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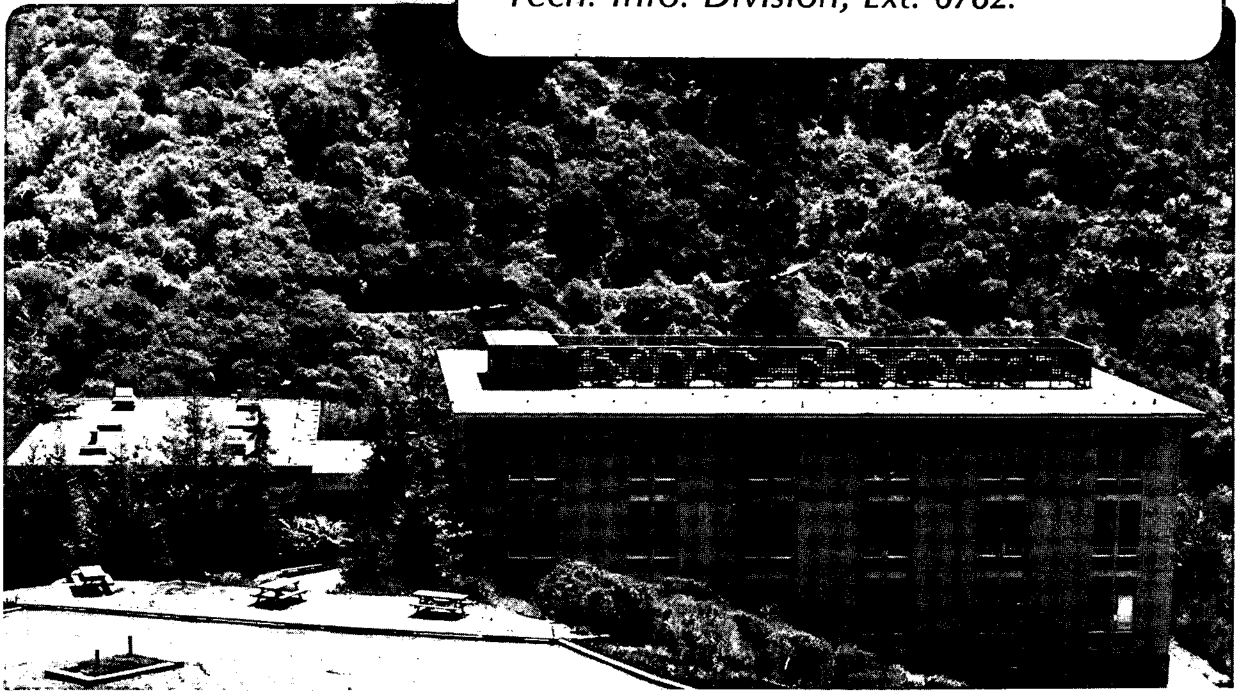

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Summary. Alkanes are plentiful enough to be considered for use as feedstocks in large-scale chemical processes, but they are so unreactive that relatively few chemical reagents have been developed which can be used to convert them to molecules having useful functional groups. Recently, however, a new iridium (Ir) complex has been synthesized which successfully converts alkanes into hydridoalkylmetal complexes ($M + R\text{-}H \longrightarrow R\text{-}M\text{-}H$). This is a dihydride having the formula $Cp^*(L)IrH_2$, where Cp^* and L are abbreviations for the ligands $(CH_3)_5C_5$ and $(CH_3)_3P$, respectively. Upon irradiation with ultraviolet light, the dihydride loses H_2, generating the reactive intermediate Cp^*IrL, which reacts rapidly with C-H bonds in every molecule so far investigated (including alkanes), leading to hydridoalkyliridium complexes $Cp^*(L)Ir(R)(H)$. Evidence has been obtained that this C-H insertion, or oxidative addition, reaction proceeds through a simple three-center transition state and does not involve organic free radicals as intermediates. In accordance with this, the intermediate Cp^*IrL reacts most rapidly with C-H bonds having relatively high bond energies, such as those at primary carbon centers, in small organic rings, and in aromatic rings. This contrasts directly with the type of hydrogen-abstraction selectivity characteristic of organic radicals. The hydridoalkyliridium products of the insertion reactions can be converted into functionalized organic molecules--alkyl halides--by treatment with mercuric chloride followed by halogens. Expulsion (reductive elimination) of the hydrocarbon from the hydridoalkyliridium complexes can be induced by Lewis acids or heat, regenerating the reactive

intermediate Cp*IrL. Oxidative addition of the corresponding rhodium complexes Cp*RhL to alkane C-H bonds has also been observed, although the products formed in this case are much less stable, and undergo reductive elimination at -20°. These and other recent observations provide an incentive for reexamining the factors which have been assumed to control the rate of reaction of transition metal complexes with C-H bonds--notably the need for electron-rich metals and the close proximity of reacting centers.

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The usual requirements for organic feedstocks in large scale metal-catalyzed processes are plentiful supply and reasonable reactivity toward transition metals. Alkenes (also called olefins or unsaturated hydrocarbons) fit these requirements well, since they are major constituents of petroleum and contain carbon-carbon double bonds, which are reactive toward a wide range of transition metal-based reagents(1). From the point of view of quantity, alkanes (saturated hydrocarbons) would also be very attractive feedstocks for catalytic synthesis of organic molecules; they are major constituents of natural gas, petroleum and coal liquefaction processes. However, they are much less often used in this way, for a very simple reason: alkanes are among the least reactive organic molecules. This unreactivity is a consequence of the high C-H bond energies in alkanes. These values range from 90 to 98 kcal/mole for primary and secondary C-H bonds; in methane, the main constituent of natural gas, the C-H bond energy is 104 kcal/mole(2). This makes methane one of the most common, but least reactive, organic molecules in nature.

The large quantity and low reactivity of methane and higher alkanes has tantalized organic and organometallic chemists for several years. In 1968, when mechanistic theory in organometallic chemistry was just developing, one leader in this area stated that, "the development of successful approaches to the activation of carbon-hydrogen bonds, particularly in saturated hydrocarbons, remains to be achieved and presently constitutes one of the most important and challenging problems in this whole field"(3). This feeling, shared by many workers in the area, has prompted many searches for clear-cut homogeneous metal-based alkane activation systems during the intervening period. However, it is only very recently that soluble transition metal systems have been found for which reaction with alkanes can be directly observed. These discoveries have stimulated an even greater intensification of interest in this problem. The purpose of this article is to summarize some of these discoveries, to discuss the advances they have led to in the fundamental understanding of reactions between alkanes and transition metal complexes, and to provide a general idea of the important, and as yet unsolved, questions which have been raised by this research.

Background

Alkanes are not completely unreactive. Free radicals capable of abstracting alkane hydrogen atoms (e.g., chlorine atoms, Eq. (1)) have been known for many years(4); these reactions lead to alkyl radicals which may then be converted into other types of organic molecules (Eq. (2)). In some cases, transition metals have been shown to mediate the formation or reactions of free radicals(5). One problem with these systems is that they are either very unselective, or in more selective cases tertiary hydrogens react much more readily than secondary or primary. A typical example of a free radical autoxidation, selective for tertiary hydrogens, is illustrated in Eq. (3). It is much more difficult to activate secondary and primary hydrogens in such processes, and only a very few systems capable of causing methane to undergo free radical reactions are known(6). Examples also exist of organic reagents which react with alkanes by apparent non-radical mechanisms; examples are ozone, superacids and fluorine(7).

In the organometallic area, the attention of many laboratories has been focused on a specific goal: the discovery of a soluble complex capable of inserting a metal center into the C-H bond of alkanes (Eq. (4)). This is one example of a general organometallic primary transformation called "oxidative addition" because the metal center is formally oxidized by two units in its conversion from starting complex to inserted product(8). An intriguing aspect of current knowledge about this reaction is that during the past ten years, many examples of intramolecular C-H oxidative addition (i.e., where the metal and reacting C-H bond are located in the same molecule (Eq. (5)) have been discovered(9). Some specific examples of this process are illustrated in Eq. (6)-(8). The largest group involves so-called "orthometallation" processes, in which insertion takes place into the C-H bond of an aromatic ring attached to an atom directly bound to the metal (Eq. (6)). A few cases are also known of insertion into a C-H bond of an alkyl chain located in the same molecule as the metal (Eqs. (7), (8)). Clearly, close proximity of the reacting C-H bond to the metal center is a critical factor favoring such cyclometallation processes. In attempts to extend these reactions to intermolecular cases, a few reactions have been found in which relatively electron-rich metal centers react with organic compounds having C-H bonds with low bond energy or high acidity (e.g., Eqs. (9), (10)). However, before the work reported here was initiated, all attempts to find a clear example of Eq. (4) involving simple alkanes had been unsuccessful.

A few examples of multi-step metal-based transformations of alkanes are known. One is the work of Shilov and his group in the Soviet Union(10) reported in the late 1960's. These intriguing reactions involve both alkane hydrogen/deuterium exchange and conversion to chlorides and acetates, catalyzed by soluble platinum salts. However, somewhat elevated temperatures (100 - 120°C) are required for these reactions. In addition, little is known about their mechanism, including whether they are truly homogeneous reactions. In much more recent work, Crabtree's group at Yale(11) and Felkin's at Gif sur Yvette in France(12) have reported the novel iridium- and rhenium-induced dehydrogenation processes exemplified by Eqs. (11) and (12). Crabtree has provided convincing evidence that these reactions are homogeneous, and has postulated that they are initiated by insertion of the metal center into an alkane C-H bond. However, this postulate has not yet been confirmed by direct observation of the oxidative addition in these systems.

Generation and Oxidative Addition Reactions of $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir$.

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 Eq. (13). Many dihydridometal complexes are known to undergo reductive elimination of H_2 upon irradiation(13). In complexes related to **2** (e.g., Cp_2MoH_2; Cp = C_5H_5) the type of intermediates generated in such reactions have been shown to insert into at least some types of C-H bonds (e.g., Eq. (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 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 characteristic resonances in the proton nuclear magnetic resonance (NMR) spectrum of the reaction mixture. The signals due to the metal-bound hydrogen atoms appear in the very high-field region of the spectrum, and each signal is doubled due to spin-spin coupling between the hydride nucleus and the phosphorus nucleus also attached to the metal. 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. Figure 1 reproduces the high-field region of the proton NMR spectrum taken on the reaction mixture during the course of irradiation. It shows the two-line pattern centered at -17.38 ppm due to starting material, and the additional two-line pattern centered at -18.67 caused by the presence of the new hydride product. A similar result was obtained in neopentane solvent.

These products are the hydridoalkyl complexes 4 and 5 shown in Eq. (14). 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 proton NMR, carbon-13 NMR and infrared spectroscopic techniques. Furthermore, they can be converted to the corresponding bromoalkyliridium derivatives (see below), which can be characterized using both spectroscopic and elemental analysis techniques(14).

Mechanism of the C-H Oxidative Addition Reaction

The conventional mechanism for the C-H insertion is shown in Figure 2. 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(15). Many radical mechanisms proceed through a step in which the radical R• 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 Figure 3. 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 the deuterium-labeled alkane cyclohexane-d_{12} was carried out. As shown in Figure 3, 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 solvent-caged radical pairs. Our best evidence against such intermediates 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(4). In view of this, cyclopropane may be used as a diagnostic substrate, since its C-H bond energy is 106 kcal/mole, even stronger than that of methane(2). Despite this, as shown in Eq. (15), 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 have led to a four-membered iridium-containing ring compound. In view of this result, a radical-cage mechanism seems extremely unlikely for these reactions.

Reductive Elimination and Functionalization Reactions of the Hydridoalkyliridium Complexes

A primary goal of this work has been the conversion of the hydridoalkyliridium complexes to functionalized organic molecules. Unfortunately, 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 **10** and **11**. This can be done smoothly at room temperature by treating them with the common reagent $CHBr_3$, as shown in Eq. (16). 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 Eq. (17). 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 studies of the selectivity of the reactive intermediate $Cp'(PMe_3)Ir$ (**6**, $Cp' = C_5Me_5$; cf. Figure 2). 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 react competitively with 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 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. Then the irradiation was carried out in a mixture (usually 1:1) of the two solvents, and the ratio of products measured by repetitive integration of the hydride resonances in the high-field region of the spectrum. The rate ratio was calculated by correcting the ratio of product yields 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 Cp'Ir(PMe_3) on one C-H bond in each of the molecules in Figure 4, 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. Reaction of Cp'(PMe_3)Ir (**6**) with unsymmetrical hydrocarbons (i.e., those having C-H bonds in different chemical environments) in general leads to several structurally different hydridoalkyliridium complexes. Because of the chemical similarity of these materials, it was not feasible to separate and identify them individually. Fortunately, however, NMR experiments on a wide range of C-H oxidative additions using symmetrical hydrocarbons (such as those summarized in the preceding paragraph) demonstrated that the NMR line position (chemical shift) due to a particular metal-bound hydride in the hydridoalkylmetal products correlated quite reliably with the type of substitution at the carbon attached to the metal. That is, secondary hydridoalkyl complexes (e.g., those formed from ring compounds such as cyclohexane, cyclopentane, etc., having general structure H-M-CHR_2) exhibit hydride chemical shifts at relatively high field, whereas primary hydridoalkyl complexes (H-M-CH_2R) invariably exhibit hydride signals at significantly lower field in the proton NMR. Oxidative addition reactions carried out on simple unsymmetrical systems confirm that this dependence holds up in more complex molecules--for example, generation of **6** in n-propane as predicted gives two new hydride signals, one in the lower-field "primary" and one in the higher-field "secondary" region of the spectrum. On the basis of this correlation, we can assign these signals with some confidence to oxidative addition products **14** and **15**, respectively (eq. (18)). Using the results of experiments such as this one, we have been able to determine that in simple acyclic systems such as n-propane, n-pentane, and 2-methyl-2-butane, **6** demonstrates measurable "anti-radical" selectivity--it inserts into primary C-H bonds about twice as fast as into secondary, and insertion into tertiary C-H bonds is apparently so slow that we have never detected hydride signals due to this type of product.

Reductive Elimination Induced by Heating: Use in Thermal C-H Activation, Enhancing Selectivity for Primary Centers, and Determination of Relative Carbon-Iridium Bond Strengths

As mentioned earlier, regeneration (reductive elimination) of hydrocarbon R-H from hydridoalkyliridium complexes such as 4 and 5 can be induced by various oxidizing agents and Lewis acids. However, it can also be induced thermally. For example, heating hydridocyclohexyl complex 4 (cf. Eq. (14)) to temperatures above 100°C in the presence of a solvent other than cyclohexane causes elimination of cyclohexane and (via the intermediacy of **6**) formation of the new hydridoalkyl complex resulting from insertion into a C-H bond of the solvent. This reaction has proven to be especially useful in enhancing the effective primary/secondary selectivity of the C-H oxidative addition process. This is illustrated with the sequence of reactions carried out using n-pentane (Fig. 5). Irradiation of **2** in n-pentane gives four new hydride resonances in the NMR spectrum, one (that due to the major product **16**) in the "primary" and three in the "secondary" region of the spectrum. Three, rather than two, secondary products are observed because the insertion of iridium into the hydrogens at C-2 of this hydrocarbon can give rise to the two structurally distinguishable diastereomers shown in the figure. 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**. This occurs because this temperature is sufficient to cause reversible reductive elimination from the secondary hydridoalkyl products, and thus the thermodynamically most stable product (i.e., the primary complex **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 Fig. 6. Under these conditions, the secondary products again disappear, but are converted into the cyclohexylhydridoiridium complex **4** instead of additional 1-pentylhydridoiridium complex **16**.

Because different hydridoalkyliridium complexes are interconverting reversibly in these experiments, it is in principle possible to measure the equilibrium constants for the reactions, and thus obtain a quantitative measure of the relative iridium-carbon bond strengths involved. We have done this for the n-pentyl/cyclohexyl system. The reversible reaction under consideration, and the equilibrium constant associated with it, are illustrated in Eqs. (19) and (20). The equilibrium was studied by first dissolving the mixture of four hydridopentyliridium products illustrated in Fig. 5 in a 92:8 mixture of cyclohexane and n-pentane. This solution was then heated. At 120°, reductive elimination and disappearance of the 2-pentyliridium complexes occurred. Heating to 140° then brought the more stable complexes **4** and **16** into interconversion with one another via reversible reductive elimination/oxidative addition. In this solvent mixture and at this temperature, the system reached equilibrium after about 120 hr; the equilibrium mixture contained 52% **4**, 48% **16**, and no detectable 2- or 3-pentyliridium complexes. Using these equilibrium concentrations and the relative molar concentrations of the two solvents, the equilibrium constant is calculated to be 10.6, as shown in Eq. (20). This corresponds to a free energy difference of about two kcal/mole at 140°. The primary C-H bond in n-pentane is about 4 kcal/mole stronger than the secondary C-H bond in cyclohexane(2). Using this number and the reaction free energy, assuming a negligible entropy difference between reactants and products we can estimate that the primary metal-carbon bond in the n-pentyliridium complex **16** is about 6 kcal/mole stronger than the secondary metal-carbon bond in **4**. Clearly the secondary metal-carbon bonds in the 2-pentyliridium complxes are even weaker than that in **4**; we do not as yet understand the reason for this unusual result.

Preliminary Results on C-H Oxidative Addition Using Rhodium Complexes

Recently we have prepared the rhodium complex **17** analogous to dihydride **2**, and found that it, too, participates in C-H oxidative addition reactions (Fig. 7). Irradiation of **17** 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 ^{1}H NMR spectrum. Preliminary studies have indicated that the C-H insertion reactions of the proposed intermediate Cp'RhL (Cp' = C_5Me_5; L = PMe_3) shown in Fig. 7 are successful(16). 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 Eq. (4), in which a soluble metal complex undergoes oxidative addition into the C-H bonds of alkanes, 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, both practical and fundamental, about the nature of C-H oxidative addition. From the practical point of view, two issues are paramount. One is the possibility of causing methane (CH_4) to react, and a second is the possibility of developing catalytic processes for conversion of alkanes to functionalized organic molecules. The chemical properties of methane are similar to those of higher alkanes, and so achieving its reaction should be quite feasible; the problem simply is that methane is a gas which liquifies at very low temperature. Its activation will therefore be achieved most conveniently when a solvent is found in which CH_4 is soluble, but which reacts with Cp'IrL much more slowly than with methane. Shilov's early work(10) and the recent report that methane is activated by a soluble lutetium complex(17) (Eq. 21) provide added encouragement that activation of methane by the iridium systems described here will be successful.

Development of catalytic processes will be more challenging. The difference between a catalytic and non-catalytic sequence of reactions is that the former is cyclic, so that the catalyst is regenerated in the final step of the sequence, and can be automatically re-used. Development of such a cyclic process, like methane activation, does not require substantial new fundamental information, but still faces difficult practical roadblocks. One of these is the fact that reagents which will convert the C-H insertion product to functionalized organic molecules often react irreversibly with the critical intermediate Cp'IrL, thus shutting down the cycle. However, research is underway aimed at finding reagents which do not have this problem.

On the fundamental side, 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. The search for additional systems which also engage in intermolecular addition is continuing in our and other laboratories, with some apparent recent success, and this should provide information which will be useful in answering this question. 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 Eq. (22), demonstrates that even a CO ligand is not electron-withdrawing enough to prevent C-H insertion(18). Finally, Watson's recent discovery of the reaction illustrated in Eq. (21) shows that methane (and other small hydrocarbons) will react with organometallic lutetium—a metal center normally considered to be very electrophilic(17). Intermolecular reactions between metal centers and alkanes are now being uncovered at an increasingly rapid rate, and with metals having a wide range of electronic character. It seems likely that several different mechanisms for alkane oxidative addition will eventually be identified(19).

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15. See, for example, (a) J. A. Labinger; R. J. Braus; D. Dolphin and J. A. Osborn *J. Chem. Soc., Chem. Commun.* (1970), p. 612; (b) F. R. Jensen and B. Knickel, *J. Am. Chem. Soc.* **93**, 6339 (1971); (c) J. A. Labinger and J. A. Osborn, *Inorg. Chem.* **19**, 3230 (1980).

16. Similar work has recently been reported independently by another group: W. D. Jones and F. J. Feher, *Organometallics* **2**, 562 (1983).

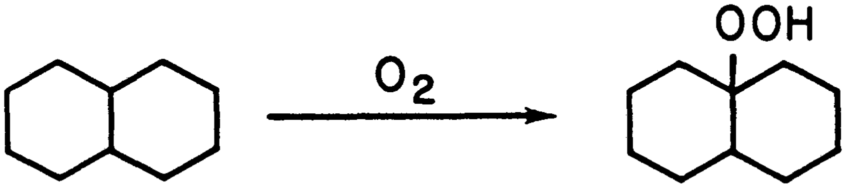
17. P. L. Watson, submitted for publication; see also P. L. Watson, *J. Chem. Soc., Chem. Commun.* (1983), p. 276.

18. J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.* **104**, 3723 (1982).

19. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

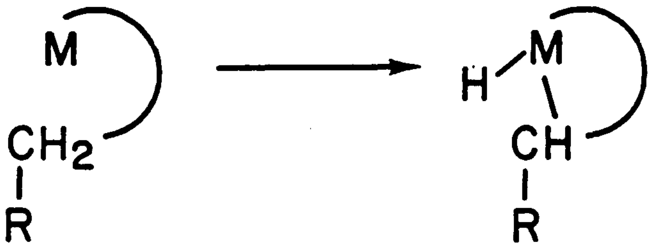
$$Cl\cdot + R{-}H \longrightarrow HCl + R\cdot \qquad (1)$$

$$R\cdot + X{-}Y \longrightarrow R{-}X + Y\cdot \qquad (2)$$

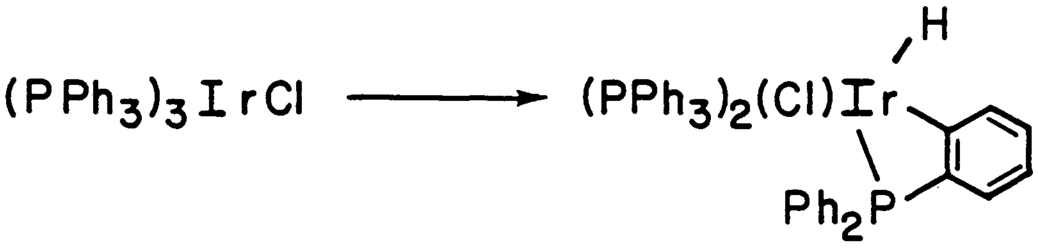


(3)

$$M + R{-}H \longrightarrow R{-}M{-}H \qquad (4)$$



(5)



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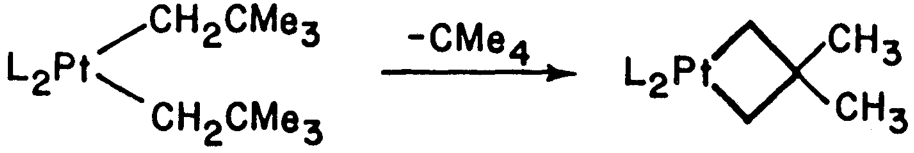

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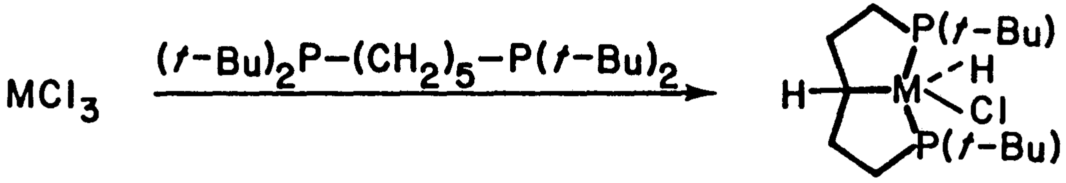
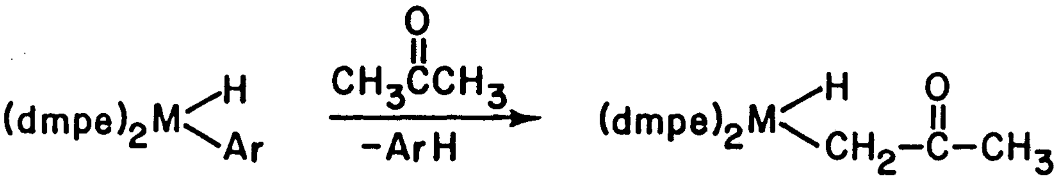


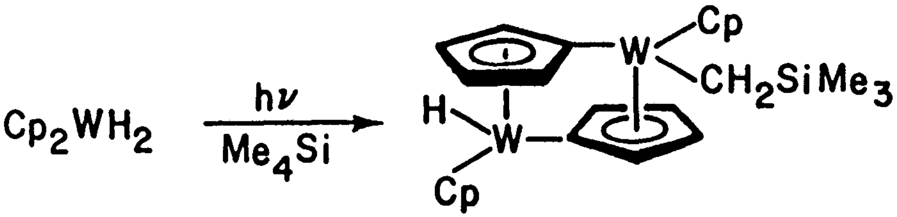
(M = Ir, Rh)

(8)

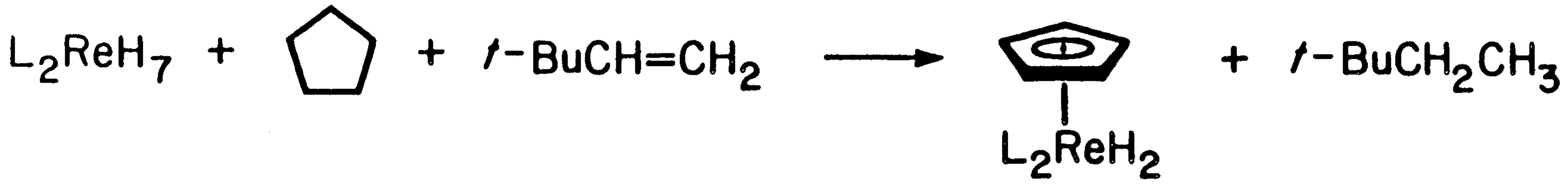


(M = Fe, Ru)

(9)

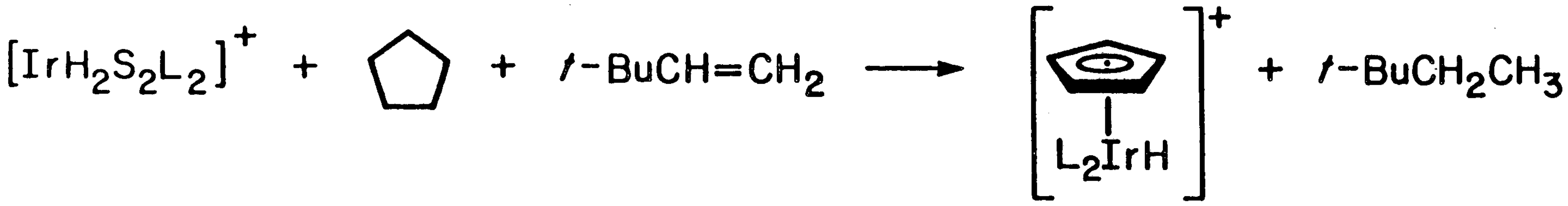


(10)



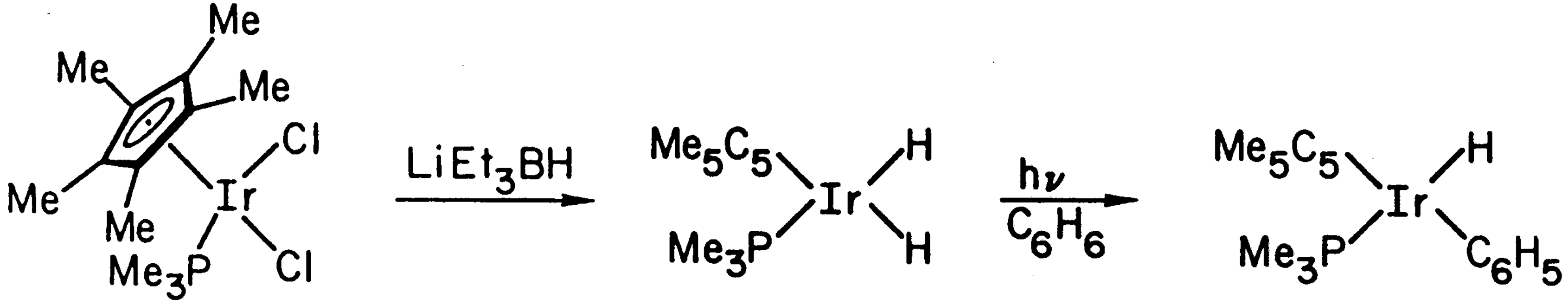
(11)

(L = PPh$_3$, PEt$_2$Ph)



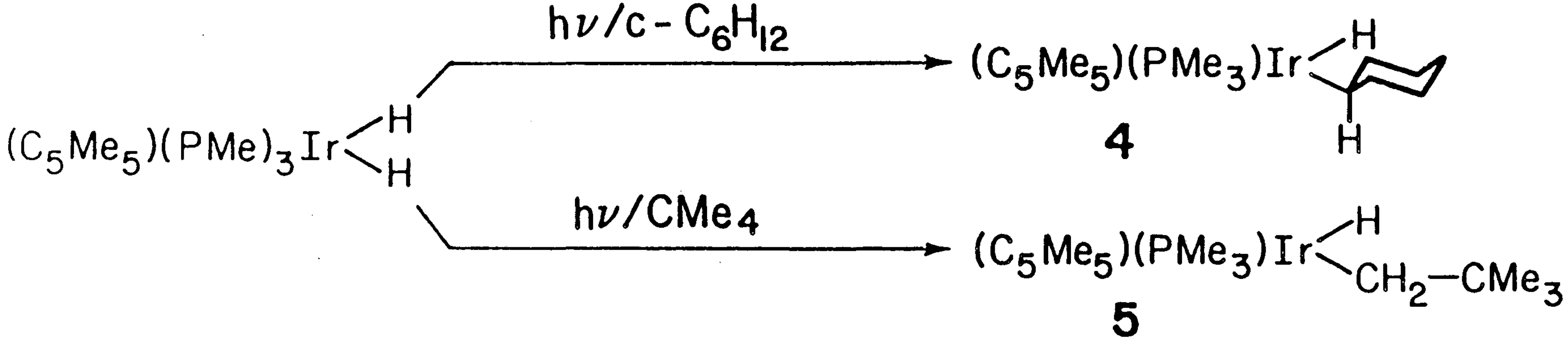
(12)

(L = PPh$_3$, S = H$_2$O or acetone)

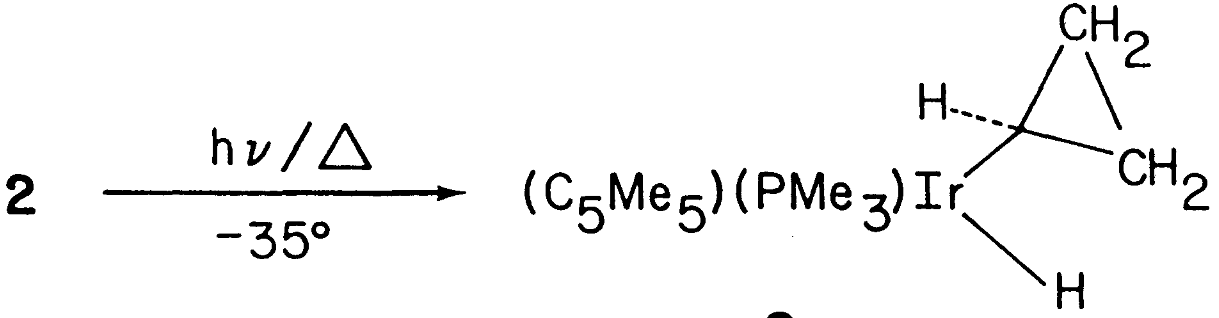

Me
Me
Me
Me
Me
Cl
Ir
Me3P
Cl
LiEt3BH
Me5C5
Ir
H
Me3P
H
hν
C6H6
Me5C5
Ir
H
Me3P
C6H5

1 2 3

(13)

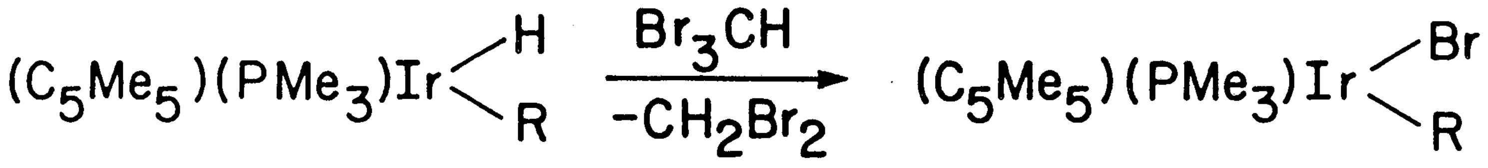

$(C_5Me_5)(PMe)_3Ir$
H
H
$h\nu/c-C_6H_{12}$
$h\nu/CMe_4$
$(C_5Me_5)(PMe_3)Ir$
H
H
4
$(C_5Me_5)(PMe_3)Ir$
H
CH_2-CMe_3
5

(14)



8

(15)



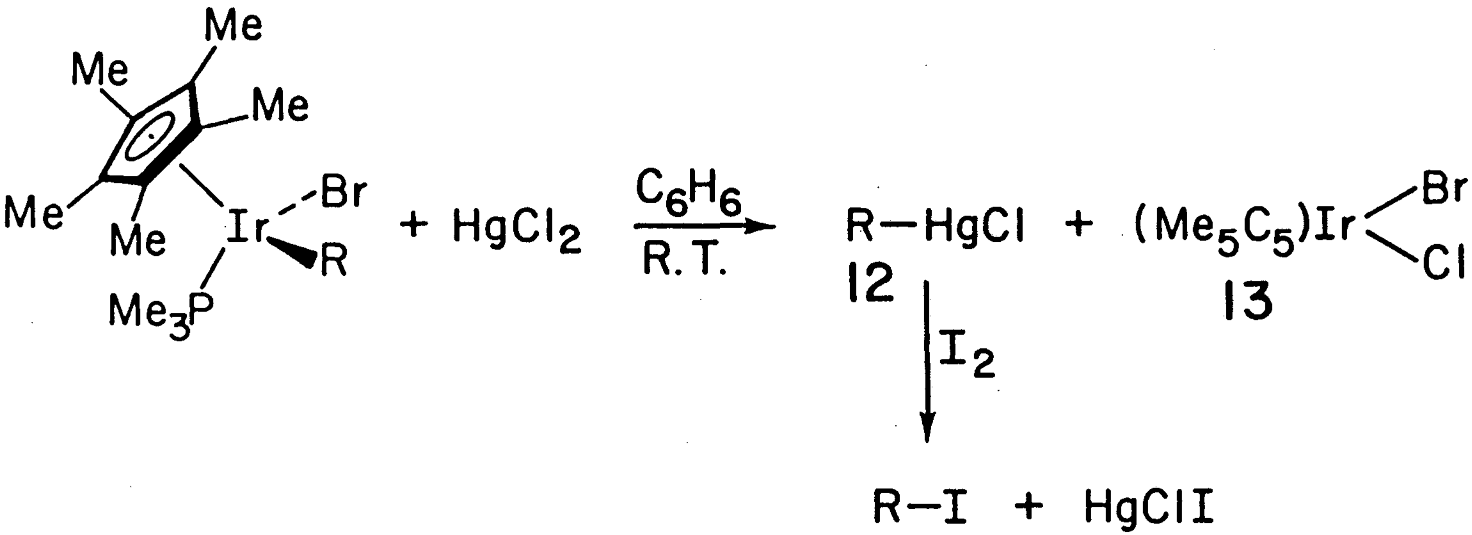
$$(C_5Me_5)(PMe_3)Ir\begin{matrix}H\\R\end{matrix} \xrightarrow[-CH_2Br_2]{Br_3CH} (C_5Me_5)(PMe_3)Ir\begin{matrix}Br\\R\end{matrix} \qquad (16)$$

4 R = C_6H_{11}

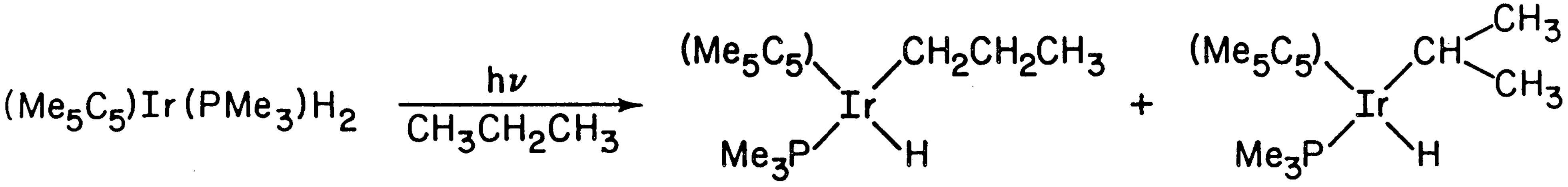
5 R = CH_2CMe_3

10 R = C_6H_{11}

11 R = CH_2CMe_3

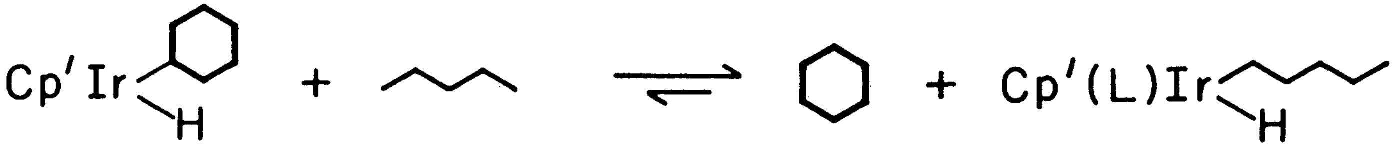

Me
Me
Me
Me
Me
Ir
Br
R
Me3P
+ HgCl2
C6H6
R.T.
R—HgCl
12
I2
R—I + HgClI
+ (Me5C5)Ir
Br
Cl
13

(17)


(Me5C5)Ir(PMe3)H2
hν
CH3CH2CH3
(Me5C5)
Ir
CH2CH2CH3
Me3P
H
+
(Me5C5)
Ir
CH
CH3
CH3
Me3P
H

(18)

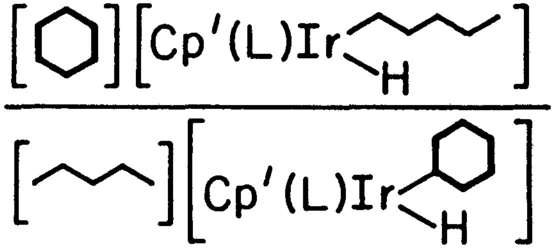
2 **14** **15**



4 **16**

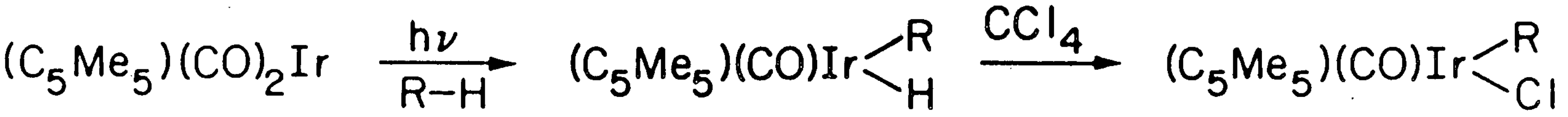
(19)

$K_{eq} =$



$= \frac{92}{8} \cdot \frac{48}{52} = 10.6$ (20)

$$(C_5Me_5)_2Lu{-}CH_3 + {}^{13}CH_4 \longrightarrow (C_5Me_5)_2Lu{-}{}^{13}CH_3 + CH_4 \qquad (21)$$



$$(C_5Me_5)(CO)_2Ir \xrightarrow[R-H]{h\nu} (C_5Me_5)(CO)Ir{<}^{R}_{H} \xrightarrow{CCl_4} (C_5Me_5)(CO)Ir{<}^{R}_{Cl} \qquad (22)$$

Figure Captions

Fig. 1. Reproduction of the high-field portion of the proton nuclear magnetic resonance (NMR) spectrum of the mixture obtained during irradiation of Cp'(L)IrH_2 (complex 2) with ultraviolet light in cyclohexane solvent. On the numbered axis at the bottom of the spectrum, the field increases moving toward the right. The position of each signal (i.e., the chemical shift of the hydrogen atom which produces that signal) is measured in parts per million distance from the single line observed for the internal standard tetramethylsilane, which appears at much lower field and is therefore not visible in this portion of the spectrum. Chemical shifts which appear at higher fields than tetramethylsilane are listed as negative numbers by convention. The lower-field doublet is due to the hydride signal for the starting dihydride **2**, and the higher-field doublet arises from the hydride signal for the C-H insertion product **4**.

Fig. 2. Proposed mechanism for the photochemical conversion of dihydride **2** to C-H insertion products.

Fig. 3. Schematic illustration of the crossover experiment (see text) carried out by irradiating dihydride **2** in a mixture of neopentane (CMe_4) and completely deuterated cyclohexane (C_6D_{12}).

Fig. 4. Relative rates of reaction of one C-H bond in each of the cyclic organic molecules illustrated with Cp'IrL.

Fig. 5. The C-H insertion products formed on irradiation of dihydride **2** in n-pentane at 6° C, followed by heating the resulting mixture to 110° in the same solvent.

Fig. 6. Illustration of the result of heating the products formed on irradiation of **2** in n-pentane to 100° C in cyclohexane solvent.

Fig. 7. The reactions observed on irradiation of the dihydridorhodium complex **17** at -50° C in various organic solvents.

FIGURE 1

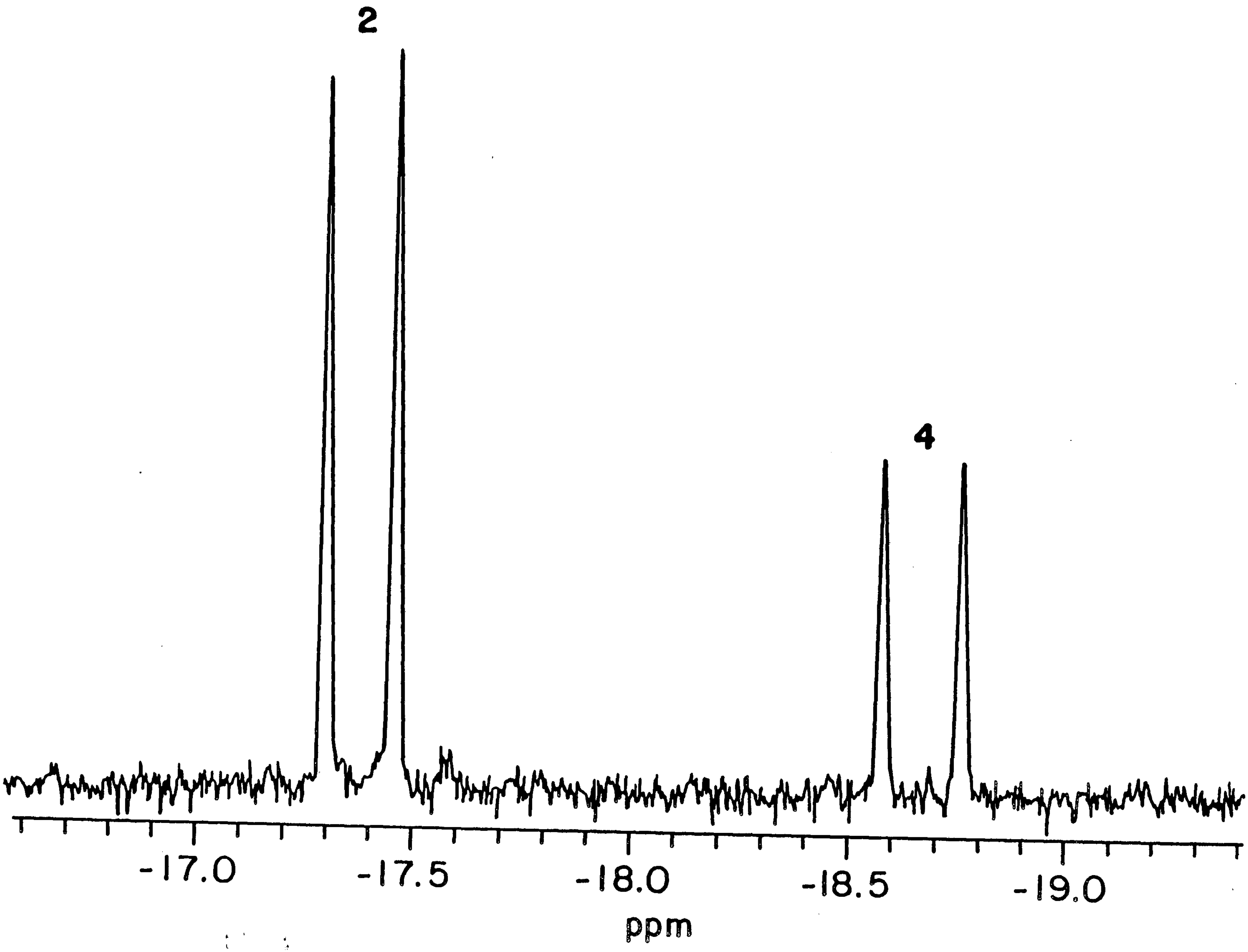


FIGURE 2

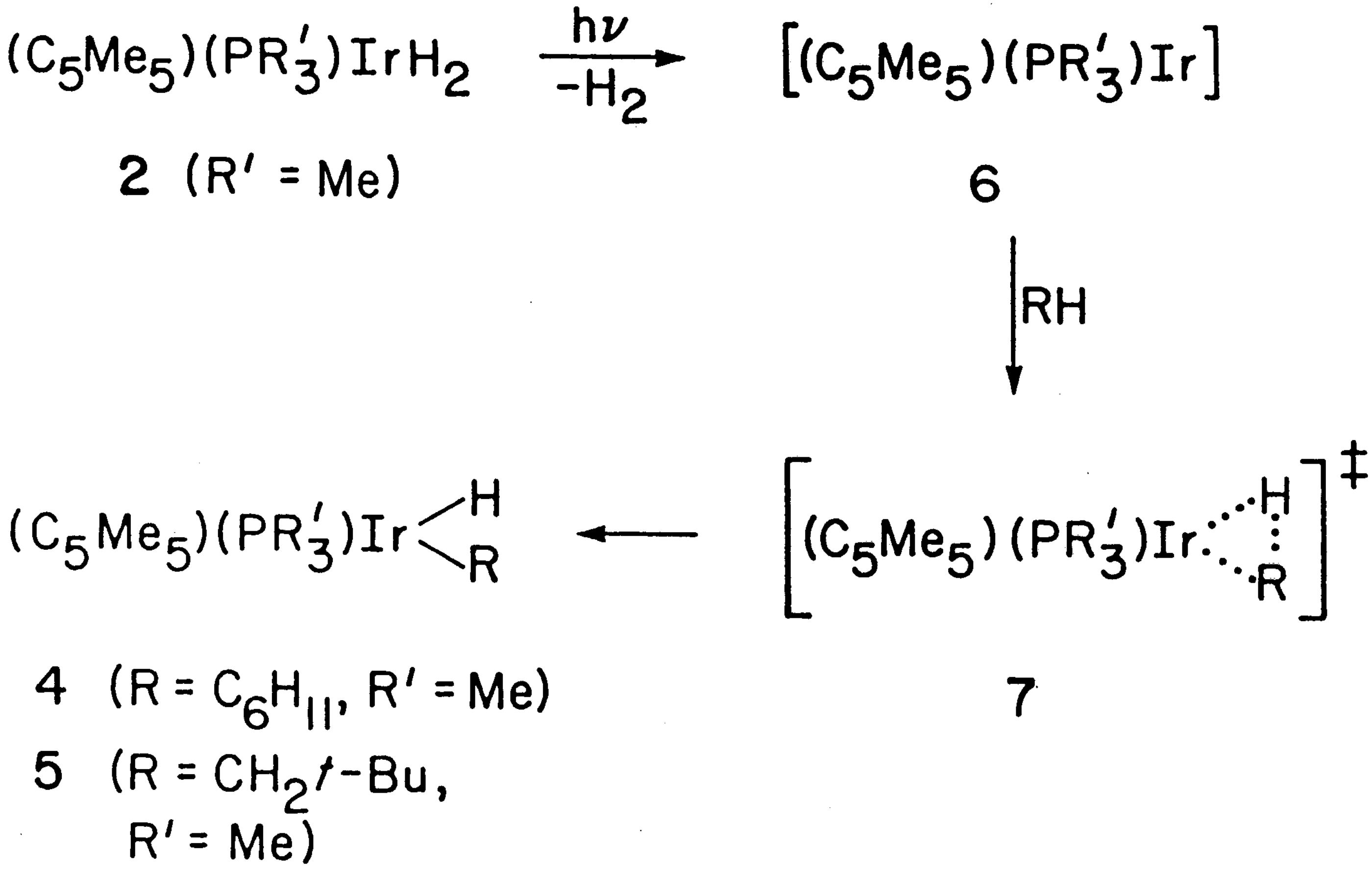
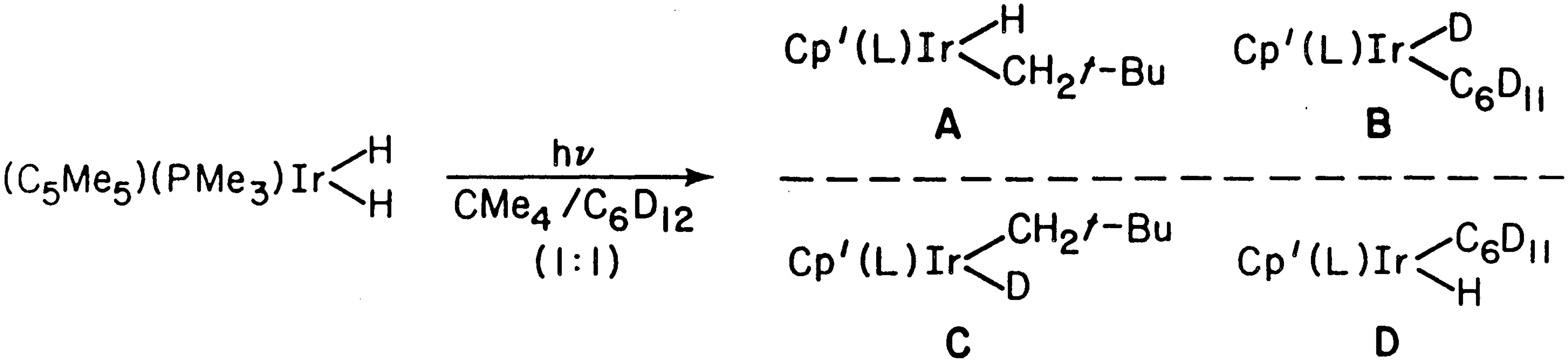

(C5Me5)(PR'3)IrH2
hν
-H2
[(C5Me5)(PR'3)Ir]
2 (R' = Me)
6
RH
(C5Me5)(PR'3)Ir H R
[(C5Me5)(PR'3)Ir H R]‡
4 (R = C6H11, R' = Me)
5 (R = CH2t-Bu, R' = Me)
7

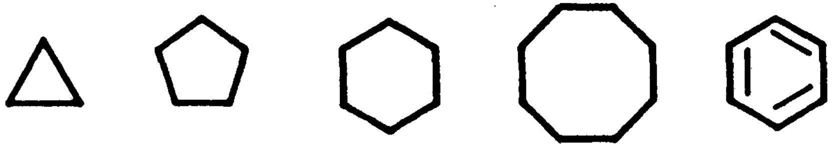
FIGURE 3



$[Cp' \equiv C_5Me_5]$

FIGURE 4

Ring Systems:



k_{rel}: 2.6 1.6 1.0 0.09 4.7

FIGURE 5

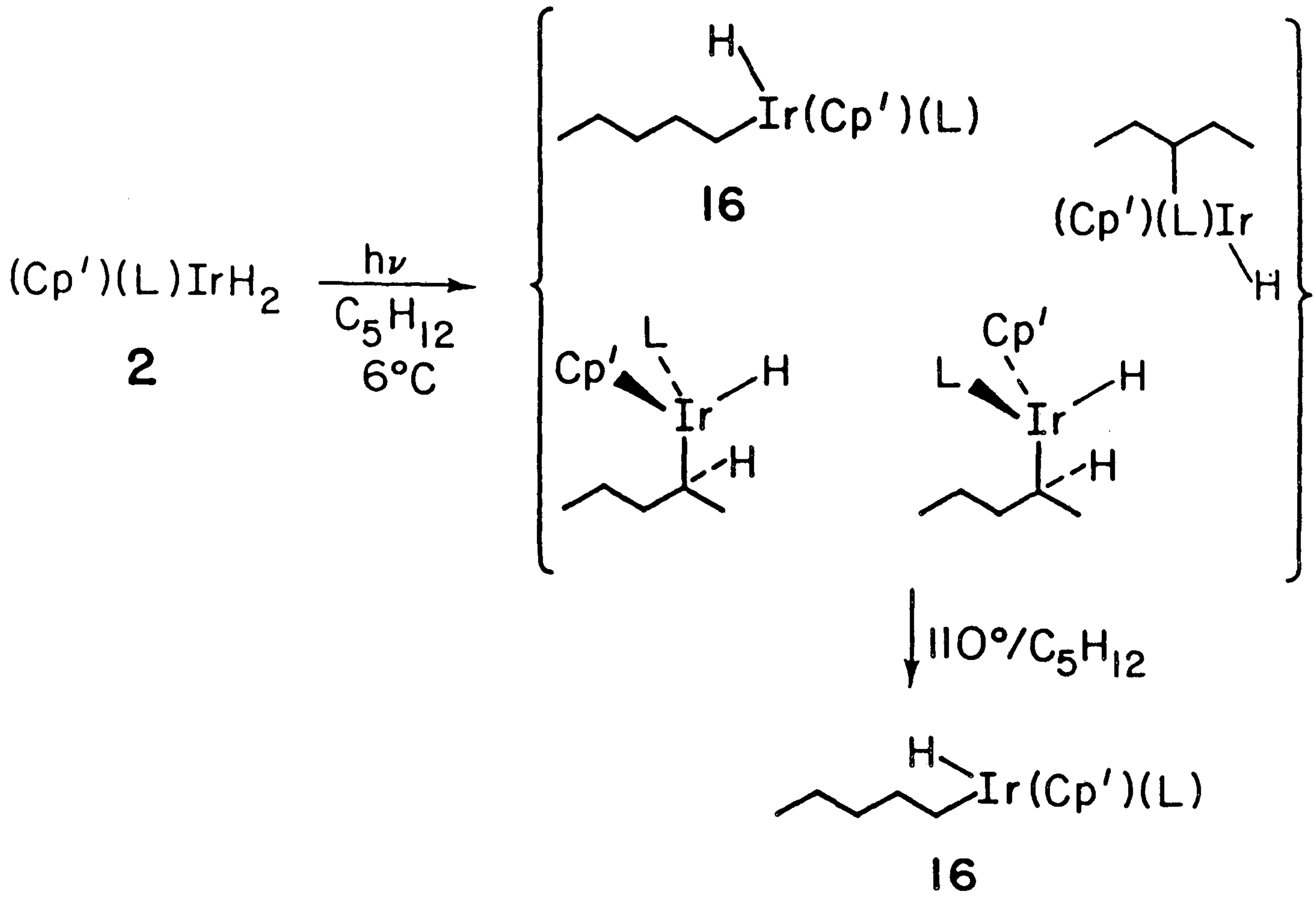
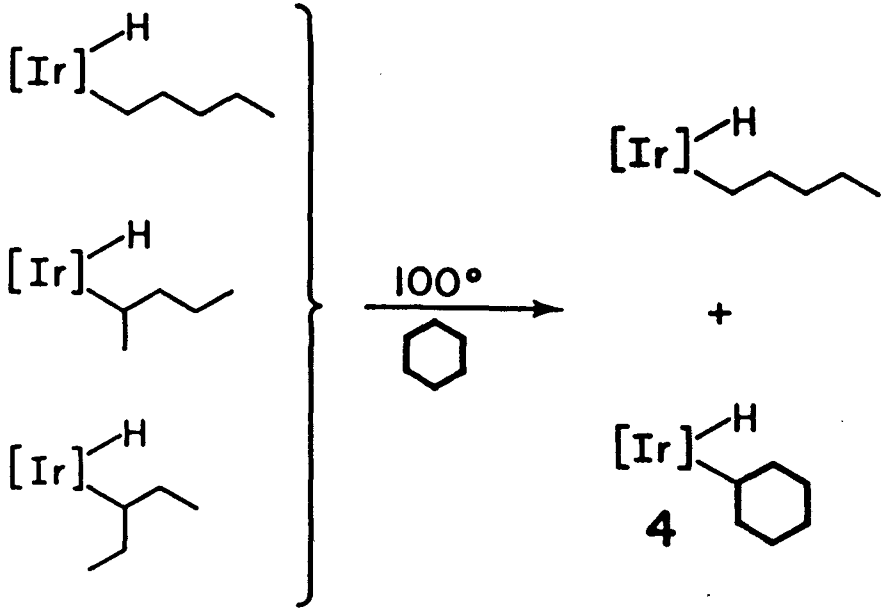
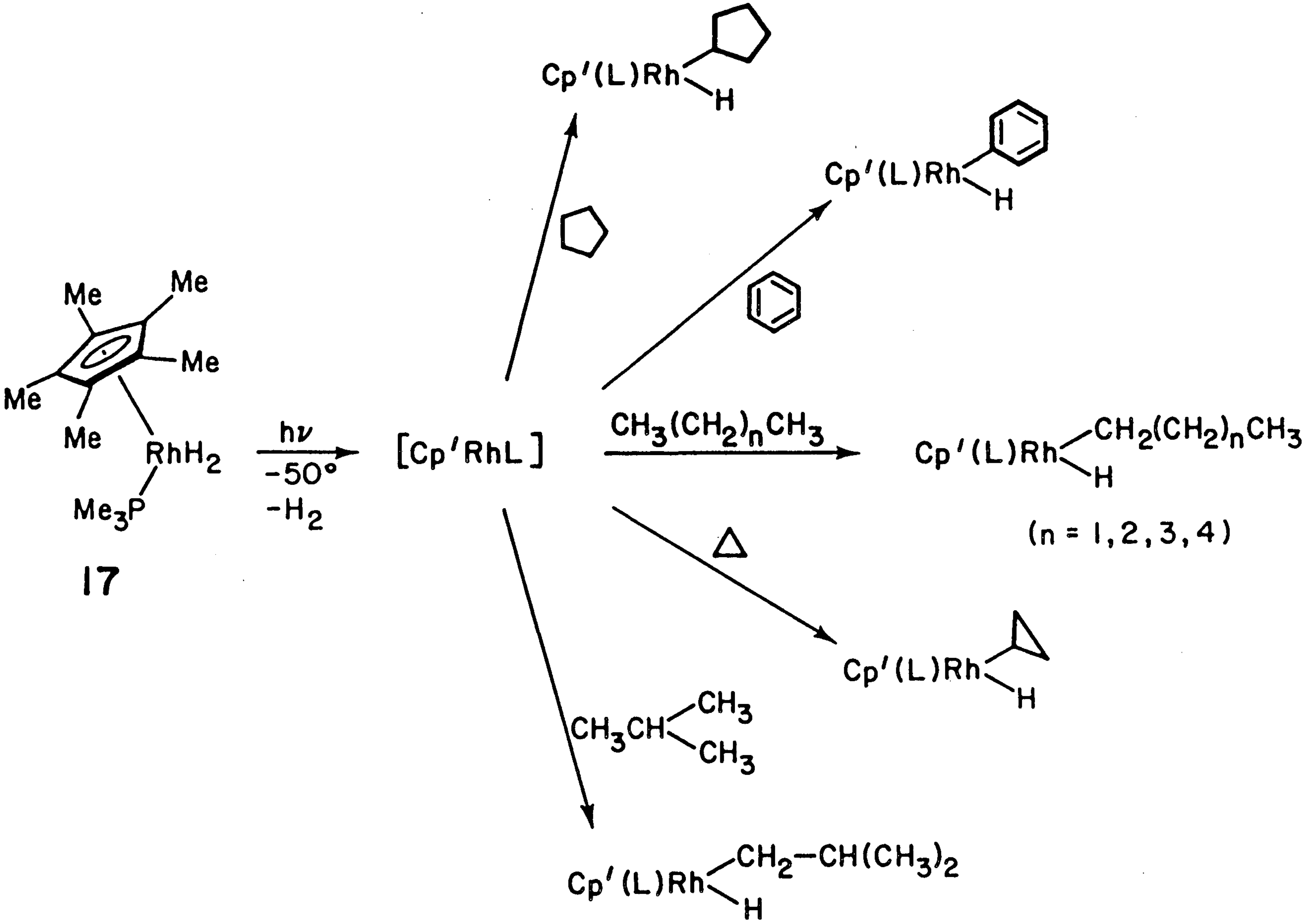

(Cp')(L)IrH$_2$
2
hν
C$_5$H$_{12}$
6°C
H
Ir(Cp')(L)
16
(Cp')(L)Ir
H
Cp'
L
Ir
H
H
Cp'
L
Ir
H
H
110°/C$_5$H$_{12}$
H
Ir(Cp')(L)
16

FIGURE 6



$[\mathrm{Ir}] \equiv (\eta^5\text{-}C_5Me_5)\mathrm{Ir}(PMe_3)$

FIGURE 7


Me
Me
Me
Me
Me
RhH2
Me3P
17
hν
-50°
-H2
[Cp′RhL]
Cp′(L)Rh
H
CH3(CH2)nCH3
Cp′(L)RhCH2(CH2)nCH3
(n = 1,2,3,4)
CH3CH(CH3)CH3
Cp′(L)RhCH2—CH(CH3)2

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