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Andrew Henry Janowicz
(Ph.D. thesis)

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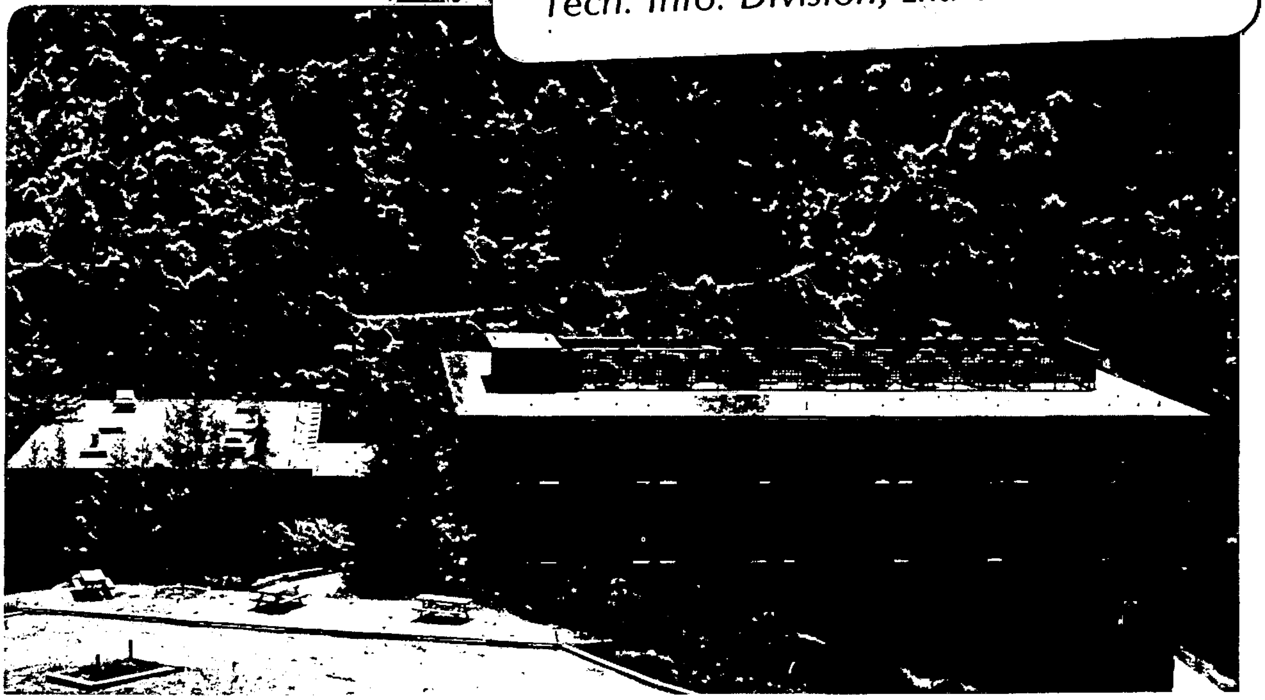

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By

Andrew Henry Janowicz

PH.D. THESIS

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MATERIALS & MOLECULAR
RESEARCH DIVISION

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A Mechanistic Study of the Formation and Cleavage of C–H Bonds: Hydrogenolysis of M–C Bonds / C–H Bond Activation of Saturated Hydrocarbons

Andrew Henry Janowicz

Abstract. To study the cleavage of metal-carbon bonds by hydrogen, the hydrogenolysis of (η^5-cyclopentadienyl)-(triphenylphosphine)dimethylcobalt(III) (**1**) has been investigated. Hydrogenolysis of **1** takes place under mild conditions and leads to two moles of methane and (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt(I) (**2**). The reaction is autocatalytic; the rate is inhibited by added phosphine and accelerated by the addition of product **2** to the initial reaction mixture. A mechanism is proposed which postulates that **2** reacts with hydrogen to give (η^5-cyclopentadienyl)(triphenylphosphine)dihydridocobalt(III) (**5**) as a transient species (generated from **1** by a loss of phosphine) and dihydride **5**. Although dihydride **5** could not be prepared to test this hypothesis directly, solutions of the corresponding pentamethylcyclopentadienyl dihydride (**7**) were generated by hydrogenolysis of **6**, the pentamethylcyclopentadienyl analogue of **1**. As predicted, **6** and **7** reacted readily to give methane. The kinetics of this reaction are consistent with a pre-equilibrium loss of phosphine followed by trapping of the unsaturated dimethyl species by dihydride. Other phosphine derivatives of the pentamethylcyclopentadienyl cobalt dihydrides and the rhodium analogue of **7** were generated by the hydrogenolysis of the correspondng dimethyl compounds.

We report the first example of intermolecular oxidative addition of a transition metal complex in homogeneous solution to single C-H bonds in saturated hydrocarbons, leading to hydridometal alkyl complexes at room temperature. Upon irradiation, (η^5-pentamethylcyclopentadienyl)(trimethylphosphine)dihydridoiridium(III) loses dihydrogen to lead presumably to the coordinatively unsaturated transient intermediate (η^5-pentamethylcyclopentadienyl)(trimethylphosphine)-iridium(I). In saturated hydrocarbon solvents, such as cyclohexane and neopentane, the unsaturated intermediate inserts into a C-H bond of the solvent leading to the corresponding cyclohexyl- and neopentyl iridium hydrides, respectively. Labelling studies indicate that the insertion is at least 92% intramolecular (concerted addition). Irradiation of the iridium dihydride in a variety of other saturated hydrocarbons yields new alkyl hydrides; in these reactions, insertion into primary C-H bonds is favored over secondary C-H bonds. In competition studies, the relative reactivities of C-H bonds were as follows: pentane (1° C-H) > cyclopentane > cyclohexane > cyclooctane. Bromoform converts to alkyl hydrides into the corresponding bromoalkyl iridium complexes. The bromoneopentyl iridium complex can be converted into neopentyl bromide by reaction with mercuric chloride, followed by treatment with bromine.

To Kathy,
my forever friend.
I love you.

Acknowledgments

There are many people whom I would like to thank for their contributions as I progressed towards my Ph.D. degree. I am indebted to Bob Bergman; during our three and a half years together, he shared his many insights into chemistry with me. When times were tough during my first year, Bob stuck with me and helped me develop as a person as well as a chemist. I am also grateful that as I progressed, Bob had enough faith in me to allow me to pursue my own ideas in the lab.

The members of the Bergman group have also been instrumental in my development. They have been there with a helpful hand and many good suggestions. Although I could not possibly name every person who has been involved, I would like to acknowledge my fellow fourth year students, Paul Becker and Klaus Theopold, and Henry Bryndza, Michael Wax, Bill Hersh and Wayne Weiner for their friendship and help throughout this whole ordeal.

On a more personal level, I would like to thank my parents, family and friends for their emotional support throughout my educational process. Last, but certainly not least, I am deeply grateful and indebted to Kathy, my wife and best friend. She was my pillar of strength, my loving wife and supportive friend throughout my quest for a Ph.D. I am absolutely certain that I could not have done as well without her. She stood right along side of me at all times; thus, I dedicate this thesis to Kathy, my forever friend.

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Table of Contents

Chapter I

HYDROGENOLYSIS OF DERIVATIVES OF (η^5-CYCLOPENTADIENYL)(TRIPHENYLPHOSPHINE)DIMETHYLCOBALT(III). AN AUTOCATALYTIC MECHANISM INVOLVING A METAL DIHYDRIDE/ METAL DIALKYL REACTION AS A CRITICAL STEP

Introduction

The hydrogenolysis of organotransition metal-carbon bonds is an important part of many catalytic processes. For example, the terminating steps in hydroformylation[1] and homogeneous hydrogenation[2] require cleavage of a metal acyl or alkyl by H_2. The (heterogeneous) Fischer-Tropsch reaction also requires several steps involving H_2 in which C-H bonds are formed, including the final release of hydrocarbon or oxygenate from the metal surface.[3]

It has commonly been assumed that M-R hydrogenolysis occurs by oxidative addition of H_2 to the metal center at which the carbon fragment is attached, followed by formation of a new C-H bond by reductive elimination (eq 1).[4] However, evidence has

$$\text{M-R} + H_2 \longrightarrow [\text{R-MH}_2] \longrightarrow \text{M-H} + \text{R-H} \qquad (1)$$

been obtained[5] that in hydroformylation, the final C-H bond forming step is a binuclear process, involving reaction between a transient cobalt acyl complex and the hydroformylation catalyst, $HCo(CO)_4$. Therefore, hydrogen is no longer the molecule interacting with the metal containing the carbon fragment; some other hydrogen carrying species is inducing C-H bond formation.

Other reactions between transition metal alkyls and hydrides have been found to lead to C-H bond formation.[6] Norton and co-workers have studied the reaction of an osmium tetracarbonyl dihydride and dialkyl.[6a,b] In this case, there is a dinuclear elimination between the dihydride and dialkyl to give alkane. They have postulated that an alkyl group migrates to a CO to form an unsaturated acyl, which in turn interacts with the hydride. It has been suggested that the interaction of the Os-H with the vacant coordination site on the other Os to form a dinuclear species (whose structure is unknown) is a key step in the dinuclear elimination.

Jones and Bergman have studied the reaction between a Mo alkyl and hydride.[6e] An important feature in the proposed mechanism is again an alkyl migration to a CO to form an unsaturated acyl. A binuclear species containing a hydride ligand bridging two Mo atoms was discussed as an important intermediate. However, when the Mo-H interacts with the vacant coordination site on the newly formed Mo acyl, the reaction product is the corresponding aldehyde.

Halpern and co-workers have studied the mechanism of C-H bond formation with Mn alkyls and hydrides.[6d] They have found that a change in solvent polarity or a slight change in one of the ligands can cause a dramatic shift in mechanism. Alkane formation was observed in two slightly different systems by (1) Mn-C bond homolysis, followed by hydrogen atom transfer from the Mn-H and (2) the interaction of Mn-H with an unsaturated Mn-R. Aldehyde formation is observed in two slightly different systems by (1) the mechanism of Jones and Bergman via an unsaturated metal acyl and (2) a radical pathway where the acyl species is made coordinatively saturated by the addition of a trapping ligand.

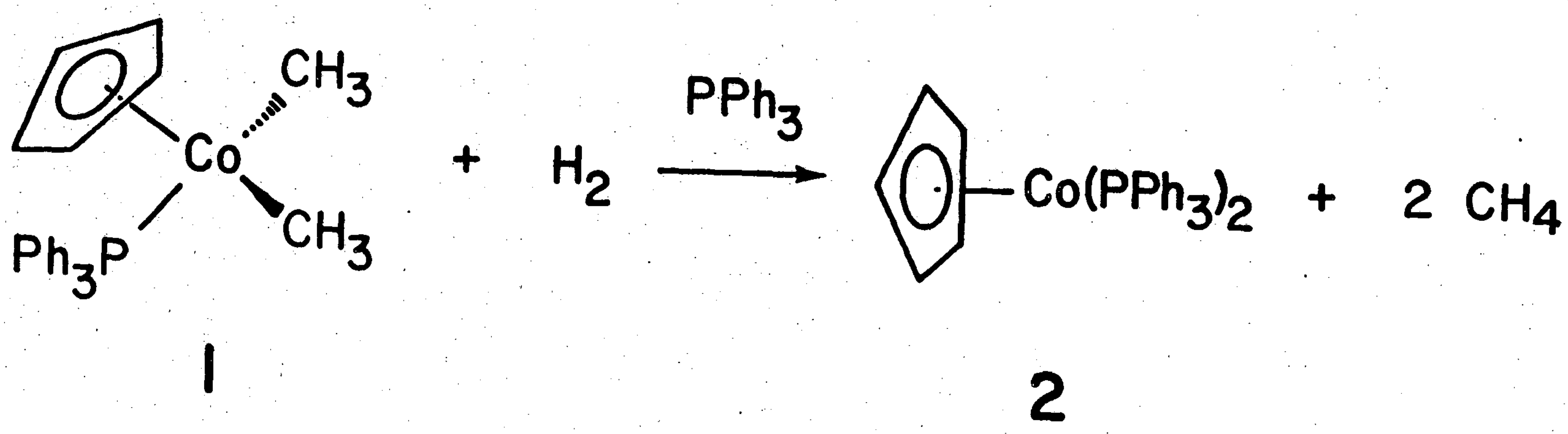
This study is aimed at directly investigating the mechanism of metal-carbon bond hydrogenolysis. The reaction of hydrogen with some Zr alkyl hydrides has been studied.[7] Both studies report a clean M-C bond cleavage with subsequent formation of alkane. We wish to report our results on the mechanism of the facile methane-forming hydrogenolysis of cyclopentadienyldimethylcobalt derivatives.[8]

Results and Discussion

Hydrogenolysis of $(\eta^5\text{-}C_5H_5)Co(PPh_3)(CH_3)_2$ (1). Reaction of $(\eta^5\text{-}C_5H_5)Co(PPh_3)(CH_3)_2$ (1)[9] with dihydrogen at 45°C yields two equivalents of CH_4 and approximately 0.5 equivalents of $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ (2). In the presence of an added equivalent of PPh_3, the rate of reaction is slower but the hydrogenolysis now gives two equivalents of CH_4 and nearly a full equivalent of 2 (Scheme I). We chose this dimethyl complex for study because upon hydrogenolysis, methane is formed and yet it seemed unlikely that this process could be occurring by loss of phosphine, followed by oxidative addition of H_2 to give a formally Co(V) intermediate (Scheme II). A Co(V) species would be highly energetic and unfavorable as an intermediate. The system apparently finds some more energetically favorable pathway to form new C-H bonds, perhaps via a binuclear M-H/M-R reaction.

Isotope labeling experiments were used to determine that the origin of the new C-H bond in the product methane is the added hydrogen gas. Treatment of 1 with D_2 under the same conditions as above gives exclusively CH_3D. The rate of reaction of 1 with

Scheme I



Scheme II

$$\underset{\mathbf{1}}{CpCo(PPh_3)Me_2} \rightleftharpoons \underset{\mathbf{3}}{CpCoMe_2} + PPh_3$$

$$\mathbf{3} + H_2 \longrightarrow CpCoMe_2H_2$$

$$CpCoMe_2H_2 \xrightarrow{PPh_3} \underset{\mathbf{2}}{CpCo(PPh_3)_2} + 2\ CH_4$$

H_2 in the presence of added triphenylphosphine was also examined. In agreement with the premise that a conventional mechanism might not be accessible for this process, an induction period was found, whose length was dependent upon the concentration of phosphine (Figure 1). Following the induction period, the rate gradually accelerated until the system began to be depleted in complex 1. Such induction periods are often characteristic of free-radical chain processes; however, the operation of a radical chain in this system seemed somewhat unlikely, because it would presumably have to involve methyl radicals. These very reactive radicals would almost certainly produce some toluene by reaction with benzene solvent; in addition, because of the comparable bond energies of H_2 and methane, H_2 should not transfer hydrogen very rapidly to methyl radicals. Nevertheless, we carried out the hydrogenolysis using D_2, $(\eta^5\text{-}C_5H_5)Co(PPh_3)(CD_3)_2$, and ten equivalents (0.95 M) of 1,4-cyclohexadiene, a very reactive reagent for transfer of hydrogen atoms to organic radicals.[10] Under these conditions the methane produced was found to be exclusively CD_4; no hydrogen from the cyclohexadiene was incorporated. This suggested that the observed induction period was not due to a radical chain process.

A second explanation for the induction period is that the hydrogenolysis is autocatalytic. To test this hypothesis, the hydrogenolysis was carried out in the presence of both an equivalent of PPh_3 and 0.17 of an equivalent of the subsequent reaction product, 2. The induction period disappears, although the overall rate still exhibits inhibition by PPh_3 (Fig. 1).

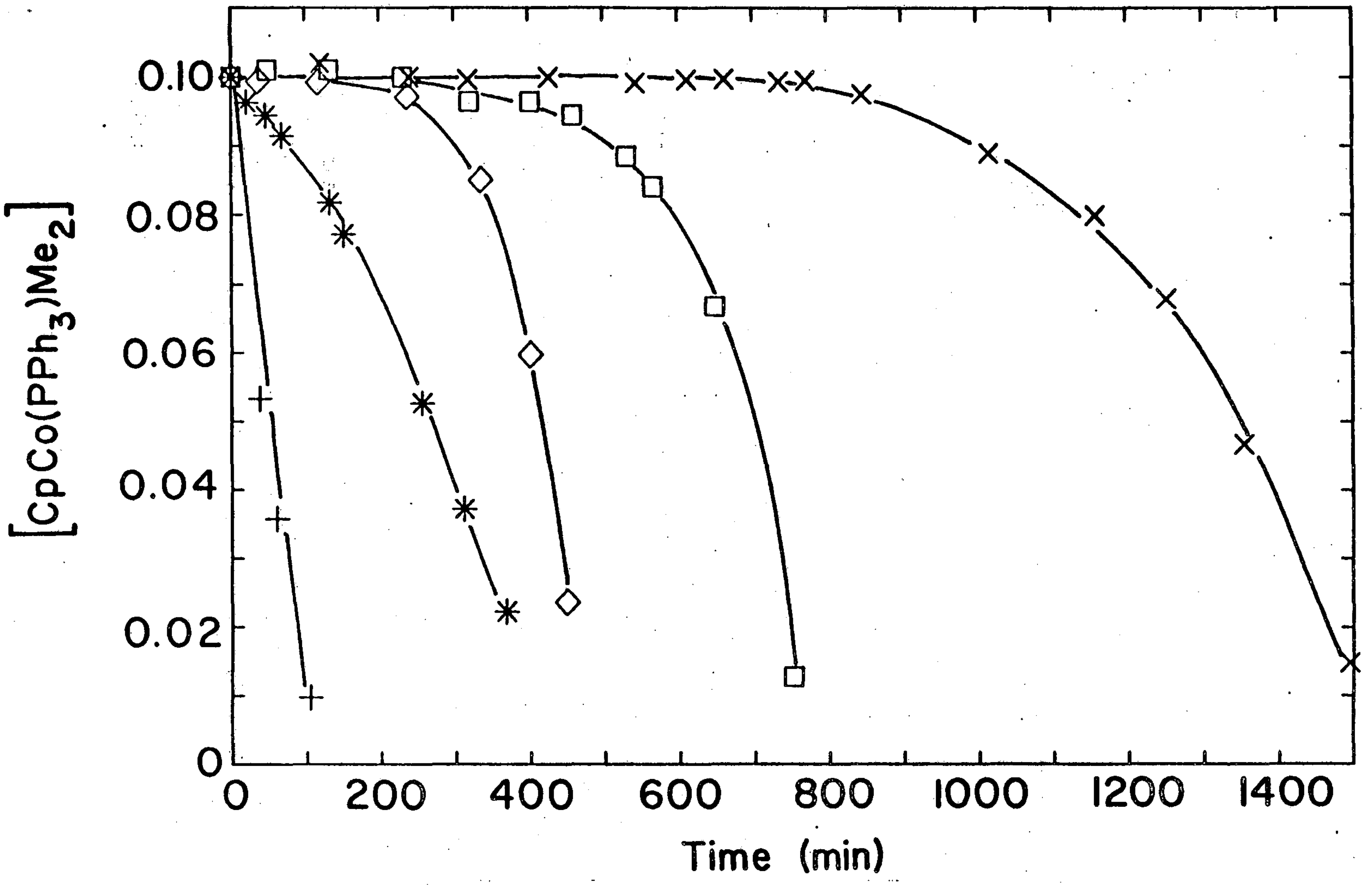


Figure 1. Concentration vs. time plots for the disappearance of complex 1 (0.10 M initial concentration, 3 atm H_2), in benzene-d_6 at 45°C, with the following additives: (+) no additives, (◇) 0.025 M PPh_3, (□) 0.50 M PPh_3, (×) 0.10 M PPh_3, (✳) 0.10 M PPh_3 and 0.017 M 2.

Clearly product 2 is a catalyst (or catalyst precursor) for the hydrogenolysis of 1.

An autocatalytic mechanism consistent with the observations reported above is outlined in Scheme III. We know that the thermal decomposition of 1 is slow at 45°C and has a complicated mechanism, but some Co(I) species are produced in this reaction.[11] We believe these initiate the hydrogenolysis, and once some $(\eta^5\text{-}C_5H_5)CoPPh_3$ (4) is produced, this takes over as the critical Co(I) species. Complex 1 is in equilibrium with small amounts of the unsaturated complex $(\eta^5\text{-}C_5H_5)Co(CH_3)_2$ (3) and PPh_3 at 45°. Complex 2 dissociates phosphine even more rapidly ($k_{dissoc} = 1.15 \times 10^{-3}$ sec^{-1} in toluene-d_8 at -60^oC) leading to 4.[12] We propose that oxidative addition of H_2 to 4 gives a reactive dihydride 5. The critical step in this mechanism involves the binuclear reaction of dihydride 5 with the unsaturated dialkyl 3, leading to methane and CpCo(I) fragments; these fragments either continue the autocatalysis or are scavenged by PPh_3 to give 2.

We sought additional support for this mechanism by attempting to prepare dihydride 5, so that we might investigate its reactions with 1 directly. Unfortunately, reaction of 1 with H_2, reaction of 2 with excess H_2, or treatment of $(\eta^5\text{-}C_5H_5)\text{-}Co(PR_3)I_2$ derivatives with hydride reagents gave no evidence for the formation of stable dihydrides. We found that another organometallic dihydride, $(\eta^5\text{-}C_5H_5)_2MoH_2$,[13] does react with 1 at 45°C in less than an hour to yield methane; therefore, an interaction between a dihydride and 3 seems plausible.

Scheme III

$$\underset{\mathbf{1}}{\mathrm{CpCo(PPh_3)Me_2}} \rightleftharpoons \underset{\mathbf{3}}{\mathrm{CpCoMe_2}} + \mathrm{PPh_3}$$

$$\underset{\mathbf{2}}{\mathrm{CpCo(PPh_3)_2}} \rightleftharpoons \underset{\mathbf{4}}{\mathrm{CpCoPPh_3}} + \mathrm{PPh_3}$$

$$\mathbf{4} + \mathrm{H_2} \rightleftharpoons \underset{\mathbf{5}}{\mathrm{CpCo(PPh_3)H_2}}$$

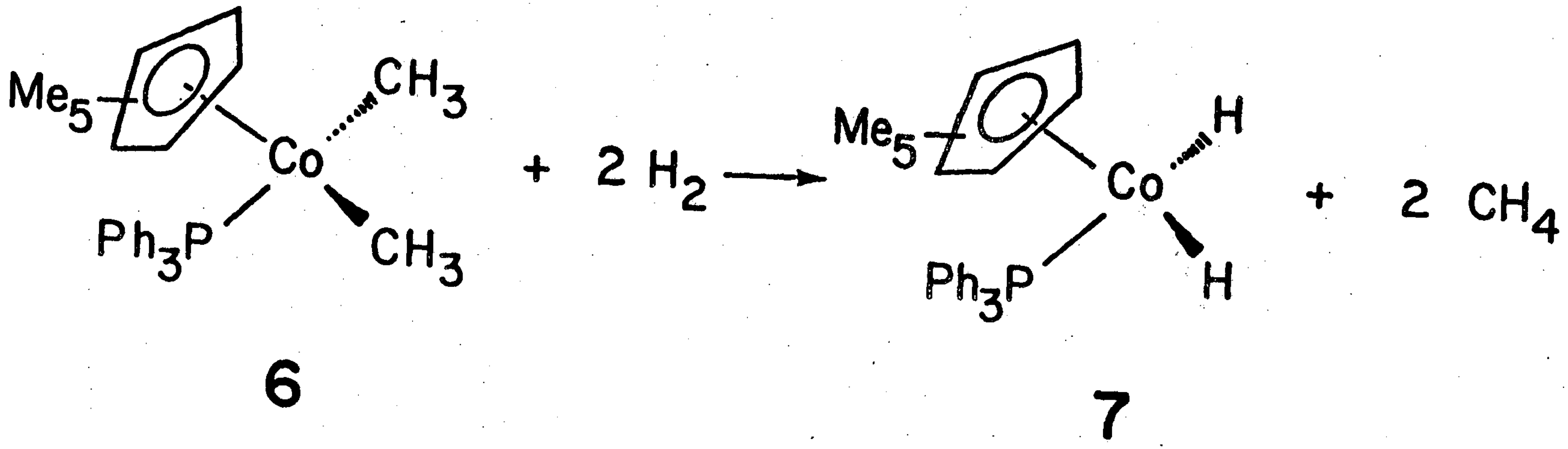
$$\mathbf{5} + \mathbf{3} \xrightarrow{\mathrm{PPh_3}} \mathbf{2} + 2\ \mathrm{CH_4}$$

Hydrogenolysis of Pentamethylcyclopentadienyl Derivatives of 1. As an alternative, therefore, we prepared (η^5-C_5Me_5)-$Co(PPh_3)(CH_3)_2$ (6), the pentamethylcyclopentadienyl analogue of 1. The synthesis of 6 did not parallel that of 1. Following the method of Yamazaki and Hagihara,[16a] we were unable to synthesize 6 from (η^5-C_5Me_5)$Co(PPh_3)I_2$ (18) and CH_3MgI in greater than 4% yield. We varied solvents and methylating agents but could not appreciably increase our yield — that is, until we tried acetonitrile. At first glance, this choice of solvent would seem inappropriate due to the facile reaction between Grignard reagents and acetonitrile. However, 6 is fairly insoluble in acetonitrile and 18 reacts much faster with CH_3MgI than does acetonitrile. Therefore, as 6 is formed, its insolubility shifts the course of the reaction towards dimethylcobalt formation. We have been able to isolate 6 in 61% yield using this method.

When 6 and excess H_2 were allowed to react in benzene-d_6 at 45°C, methane was again produced, along with a new material whose proton NMR spectrum [δ 1.77 (15 H, s), 6.90-7.10 (9 H, m), 7.70-7.83 (6 H, m), -16.54 (2 H, d, J_{P-H} =87 Hz)] was consistent with its formulation as (η^5-C_5Me_5)$Co(PPh_3)H_2$ (7) (Scheme IV). This material showed a strong absorption in the IR at 1908 cm^{-1}. This was assigned as ν_{M-H} on the basis of its shift to 1376 cm^{-1} when metal-bound hydrogen was replaced with deuterium.[14]

Evaporation of the benzene solvent left the dihydride as a green oil; however, this material decomposed rapidly in the absence of a hydrogen atmosphere. Supportive evidence that H_2 is lost rapidly from 7 came from the finding that in benzene

Scheme IV



solution, it easily yielded $(\eta^5\text{-}C_5Me_5)Co(PPh_3)D_2$ upon exposure to an atmosphere of deuterium gas. Although this property has prevented us from isolating 7 as a pure solid, benzene solutions of the dihydride are stable for relatively long periods of time under H_2. Complex 7 is one of the few mononuclear dihydridocobalt complexes which have been prepared.[15]

Other phosphine analogues of 7 [PPh_2Me (9), $PPhMe_2$ (10), PMe_3 (11)] can also be prepared. These dihydrides arise by the hydrogenolysis of the corresponding dimethyl species [PPh_2Me (12), $PPhMe_2$ (13), PMe_3 (14)], prepared by phosphine substitution of 6 (Table 1). Unfortunately, even with the more donating phosphines, these dihydrides also decomposed by loss of H_2 upon attempted purification.

Hydrogenolysis of 6 is also autocatalytic. However, this system provided an opportunity for testing the mechanism analogous to that proposed for 1 (Scheme V) by directly examining the interaction of dimethyl complex 6 with 7. Dialkyl 6 and dihydride 7 reacted readily at 45°C, as predicted by Scheme III, to give two moles of methane and numerous uncharacterized organometallic products. A steady-state analysis of the proposed mechanism gives the rate law shown in Scheme V. Under pseudo-first-order conditions -- excess 7 and PPh_3 -- the reciprocal of the pseudo-first-order rate constant k_{obsd} should depend upon the dihydride and PPh_3 concentrations (Scheme V). In the presence of excess 7 and PPh_3, the rate of disappearance of 6 (as determined by ^1H NMR spectroscopy) showed good pseudo-first-order kinetics. The rate constant k_{obsd} for each reaction was, therefore,

Table 1. ^{1}H NMR Data for Cobalt Dihydrides and Dialkyls[a]

$(C_5Me_5)Co$	Me_5C_5[b]	PPh[c]	PMe[d]	CoMe[e]	CoH[f]
$(PPh_3)Me_2$ 6	1.32	7.03, 7.50		0.11	
$(PPh_3)H_2$ 7	1.77	7.00, 7.76			−16.54
$(PPh_2Me)Me_2$ 12	1.40	7.05, 7.36	1.53	0.08	
$(PPh_2Me)H_2$ 9	1.85	7.03, 7.56	1.62		−16.60
$(PPhMe_2)Me_2$ 13	1.36	7.02, 7.24	1.16	0.03	
$(PPhMe_2)H_2$ 10	1.87	7.10, 7.51	1.29		−16.76
$(PMe_3)Me_2$ 14	1.56		0.95	−0.12	
$(PMe_3)H_2$ 11	2.00		1.05		−16.99

[a] C_6D_6 solvent. [b] broad singlets. [c] center of multiplets. [d] doublets, (10, 12, 13) J=8 Hz, (9,11, 14) J=9 Hz. [e] doublets, J=6 Hz. [f] broad doublets, (9) J=85 Hz, (10) J=90 Hz, (11) J=93 Hz.

Scheme V

$$\underset{\mathbf{6}}{(C_5Me_5)Co(PPh_3)Me_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{8}}{(C_5Me_5)CoMe_2} + PPh_3$$

$$\underset{\mathbf{7}}{(C_5Me_5)Co(PPh_3)H_2} + \mathbf{8} \xrightarrow{k_2} 2\,CH_4 + (C_5Me_5)Co_n(PPh_3)_m$$

$$\text{Rate} = \frac{k_1 k_2 [\mathbf{7}]}{k_{-1}[PPh_3] + k_2[\mathbf{7}]}\,[\mathbf{6}]$$

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}[PPh_3]}{k_1 k_2 [\mathbf{7}]}$$

determined and plotted according to the equation in Scheme V. As shown in Figure 2, the predicted linear behavior is observed. From the slope and intercept of the plot, we calculate $k_1 = 1.83 \times 10^{-4}$ sec^{-1} and $k_{-1}/k_2 = 1.44$. Thus (kinetically at least), the unsaturated intermediate (8) exhibits a comparable affinity for PPh_3 and dihydride 7.

Scheme V and the corresponding rate law posit a specific level of unsaturation of each reacting partner in the rate-determining step associated with microscopic rate constant k_2; i.e., the dialkyl reactant is coordinatively unsaturated, whereas the hydride is saturated. The rate law rules out the possibility that both reactants are unsaturated; reversible dissociation of phosphine from both 7 and 6, followed by reaction of the two unsaturated species so produced, would give an inverse squared dependence upon the concentration of phosphine, which is not observed. That it is the dialkyl complex, rather than the dihydride, which is unsaturated, is consistent with the following observations: (1) substitution of PPh_3 by more electron-donating phosphines occurs much more rapidly in 1 and 6 than in 7; (2) the dimethyl complexes 6 and 12-14 hydrogenolyze more slowly as the electron-donating ability of the bound phosphine increases, (e.g., hydrogenolysis of 14 is slower than 6 by a factor of about 100); (3) the rhodium analogue, $(\eta^5\text{-}C_5Me_5)Rh(PPh_3)(CH_3)_2$ (15),[16] hydrogenolyzes approximately 500 times more slowly than 6 to yield $(\eta^5\text{-}C_5Me_5)Rh(PPh_3)H_2$ (16) and methane; and (4) 1 reacts rapidly with a coordinatively saturated dihydride, $(\eta^5\text{-}C_5H_5)_2MoH_2$, to give methane.

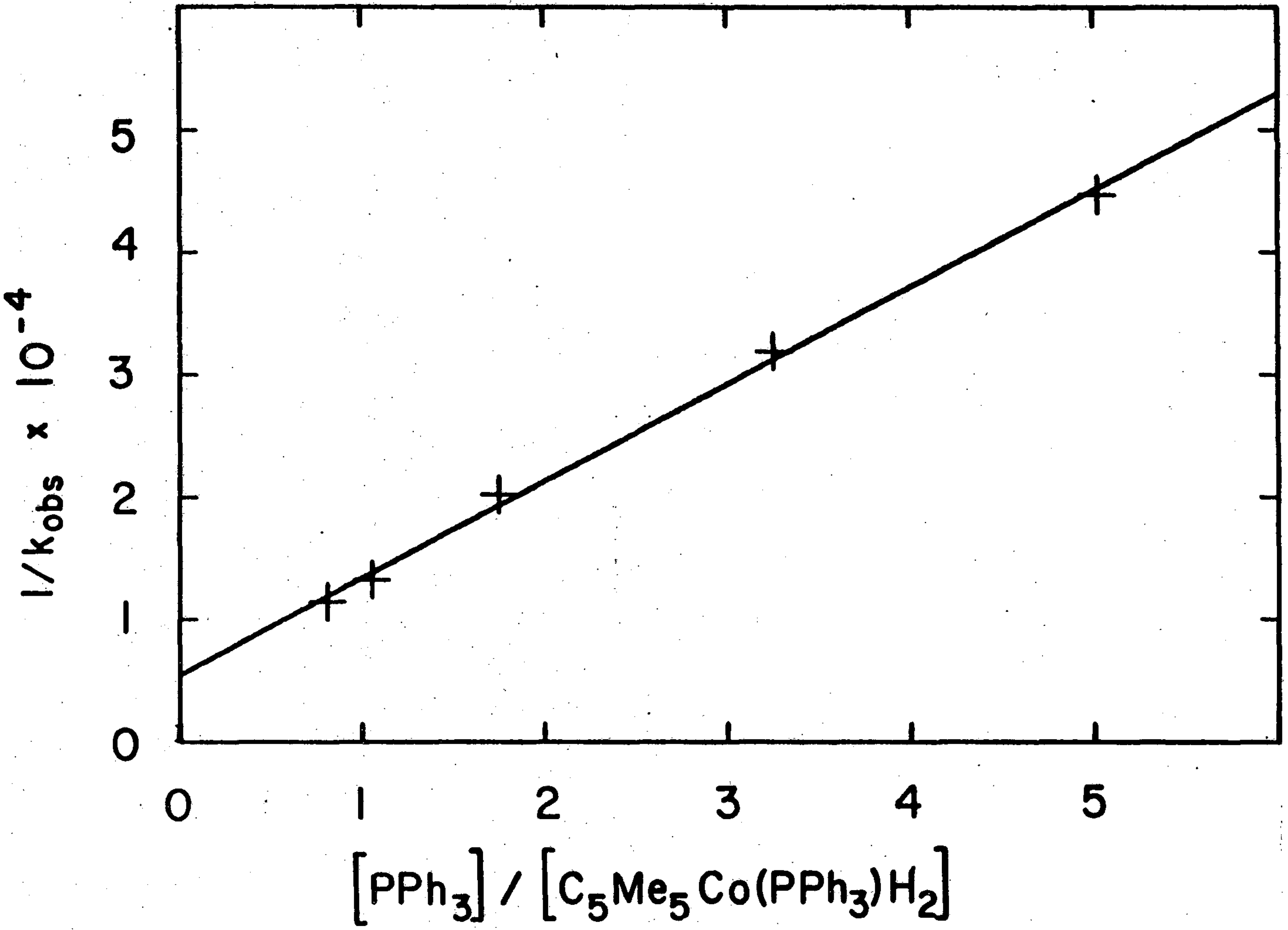


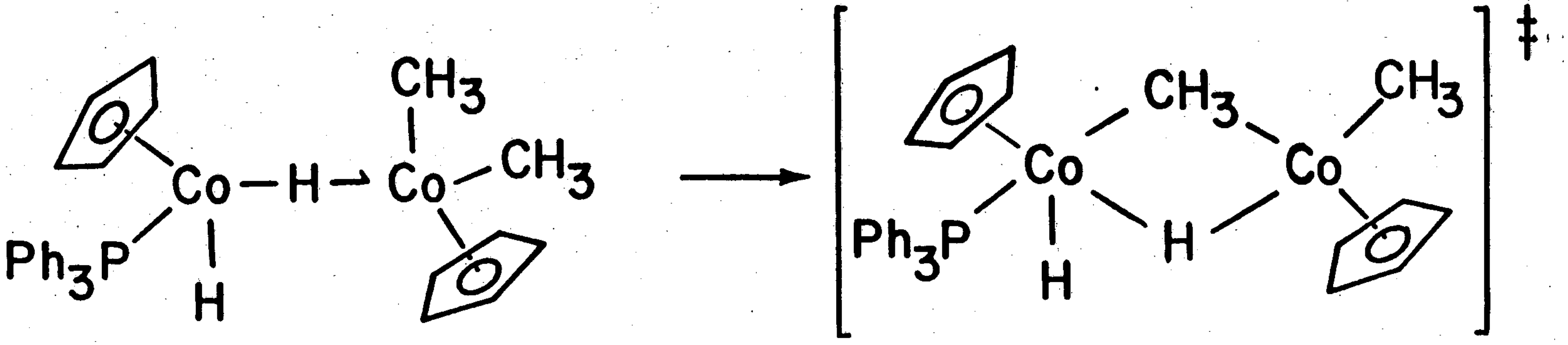
Figure 2. Dependence of the pseudo-first-order rate constant for reaction of dimethyl 6 and dihydride 7 (measured in the presence of excess 7 and PPh_3) upon the ratio of PPh_3 to 7.

Conclusion

Even though the inaccessibility of the formal Co(V) oxidation state prevents oxidative addition of H_2 to cyclopentadienylcobalt(III) derivatives, they still undergo facile hydrogenolysis. A critical step in this hydrogenolysis involves a reaction between a metal alkyl and a metal hydride. The lack of metal hydride reagent present at the beginning of the hydrogenolysis reaction of 1 and 6 leads to an autocatalytic mechanism; this produces hydride 5 and 7, respectively, as the hydrogen carrying species. In the case of the C_5Me_5 derivatives, one can observe the direct reaction between dialkyl and dihydride species.

As in other reactions involving interaction of a metal hydride with a coordinatively unsaturated alkyl,[6] we do not yet know the precise structure of the intermediate involved in the M-R/M-H step, but we assume interaction initially involves entry of the hydride end of the M-H bond into the vacant coordination sphere of the dialkyl, forming a bridging hydride. This seems likely, since on the basis of the relative rate constant ratio k_2/k_{-1} measured in our kinetic study, PPh_3 reacts with the unsaturated intermediate 8 only slightly more rapidly than does the dihydride 7. Perhaps after the dihydride enters the coordination sphere of the unsaturated dimethyl cobalt to give 19 (Scheme VI), this species rearranges to a doubly bridging species 20, similar to the one proposed for reversible metal to metal methyl transfer in these dimethyl cobalt complexes.[17] After a pairwise exchange of a H for a CH_3 group, we envision the

Scheme VI



19 20

$$20 \longrightarrow \mathrm{CpCo(PPh_3)(CH_3)H} + \mathrm{CpCo(CH_3)H}$$

21 22

formation of mononuclear alkylhydridocobalt species **21** and **22**. These complexes should undergo rapid reductive elimination to yield methane. The precise structure of these intermediates and how reductive elimination occurs is speculative at this point. In any case, our results reinforce the idea that M-H/M-R reactions are relatively facile and binuclear steps should be given serious consideration as alternatives to mononuclear steps in homogeneous catalytic processes involving C-H bond formation.

Experimental Section

General. All manipulations of oxygen or water sensitive materials were conducted under a pre-scrubbed recirculating atmosphere of nitrogen in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or using standard Schlenk or vacuum line techniques.

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian EM-390 90 MHz spectrometer or a 250 MHz high field Fourier Transform instrument. The high field system consisted of a Cryomagnets Inc. magnet, Nicolet Model 1180 data collection systems and electronics assembled by Mr. Rudi Nunlist (U. C. Berkeley). All chemical shifts are reported relative to tetramethylsilane. Infrared (IR) spectra were recorded on a Perkin-Elmer 283 grating spectrometer using NaCl solution cells.

Gas-liquid chromatography (GC) analyses were performed using a Perkin-Elmer 3920 gas chromatograph equipped with a flame ionization detector and interfaced with a Spectra Physics Autolab System 1 computing integrator. Gas samples were handled in a gas-tight Pressure Lok syringe (Precision Sampling Corp). The column used was a 9' x 1/8" stainless steel column packed with Porapak Q (Waters Assoc) that was heated to 67°C for the analysis.

Mass spectroscopic (MS) analyses were conducted on an AEI MS-1 spectrometer interfaced with a Finnegan 2300 Data System. Elemental analyses were performed by the U. C. Berkeley analytical facility.

Preparative column chromatography was performed on silica gel 60 that was degassed before being taken into the dry box. All columns were packed and chromatograms run under air-free conditions.

Benzene-h_6 and -d_6, tetrahydrofuran-h_8 and -d_8, diethyl ether, hexane and toluene were purified before use by vacuum transfer from sodium-benzophenone ketyl. Prior to vacuum transfer from the ketyl, hexane was stirred continuously over concentrated sulfuric acid for 2 x 12 hours; stirred with saturated potassium permanganate in 10% sulfuric acid for 2 x 6 hours; washed in sequence with distilled water, saturated sodium carbonate solution, and distilled water; and dried over $MgSO_4$. Methylene chloride was distilled from CaH_2 under nitrogen. Chloroform-d_1 and 1,4-cyclohexadiene were vacuum transferred from molecular sieves under nitrogen. Acetonitrile was dried over molecular sieves and distilled under nitrogen from P_2O_5.

PPh_3 (MCB) was recrystalized from hexane, and PMe_3, $PPhMe_2$, and PPh_2Me (Strem) were redistilled and stored under nitrogen. 1,[9] 2,[18] 17,[13] $(\eta^5-C_5Me_5)Co(PPh_3)I_2$ (18),[19] and $(\eta^5-C_5Me_5)$-

$Rh(PPh_3)Cl_2$[16] were prepared by literature methods. H_2, D_2 and ethylene (Matheson) were used as received.

NMR tube reactions. Experiments carried out in NMR tubes were run as follows: a 5 mm NMR tube, fused to a 14/20 ground glass joint, was loaded with solid starting materials in the dry box. The tube was capped with a teflon vacuum stopcock and taken from the dry box to a high vacuum line, where the materials were degassed, and solvent was added by vacuum transfer. Any other volatiles, such as hydrogen, were then added by expansion of the gas into the NMR tube, which was cooled to −196°C. The tube was flame sealed and thawed. Only deviations from this routine will be further noted.

Constant temperatures were maintained using a Precision Scientific circulating water bath.

Reaction of 1 and H_2. The NMR tube procedure was followed as above using 1 (50.0 mg, 0.012 mmol), ferrocene (13.4 mg, 0.0072 mmol) as an internal standard, benzene-d_6 (0.728 mL) and H_2 (2.91 atm, 0.024 mmol). The reaction was heated at 45°C in a constant temperature bath, and the course of the reaction was followed by ^1H NMR. After 132 min, the reaction was 95% complete, yielding 2 (δ 4.54 ppm) (39% yield) and methane (δ 0.30 ppm).

A similar reaction run in THF-d_8 gave similar results.

Reaction of 1 and H_2 to quantify the yield of methane. 1 (29.8 mg, 0.00716 mmol) was added to a 25 mL round bottomed flask equipped with a stirring bar and a vacuum stopcock. The flask was evacuated, one mL benzene-d_6 was transferred in, and H_2

(0.079 mmol, 0.58 atm) was added to the reaction mixture cooled to −196°C. After sealing, the reaction solution was stirred and heated at 50°C in an oil bath. After three hours, the reaction mixture was frozen, and the volatiles were collected with a Toepler pump through two −78° traps. To insure complete collection of the product gases, the mixture was taken through three freeze/pump/thaw cycles. Ethylene (0.1065 mmol) was added to the reaction gases as an internal standard via a Toepler pump. The total gas mixture was then recycled through a −78°C trap to ensure good mixing. A GC analysis yielded two moles (1.99 ± 0.02) of methane per mole of 1.[20] No ethane was detected by GC or MS. The methane and ethylene were recycled through a −196°C trap for three hours to remove the ethylene. A mass spectrum of the resulting methane yieded 100% CH_4 with no D incorporation from the solvent. MS: m/e (70 and 15 eV); 17 (1%), 16 (100%).

Reaction of 1 and D_2. 1 (20.5 mg, 0.0492 mmol) was added to a 25 mL round bottomed flask equipped with a stirring bar and vacuum stopcock. The flask was evacuated, one mL benzene was transferred in, and D_2 (0.53 mmol, 0.43 atm) was added to the reaction mixture cooled at −196°C. The reaction solution was stirred and heated to 50°C. After three hours, the reaction mixture was frozen and the volatiles collected with a Toepler pump through two −196°C traps. To ensure complete collection of the product gases, the solution mixture was taken through three freeze/pump/thaw cycles. The collected gas was analyzed by MS to give 98 ± 3% CH_3D. MS: m/e (50 eV); 17 (100.0%), 16 (78.7%), 15(26.6%), 14 (12.5%), 13 (6.6%), 12 (2.5%), corrected for natural abundance of ^{13}C.

The percentage of CH_3D was calculated by comparison of the product MS with that of an authentic CH_3D sample, run immediately afterward to minimize instrument fluctuation. CH_3MgI (Mg, 248 mg; CH_3I, 0.90 mL) in ether (12 mL) was transferred by cannula into a three neck round bottomed flask equipped with a septum, glass stopper and a vacuum stopcock. Prior to the use of a manifold on the vacuum line, the manifold was evacuated, filled with D_2O vapors for one hour, evacuated and refilled with D_2O for an additional 45 min to free the surface of the glass from protic sites. D_2O (0.11 mL, 0.60 equivalents) was vacuum transferred into the flask with the Grignard solution. Less than one equivalent of D_2O was used to ensure maximum isotopic purity of the resulting methane. Upon thawing, CH_3D was liberated and Toepler pumped through two liquid nitrogen traps. MS: m/e (50 eV); 17 (100.0%), 16 (77.4%), 15 (24.9%), 14 (11.4%), 13 (6.3%), 12 (2.4%), corrected for ^{13}C natural abundance.

Radical trapping experiment. $(\eta^5\text{-}C_5H_5)Co(PPh_3)(CD_3)_2$ ($1\text{-}d_6$)[15] (20 mg, 0.047 mmol) was added to a 44 mL glass bomb (with a built-in vacuum stopcock) in the dry box. 1,4-Cyclohexadiene (0.045 mL, 0.48 mmol) and benzene (0.455 mL) were added to the bomb by syringe. The bomb was removed from the dry box, and the reaction mixture was put through three freeze/pump/thaw cycles to degas the solution. D_2 (1.03 mmol, 0.57 atm) was added, and the reaction mixture was heated at 45°C. After 16 hours, the mixture was frozen, and the volatiles were collected with a Toepler pump through two −196°C traps. To ensure complete collection of the product gases, the mixture was taken through three freeze/pump/thaw cycles. The collected gas was analyzed by MS to give methane as 99 ± 3% CD_4. MS: m/e (15 eV); 20 (100.0%), 19 (3.4%), corrected for ^{13}C natural abundance.

The ratio of CD_4 to CD_3H was calculated by comparing the MS of the product methane with the amount of CD_4 expected from total deuterium incorporation with the D_2 (97.5% D) used.

Reaction of 1, H_2 and added PPh_3. A stock solution of 1 (125 mg, 0.300 mmol) in benzene-d_6 (3.00 mL) with TMS (13.5 uL) as an internal standard was prepared in the dry box. To each of five NMR tubes with joints, the respective amounts of PPh_3 (Table 2) were weighed on an analytical balance and, therefore, added outside of the dry box. The tubes were then brought into the dry box for further manipulation. 2 (0.006 g, 0.51 mmol) was added to tube 5. 0.500 mL of stock solution was syringed into each NMR tube. Each tube was then topped with a vacuum stopcock and taken from the dry box to the vacuum line. After cooling to -196°C, the tubes were evacuated. H_2 (0.155 mmol, 1.89 atm) was expanded into the tubes, sealed and stored at -196°C until the experiment began. The reactions (followed by ^1H NMR on the U. C. Berkeley 250 MHz spectrometer) were heated at 45°C in a circulating constant temperature bath. When the tubes were to be placed in the spectrometer, they were quenched in ice water and centrifuged for one to two minutes before the spectrum was taken. The rate of the reaction was monitored by integrating the methyl resonance of 1 versus the resonance of the TMS standard. The data is plotted in Figure 1.

Reaction of 1 and $(\eta^5-C_5H_5)_2MoH_2$ (17). The NMR tube

Table 2. Reaction of 1, H_2 and additives.

Tube	[1][a]	PPh_3 mg	[PPh_3][a]	2 mg	[2]
1	0.100	0	0	0	0
2	0.100	14.4	0.100	0	0
3	0.100	3.6	0.025	0	0
4	0.100	7.2	0.050	0	0
5	0.100	14.4	0.100	6.0	0.017

[a] Molarity.

procedure was followed using **1** (25 mg, 0.060 mmol), **17** (14 mg, 0.061 mmol), toluene (6.0 µl, 0.056 mmol) as an internal standard, and benzene-d_6 (0.448 mL). N_2 (0.43 atm) was added as an inert gas and the tube was sealed. The reaction mixture was heated at 45°C in a circulating bath. By NMR, **1** was 93% reacted in 36 min. Although the organometallic products were not identified, methane (δ 0.30 ppm) was the organic product of the reaction.

Preparation of $(\eta^5\text{-}C_5Me_5)Co(PPh_3)(CH_3)_2$ (6). $(\eta^5\text{-}C_5Me_5)$-$Co(PPh_3)I_2$ (1.662 g, 0.234 mmol) and CH_3CN (45 mL) were added to a 100 mL round bottomed flask equipped with a stirring bar in the dry box. The flask was cooled to −40°C in the dry box freezer. Upon its removal, CH_3MgI (5.0 mL of a 1.5 M solution in ether), also cooled to −40°C in the dry box freezer, was added dropwise to the stirring slurry over a period of 3-4 min. The reaction mixture turned orange/brown, and at the end of the addition, an evolution of gas (perhaps methane from the protonation of CH_3MgI) occurred. The flask was returned to the freezer for ten minutes; it was removed, and the red precipitate was filtered. The flask was again put back in the freezer for an hour, and again the precipitate was filtered. The combined solid from both filtrations was dissolved in toluene and filtered to remove any magnesium salts. Most of the toluene was removed in vacuo, and hexane was added. The solid was crystallized from this toluene/hexane mixture. The crystals were filtered, washed with 2 x 10 mL portions of hexane, and placed on a vacuum line to remove any traces of solvent. It was obtained in a 61% yield

(693 mg) as red crystals, m.p. 148. For ^1H NMR data, see Table 1. Anal: Calcd for $C_{30}H_{36}CoP$: C, 74.06; H, 7.46. Found: C, 74.24; H, 7.61.

Reaction of 6 and H_2. The NMR tube procedure was followed using 6 (17 mg, 0.035 mmol), toluene (5.0 µL) as an internal standard and benzene-d_6 (0.50 mL). H_2 (2.9 atm, 0.24 mmol) was expanded into the reaction mixture, and the tube was sealed. After four hours, NMR analysis showed methane and an organometallic product (88%), whose spectrum (see text) was consistent with its assignment as 7. The dihydride could not be isolated using column chromatography, sublimation or crystallization. Benzene solutions of 7 in a sealed system were stable for at least eight hours at 45°C. The IR absorption at 1908 cm^{-1} (v_{M-H}) disappeared, and a new band at 1376 cm^{-1} (v_{M-D}) appeared when H_2 was removed from a frozen solution of 7, D_2 added, and the solution stirred at room temperature for thirty min.

Kinetic Experiments with 6, 7 and PPh_3. A stock solution (#1) of 6 was prepared by dissolving 6 (35 mg, 0.072 mmol) in benzene-d_6 in a 10 mL volumetric flask also containing neohexane (4.0 µL, 0.030 mmol) as an internal standard. A second stock solution (#2) of 7 was prepared in the following way. 6 (304 mg, 0.0625 mmol) was first dissolved in benzene-d_6 (2.10 mL) in a 25 mL glass bomb, containing a stirring bar, in the dry box. This solution was removed from the dry box and placed on a vacuum line, where it was immersed in a −196°C bath and evacuated. H_2 (2.29 atm, 2.55 mmol) was allowed to expand into the evacuated bomb. The reaction mixture was then stirred for 20 hours.

Five NMR tubes with fused joints were prepared containing differing amounts of PPh_3 (Table 3) and taken into the dry box. Stock solution #1 (125 µL, 0.0164 M) was added to each of the tubes. The benzene solutions were then frozen, and stock solution #2 and benzene-d_6 (Table 3) were added to the tubes by syringe. The tubes were topped with a vacuum stopcock, removed from the dry box, cooled to −196°C, evacuated, and sealed. The $[PPh_3]/[7]$ ratios were measured by NMR, by integrating the ortho protons of free PPh_3 and the ortho protons of bound phosphine in **7**. For the kinetic experiments, each tube was immersed in a circulating constant temperature bath, held at 45°. The rate of the reaction was monitored by integrating the cobalt dimethyl resonance of **6** versus the methyl resonances of the neohexane internal standard. For each measurement, a tube was cooled in an ice water bath and centrifuged for one to two minutes before being placed in the probe of the NMR spectrometer. The spectrum was recorded and the tube was replaced in the bath. For the observed rate constants, see Table 3.

Phosphine complexes $(\eta^5\text{-}C_5Me_5)Co(PR_3)(CH_3)_2$. A typical preparation of **12** ($PR_3=PPh_2Me$) is given as follows: **6** (100 mg, 2.04×10^{-4} mol) and toluene (10 mL) were added to a 25 mL round bottomed flask with a stir bar in the dry box. PPh_2Me (41.5 mg, 2.07×10^{-4} mol) was added dropwise to the stirring solution. After stirring for two hrs, the solvent was removed in vacuo. The residue was crystallized from toluene/pentane at −40°C to give red crystals in 88% yield (70.8 mg), m.p. 139. Anal: Calcd

Table 3. Kinetic experiments between 6 and 7, in the presence of excess 7 and PPh_3.

Tube	#2[a]	C_6D_6[a]	PPh_3[b]	$[PPh_3]/[7]$	k_{obs} (s^{-1})
1	300	125	23.2	1.76	4.94×10^{-5}
2	300	125	46.4	3.26	3.14×10^{-5}
3	300	125	91.3	5.03	2.24×10^{-5}
4	300	125	11.5	1.06	7.54×10^{-5}
5	300	0	11.5	0.812	8.73×10^{-5}

[a] uL. [b] mg.

for $C_{25}H_{34}CoP$: C, 66.29; H, 8.90. Found: C, 64.79; H, 8.64. The other dimethyl complexes **13** and **14** were prepared via a similar procedure and characterized by ^1H NMR. For ^1H NMR data of all the dimethyl complexes, see Table 1.

Phosphine complexes $(\eta^5\text{-}C_5Me_5)Co(PR_3)H_2$. A typical preparation of **9** ($PR_3=PPh_2Me$) is as follows: **12** (27 mg, 6.36 x 10^{-5} mol), ferrocene (8 mg) as an internal standard, and benzene-d_6 (0.50 mL) were placed in an NMR tube, fused to a ground glass joint, and topped with a vacuum stopcock in the dry box. The reaction solution was removed from the box, cooled to -196°C, and evacuated on a vacuum line. H_2 (2.6 atm, 2.2 x 10^{-4} mol) was expanded into the tube, and the tube was sealed. After 12 days at room temperature, the reaction was 93% complete yielding **9** (NMR yield: 96%). The reaction tube was returned to the dry box, broken open, and the contents were chromatographed on alumina (V). The dihydride decomposed on the column. Crystallization from hexane was attempted with another batch of **9**. Upon removal of the solvent in vacuo, the dihydride decomposed. The other dihydrides were prepared in a similar way. For ^1H NMR data on **9**, **10** and **11**, see Table 1.

Reaction of $(\eta^5\text{-}C_5Me_5)Rh(PPh_3)(CH_3)_2$ (15) and H_2. **15** (10.0 mg, 1.89 x 10^{-5} mol) and benzene-d_6 were added to an NMR tube, fused to a ground glass joint, and topped by a vacuum stopcock in the dry box. After the reaction solution was removed from the dry box, it was cooled to -196°C and evacuated on a vacuum line. H_2 (1.9 atm, 1.6 x 10^{-4} mol) was expanded into the tube and the tube was sealed. After 24 hrs at room temperature and 80 min at

60°C, by NMR a reaction had started to occur (10%) giving methane and what has subsequently been identified as $(\eta^5\text{-}C_5Me_5)Rh(PPh_3)H_2$ (**16**). After 36 days at room temperature and 28 hrs at 60°C, the reaction was 66% completed, and **16** has grown in (NMR yield: 83%).

Preparation of $(\eta^5\text{-}C_5Me_5)Rh(PPh_3)H_2$ (16). **16** can be synthesized by the following independent method. $(\eta^5\text{-}C_5Me_5)$-$Rh(PPh_3)Cl_2$ (1.50 g, 2.63 mmol) and THF (100 mL) were added to a 250 mL round bottomed flask with a stir bar in the dry box. $LiEt_3BH$ (5.5 mL of 1 M solution in THF) was added dropwise to the stirring slurry. After stirring for three hrs, the THF was removed in vacuo. The residue was taken up in benzene and filtered through silica gel. The benzene was removed in vacuo, and the resulting solid was recrystallized from ether to give tan crystals, m.p. 154. ^1H NMR (C_6D_6): δ 1.87 (broad s, C_5Me_5), 7.01 and 7.73 (two m, PPh_3), -13.00 (dd J=39, 28 Hz, RhH_2). IR (C_6H_6): 2000 cm^{-1} (ν_{Rh-H}).

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20) The response factors were determined by injecting known amounts of the gases on the aforementioned column and correlating the amounts with the respective peak integrations.

Chapter II

C-H ACTIVATION IN COMPLETELY SATURATED HYDROCARBONS: FIRST DIRECT OBSERVATION OF M + R-H $\longrightarrow$ M(R)(H)

Introduction

One of the most intriguing goals of homogeneous organotransition metal chemistry is the possibility of carrying out selective chemical transformations on, or functionalizing, very unreactive materials such as saturated hydrocarbons.[1] The longest-known examples of intermolecular C-H activation in saturated hydrocarbons are those involving the use of soluble platinum salts at relatively high temperatures,[2] and more recently porphyrin complexes.[3] However, in none of these cases has it been possible to detect intermediate hydridoalkyl metal complexes formed by direct oxidative addition to a C-H bond, and in some there is evidence for free radical mechanisms.[3f,4]

There are a number of cases known involving <u>intramolecular</u> oxidative addition to unactivated C-H bonds.[5] The reaction of unsaturated transition metal fragments with the C-H bonds of their own bound phosphine ligands is not uncommon. In fact, α- and β- elimination are common examples of intramolecular oxidative additions. However, in most of these systems there is no reaction with C-H bonds not present in the same molecule as the metal center. In recent work, it was observed that reactive species generated from certain Ir and Re precursors react with completely saturated hydrocarbons.[6] However, both of these systems involve multiple hydrogen-atom loss in the hydrocarbon, and require an added alkene as hydrogen acceptor. Direct, one-stage oxidative addition (eq. (1)) has been observed so far only at C-H bonds which can be considered at least weakly activated,[7] either because they are aryl or vinyl C-H, or because they are adjacent to activating groups or atoms (e.g., aryl, carbonyl, cyano, R_3Si, or the metals themselves, as in α- or β-elimination). We now wish to discuss the discovery of an

$$M + R\text{-}H \longrightarrow M(R)(H) \qquad (1)$$

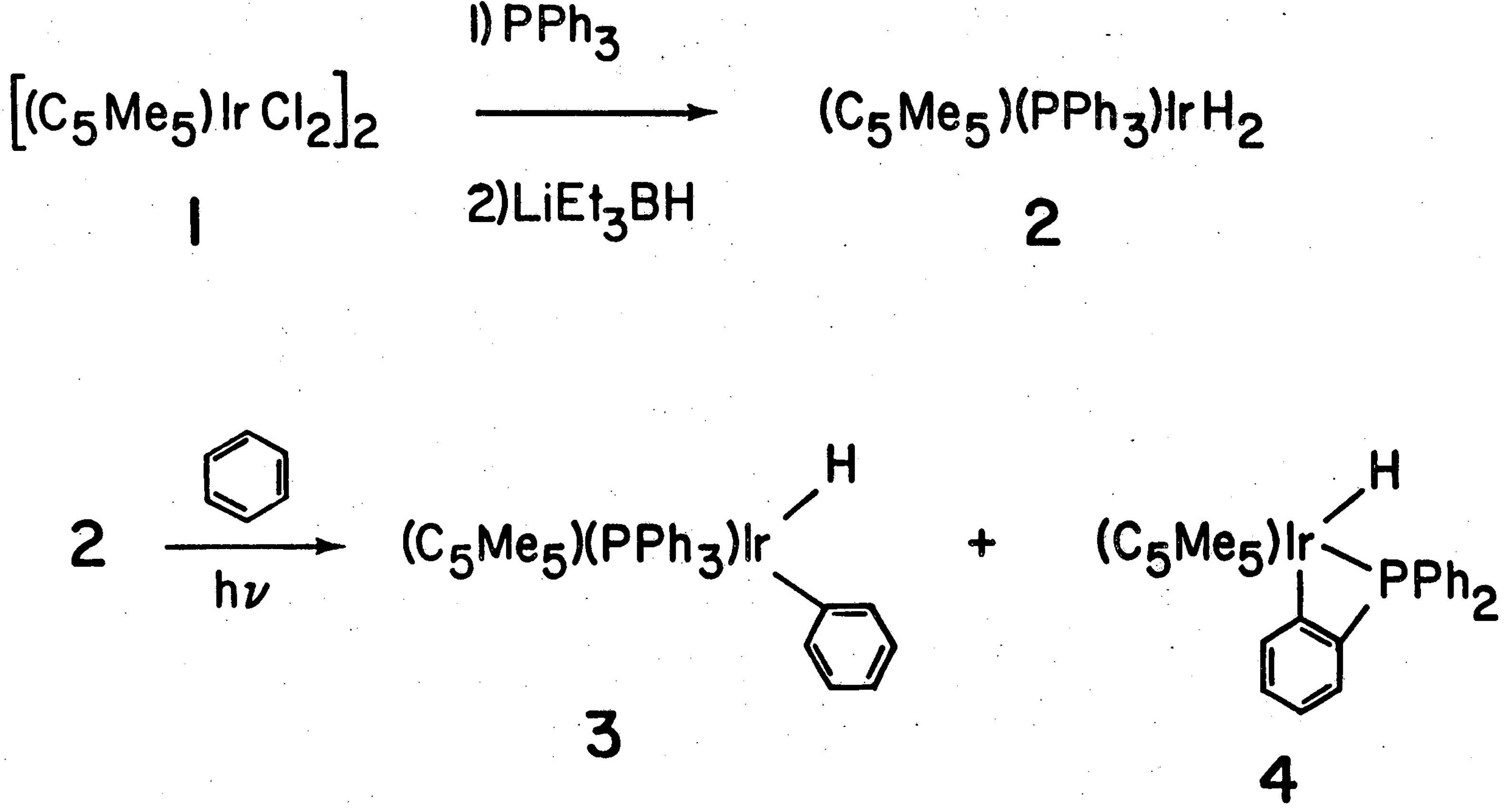
organotransition metal system capable of <u>intermolecular oxidative addition to single C-H bonds in saturated hydrocarbons</u>, leading to hydridoalkylmetal complexes in high yield at room temperature in homogeneous solution.[8]

Results and Discussion

Synthesis and reactions of $(\eta^5\text{-}C_5Me_5)Ir(PPh_3)H_2$ (2). The initial experiments centered around the previously unknown iridium dihydride 2. As shown in Scheme I, complex 2 was prepared in 42% yield by treatment of the dichloride dimer 1[9] with PPh_3, followed by two equivalents of $LiEt_3BH$. Irradiation (λ_{max} = 275 nm; high pressure Hg lamp, pyrex filter) of this material in benzene resulted in extrusion of dihydrogen. The loss of hydrogen upon the photolysis of transition metal di- and polyhydrides is a well documented process.[7a,b;10] The resulting organometallic products were the hydridophenyl complex 3 and the ortho-metallated complex 4 in a ratio of 47:53, respectively (Scheme I).

These materials were formed presumably via the

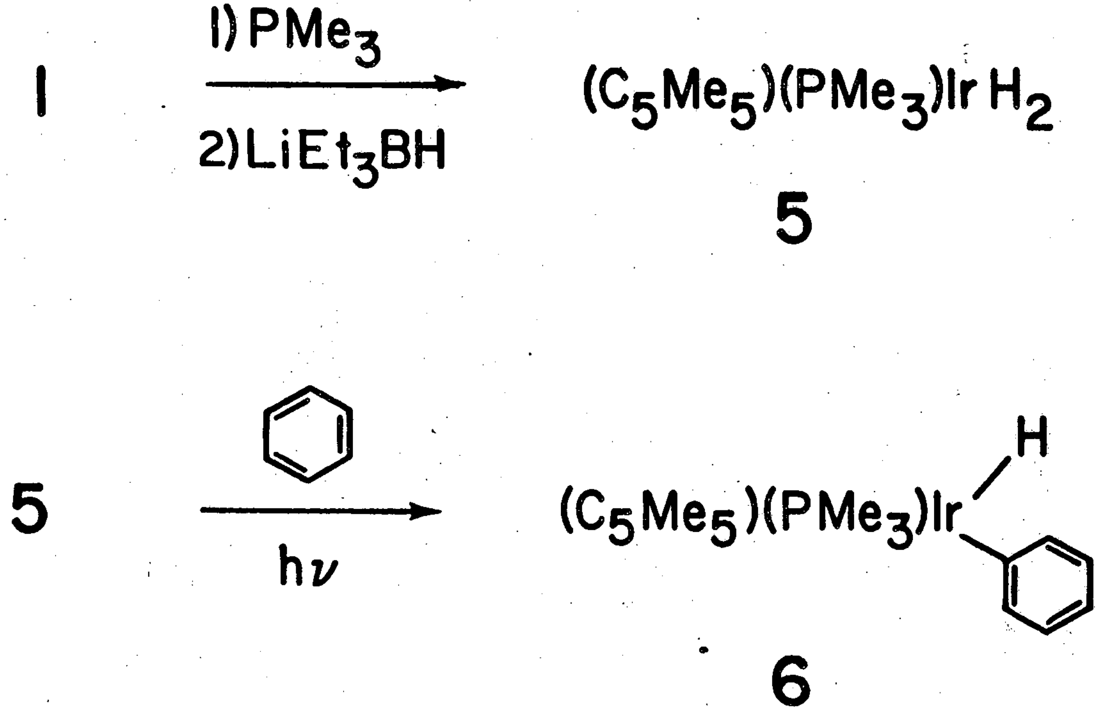
Scheme I


$[(C_5Me_5)IrCl_2]_2$
1
1) PPh_3
2) $LiEt_3BH$
$(C_5Me_5)(PPh_3)IrH_2$
2
2
$h\nu$
$(C_5Me_5)(PPh_3)Ir$
H
3
+
$(C_5Me_5)Ir$
H
PPh_2
4

coordinatively unsaturated intermediate (η^5-C_5Me_5)Ir(PPh_3). Complex 3 is the result of an intermolecular reaction of the intermediate with the C-H bonds in benzene, whereas complex 4 results from an intramolecular C-H bond activation. Thus, even in the presence of a bound triphenylphosphine group, there was considerable intermolecular reaction with the benzene solvent. Irradiation in other solvents (e.g., acetonitrile, cyclohexane) gave either all or mostly the ortho-metallated product 4. However, in the case of cyclohexane, a significant amount (30%) of a new hydride was also formed in this reaction. Its ^1H NMR in benzene-d_6 showed a broad singlet at δ 1.71 for the C_5Me_5 group (15 H), broad resonances from δ 1.50-2.30 (11 H), multiplets at 7.00 and 7.57 for the bound PPh_3, and a doublet (J=35 Hz) at δ -17.91 for the new hydride (1 H). This NMR data suggests that this material is the intermolecular C-H activation product, (η^5-C_5Me_5)Ir(PPh_3)(H)C_6H_{11}. Thus, even in the presence of a proximate aromatic group (PPh_3), it appears to be possible for the unsaturated iridium center to undergo intermolecular reaction with a saturated hydrocarbon.

Synthesis and reactions of (η^5-C_5Me_5)Ir(PMe_3)H_2 (5). In an effort to make ortho-metallation less favorable, we prepared the complex analogous to 2, containing a trimethylphosphine ligand in place of the PPh_3 group (5). As in the synthesis of 2, treatment of 1 with trimethylphosphine, followed by $LiEt_3BH$, gave 5 in 54% yield.[11] Irradiation of 5 in benzene resulted in clean loss of H_2 and attack on the solvent, leading to the hydridophenyliridium complex 6 as shown in Scheme II. We detected only the

Scheme II



intermolecular product; no evidence for any intramolecular reaction was found.[12] Next, the irradiation was carried out in cyclohexane, a compound with completely unactivated C-H bonds. A new material was formed (90% yield at 68% conversion of starting material after 5.5 hr irradiation) in which both the PMe_3 and C_5Me_5 ligands were clearly intact. Although thermally stable at room temperature, it was very sensitive both to air and chromatography supports (reductively eliminating cyclohexane in certain cases, which will be discussed later). Purification was finally effected, although with significant loss of material, by rapid chromatography using 4% THF/cyclohexane eluent on alumina III under air-free conditions, followed by evaporation of solvent. The structure of this material was confirmed as that of $(\eta^5\text{-}C_5Me_5)(PMe_3)$(hydrido)cyclohexyliridium(III) (7, Scheme III) on the basis of spectral data (Table 1) and chemical conversion to the more sparingly soluble bromocyclohexyl complex 9 (Scheme IV). Thus, the intermediate formed on irradiation of 5, presumably $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)$, reacts cleanly with unactivated C-H bonds.

An interesting feature of these alkyl hydrides can be seen in examining the ^{13}C NMR spectrum of 7. With four different substituents on the iridium, it is a chiral center. Thus, the β and γ carbon atoms form pairs of diastereomeric carbon atoms, and two signals appear for each set of carbons in the ^{13}C NMR spectrum of 7 (Table 1).

Irradiation of 5 in neopentane solvent gives, after 5.3 hr irradiation time (80% NMR yield after 83% conversion), a new

Scheme III

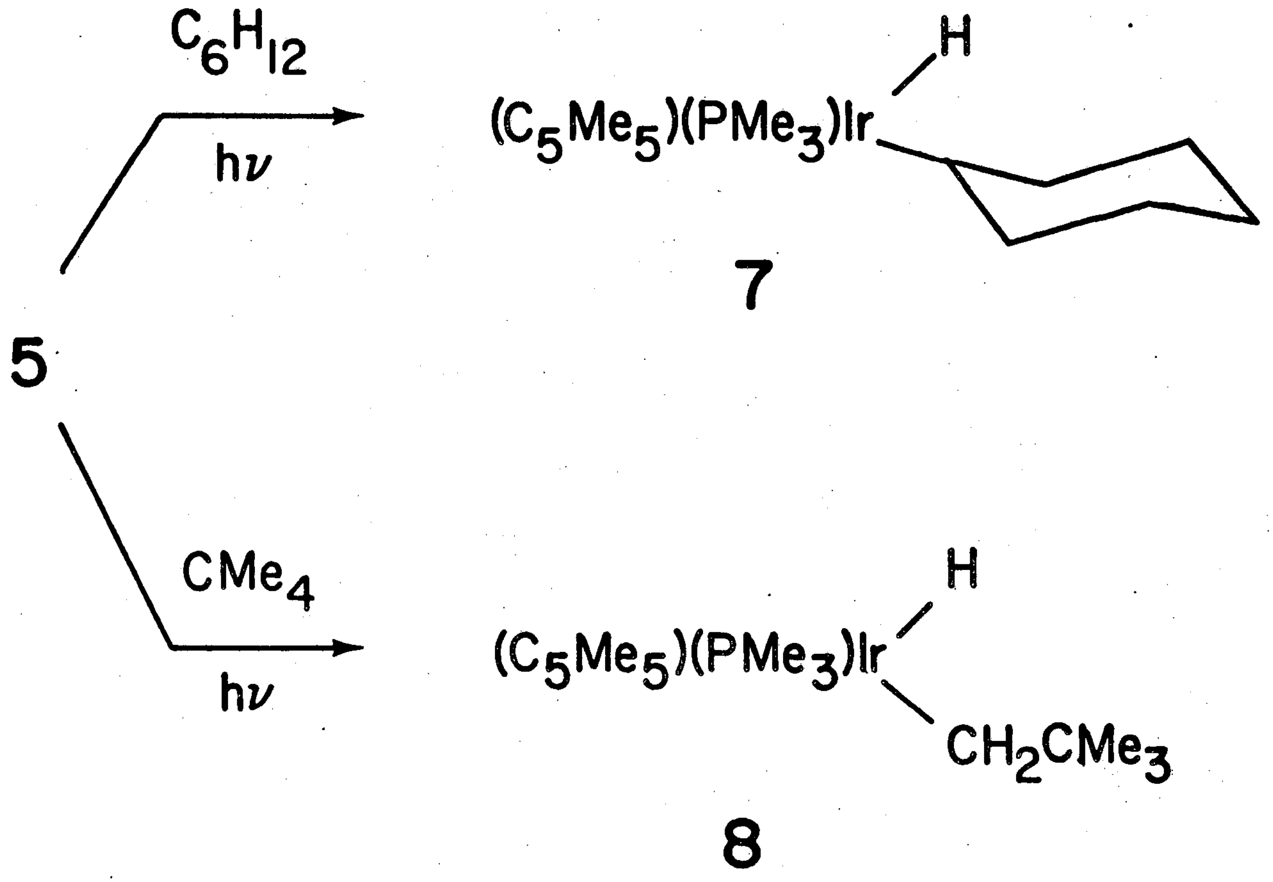
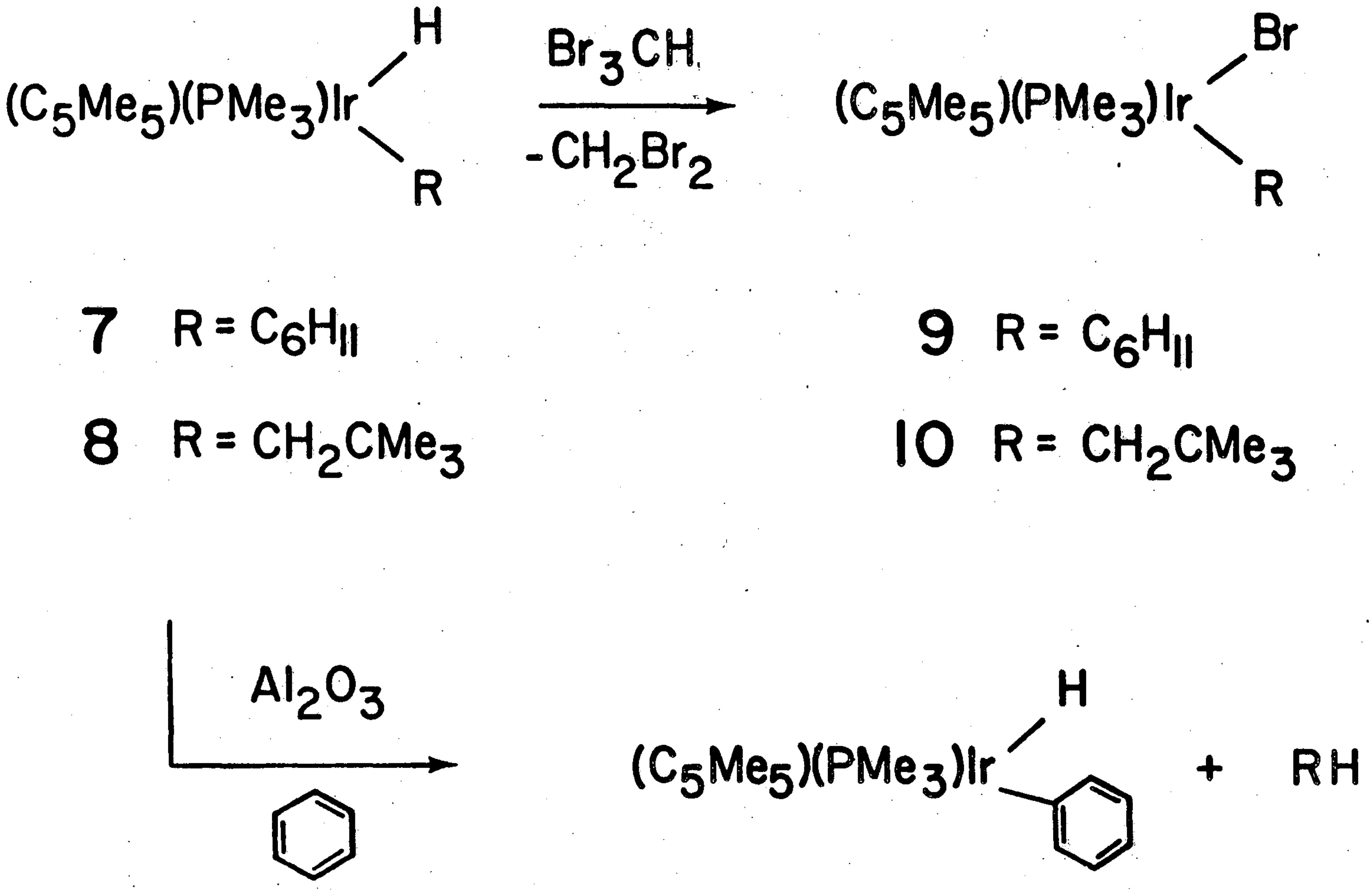


Table 1. ^{1}H and ^{13}C NMR spectra for $(\eta^{5}-C_5Me_5)Ir(PMe_3)(C_6H_{11})H$ (7) and $(\eta^{5}-C_5Me_5)Ir(PMe_3)(CH_2CMe_3)H$ (8).[a]

$^{1}\underline{H}$ spectra	7	8
C_5Me_5	1.87 dd (1.8,0.7)	1.82 dd (1.7,0.7)
PMe_3	1.24 d (9.5)	1.21 d (9.6)
Ir–H	–18.67 d (37.0)	–17.67 d (37.1)
Ir–R	1.50–2.30 broad	1.28 s (CMe_3)
		1.5 m (CH_2)
$^{13}\underline{C}$ spectra		
$\underline{C}_5Me_5$	92.36 d (3.4)	92.00 d (3.4)
$C_5(\underline{C}H_3)_5$	10.75 s	10.62 s
$P(\underline{C}H_3)$	19.69 d (35.7)	19.68 d (36.7)
Ir–R	3.27 d (7.1) α–C	6.20 d (7.1) CH_2
	44.58 d (4) β–C	33.83 s $(\underline{C}H_3)_3$
	43.96 d (2) β–C	35.71 s $\underline{C}(CH_3)_3$
	32.85 s γ–C	
	32.92 s γ–C	
	28.33 s δ–C	

[a] All spectra recorded in C_6D_6, coupling in Hz.

Scheme IV



7 R = C_6H_{11}

8 R = CH_2CMe_3

9 R = C_6H_{11}

10 R = CH_2CMe_3

complex once again seen by NMR to contain alkyl and hydride ligands, and intact C_5Me_5 and PMe_3 groups. Its structure is assigned as 8, the neopentyl hydride (the hydridoalkyl complex analogous to 7 (Scheme III)), on the basis of spectral data (Table 1) and conversion to the corresponding bromoneopentyl complex 10 (Scheme IV).

Treatment of 7 and 8 with reagents such as $ZnBr_2$, H_2O_2, Br_2, HBF_4, or O_2 results in reductive elimination of the hydrocarbon. In a particularly mild reaction, which accounts for part of the difficulty encountered in purification by chromatography, stirring 7 or 8 with Al_2O_3 in benzene solution for one hr generates the hydridophenyl complex 6 and cyclohexane (95% yield) or neopentane (98% yield), respectively (Scheme IV).

Photochemical reaction of 5 with a variety of other organic compounds was investigated briefly by NMR (Table 2). A single hydride product was formed in the presence of both acetonitrile and tetramethylsilane. In the case of tetahydrofuran, four new hydride resonances were detected by NMR. We assume these are products formed by attack at both the 2- and 3- positions, yielding two pairs of diastereomers. With methanol, the products expected of simple C-H activation, the hydoxymethyl hydride or the methoxyl hydride, were not detected. The organometallic product, as yet uncharacterized, by ^1H NMR contains only intact C_5Me_5 and PMe_3 groups. NMR (C_6D_6): δ 2.00 (d J=1.4 Hz, C_5Me_5), 1.26 (d J=9.7 Hz). Preliminary evidence points to some type of oxygen containing iridium complex because the organic products of the photolysis are hydrogen and methane. Thus, the iridium seems

Table 2. ^{1}H NMR shifts for the alkyl hydrides produced upon reaction of 5 and other "non-saturated hydrocarbon" organic substrates.[a]

Substrate	C_5Me_5(J)[b]	PMe_3(J)[c]	IrH(J)[d]
benzene[e]	1.81(1.8,0.8)	1.09(10.0)	−17.04(36.8)
acetonitrile	1.72(1.3)[f]	1.22(10.1)	−17.23(36.5)
tetramethylsilane[g]	1.80(1.9)[f]	1.17(9.8)	−17.08(38.4)
tetrahydrofuran	1.80[h]	1.42(10.3)	−16.64(34)
	1.87	1.34(10.3)	−17.09(34)
	1.94	1.15(10.2)	−17.65(36)
		1.14(9.5)	−18.07(36)

[a] C_6D_6. [b] doublet of doublets, coupling in Hz. [c] doublet, coupling in Hz. [d] doublet, coupling in Hz. [e] phenyl resonances are multiplets centered at δ 7.09 and 7.74. [f] unable to detect the smaller coupling. [g] trimethylsilyl resonance is a singlet at δ 0.35. [h] overlapping peaks prevent the assignment of all the C_5Me_5 resonances and accurate measurement of the coupling constants.

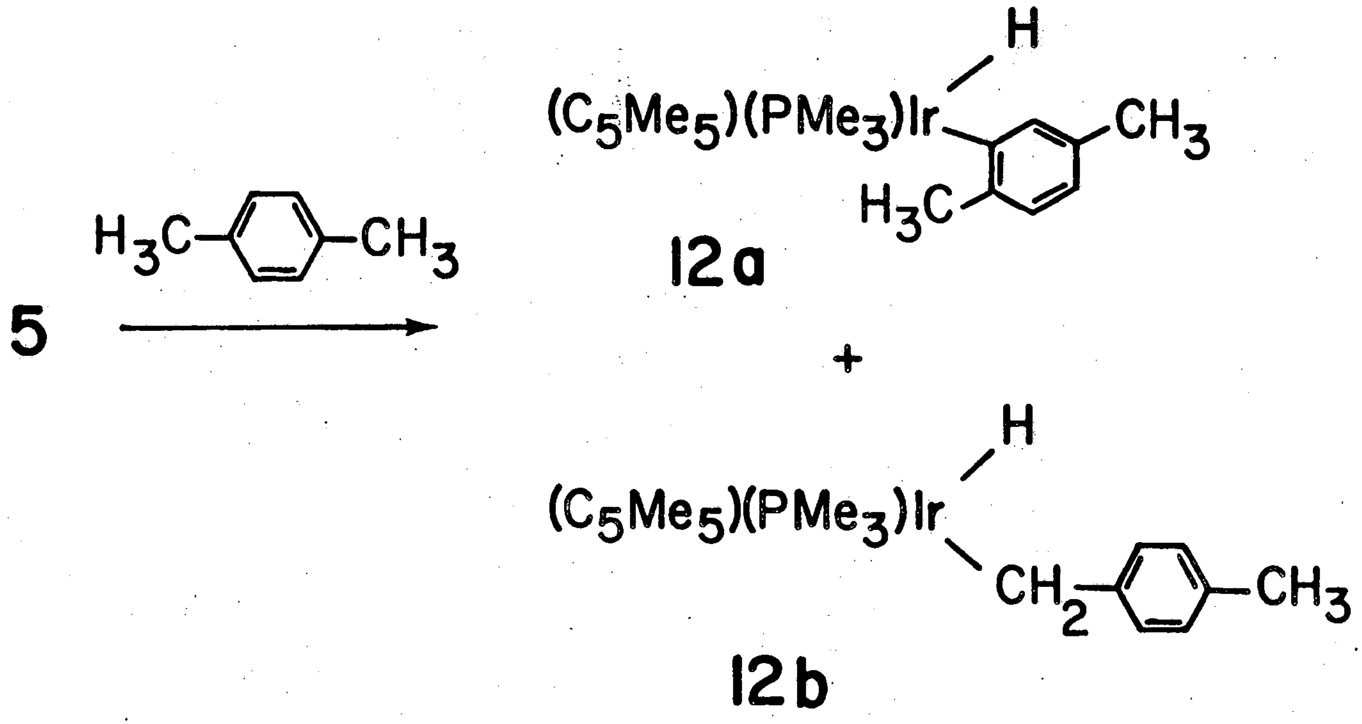
to be deoxygenating the methanol; further characterization of the organometallic product will be required to determine in what fashion the oxygen is bound to the metal.

Selectivity experiments. We next directed our attention to the question of selectivity, the relative rates at which the unsaturated iridium intermediate reacts with different types of C-H bonds. Our first experiment along these lines dealt with competition between aromatic and aliphatic C-H bonds. p-Xylene was chosen as the substrate, because it contains only a single type of aliphatic and aromatic C-H bond. Upon irradiation of **5** in p-xylene, two hydride products, **12a** and **12b**, were produced in ratio of 3.7 to 1.0 (Scheme V). Thus, reaction at the aromatic C-H bond is slightly favored over reaction at the benzylic position.

This ratio was calculated by integration of the product hydride resonances in the ^{1}H NMR spectrum. The hydride resonance for **5** appears at δ -17.38. The new resonance at lower field in the hydride region (δ -16.68) was assigned to the hydridoaryl complex **12a** because in both phenyl hydrides **3** and **6**, the hydride resonances appear downfield of the resonances for **2** and **5**, respectively. The hydride resonance upfield (δ -17.56) of that for **5** was subsequently assigned to that of the hydridobenzyl product **12b**, because of its similarity to the upfield shifts seen in all the other aliphatic iridium hydrides.

Perhaps there is some interaction between the pi system of the aromatic ring and the unsaturated iridium center that favors reaction at the ring. In any case, a purely free radical

Scheme V


5
H_3C–C_6H_4–CH_3
$(C_5Me_5)(PMe_3)Ir$
H
CH_3
H_3C
12a
+
$(C_5Me_5)(PMe_3)Ir$
H
CH_2
CH_3
12b

reaction does not appear to be occurring since we believe it would favor reaction at the benzylic position.[13]

Next we examined the relative rates of reaction of the unsaturated iridium intermediate with different types of C-H bonds in saturated hydrocarbons (Tables 3 and 4). The first reaction we ran was the photolysis of 5 in pentane. With pentane, we could directly measure the primary C-H bond versus secondary C-H bond selectivity. In this reaction, we detected only one new hydride, by its ^1H NMR resonance at δ -17.81. On the basis of comparing this with the primary alkyl hydride resonance of 8 (δ -17.67) versus that of the secondary alkyl hydride resonance of 7 (δ -18.67), we assign this resonance to that of the primary C-H bond activated product, the n-pentyl hydride (13). In order to have a second check on the validity of this assignment, we treated 13 with bromoform to produce (η^5-C_5Me_5)Ir(PMe_3)(n-pentyl)Br (14) (analogous to the reaction products 9 and 10). Upon treatment of 14 with DSO_3F, an NMR analysis revealed that the pentane produced was $CH_3(CH_2)_3CH_2D$ (integration CH_3/CH_2 = 0.86). Thus, we are confident that the product of the photolysis of 5 in pentane is that which results from primary C-H activation. By ^1H NMR, there is no detectable product due to reaction at any of the secondary positions; thus attack at the primary C-H bond is preferred by a factor of at least 15.

Next we investigated the relative rates of attack of the iridium intermediate upon the different types of primary C-H bonds in neohexane and isopentane (Scheme VI). In the photolysis

Table 3. ^{1}H NMR shifts for the alkyl hydrides produced in the selectivity experiments.[a]

hydrocarbon	C-H[b]	C_5Me_5(J)[c]	PMe_3(J)[d]	IrH(J)[e]
pentane	Me	1.89(1.8,0.6)	1.24(9.6)	-17.81(37.1)
neopentane	Et	1.88(1.8,0.7)	1.25(9.7)	-17.88(40.5)
	tBu	1.82(1.9,0.7)	1.22(9.6)	-17.69(37.4)
isopentane	Et	1.88(1.9,0.7)	1.25(9.9)	-17.84(37.1)
	iPr	1.86(1.8,0.4)[g]	1.21(9.6)	-17.51(33.0)
			1.20(9.7)	-17.69(33.6)
methylcyclohexane	Me	1.87[f]	1.20(9.6)	-17.60(37.4)
	ring		1.24(9.5)	-18.64[f]
			1.25[f]	
			1.26[f]	
1,1-dimethylcyclohexane	Me	1.82(1.9,0.5)	1.22(9.6)	-17.70(36.4)
	ring	1.88(1.9,0.7)	1.259(9.4)	-18.62(36.9)
		1.86(1.9,0.7)[g]	1.256(9.4)	-18.66(37.0)
			1.252(9.5)	-18.75(37.4)
methylcyclopentane	Me	1.87[f]	1.21(9.6)	-17.57(37.4)
	ring		1.20(9.5)	-18.19(38.0)[f]
			1.22(9.6)	
			1.23(9.5)	-18.26(35.6)[f]
			1.24(9.6)	
p-xylene	Me	1.78(1.8,0.8)	1.14(9.6)	-17.56(38.6)
	ring	1.80(1.9,0.7)	1.06(9.9)	-16.68(39.0)

[a] C_6D_6 solvent. [b] primary C-H bond in the hydrocarbon at which reaction has occurred. [c] doublet of doublets, coupling in Hz. [d] doublets, coupling in Hz. [e] doublets, coupling in Hz. [f] resonances overlapping. [g] coincident resonances for C_5Me_5.

Table 4. Relative rates for internal C-H bond selectivity.[a]

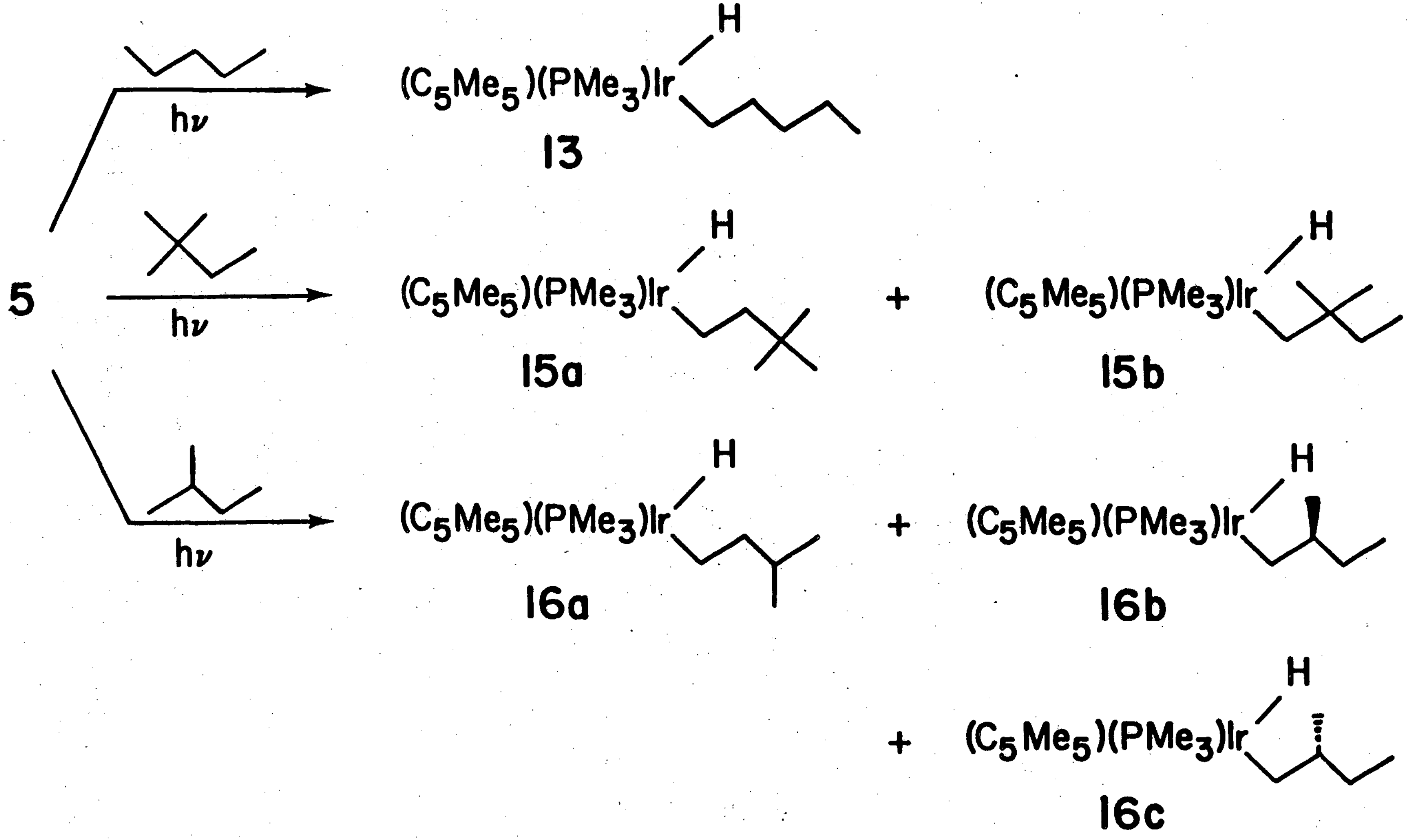
Hydrocarbon	Attack Position	Relative Rate Ratio
neohexane	Et/tBu	2.4
isopentane	Et/iPr	1.3
methylcyclohexane	$1^\circ/2^\circ$	3.5
1,1-dimethylcyclohexane	$1^\circ/2^\circ$	1.7
methylcyclopentane	$1^\circ/2^\circ$	1.7
p-xylene	Arom/Me	3.7

[a] corrected for the number of hydrogens.

of 5 in neohexane, we detected only two product hydrides by ^1H NMR (δ −17.88 and −17.69). Both are in the region characteristic of primary alkyl hydrides, and as with n-pentane, no secondary product was detected. The lower field resonance was assigned to that of the product of reaction at the t-butyl C-H bond (**15b**) due to its almost coincident resonance with that of the neopentyl hydride **8**. The former resonance was then attributed to that resulting from attack at the 4- position (**15a**) (the ethyl group C-H bond). This assignment is consistent with the hydride resonance of the straight chained n-pentyl hydride **13**. We can now compare the selectivity between the C-H bonds of the t-butyl group with those of the ethyl group. Corrected for the number of hydrogens, attack at the ethyl C-H bond to give **15a** is favored over the t-butyl C-H bond to give **15b** by a factor of 2.4. Perhaps a lower steric bulk plays a role in favoring the less congested C-H bonds.

In order to check our assumption that the steric accessibility of the C-H bond seems to be important, we irradiated 5 in isopentane. We predict the C-H bonds in the ethyl group of isopentane would be favored over those of the isopropyl group, but by a factor less than the 2.4 found in neohexane. Again, no secondary attack was observed, but three primary hydride products were detected by ^1H NMR (δ −17.84, −17.51 and −17.69). The reason is that even though only two types of primary C-H bonds are present in isopentane, reaction at a primary C-H bond in the isopropyl group brings about the formation of diastereomers, due to the chirality of the iridium

Scheme VI


5
hν
hν
hν
(C$_5$Me$_5$)(PMe$_3$)Ir
H
13
(C$_5$Me$_5$)(PMe$_3$)Ir
H
15a
+
(C$_5$Me$_5$)(PMe$_3$)Ir
H
15b
(C$_5$Me$_5$)(PMe$_3$)Ir
H
16a
+
(C$_5$Me$_5$)(PMe$_3$)Ir
H
16b
+
(C$_5$Me$_5$)(PMe$_3$)Ir
H
16c

center and the chirality of the 2- carbon in the resulting alkyl hydride (Scheme VI). By the same method of comparing the hydride shifts to those of known compounds, we assign the δ −17.84 resonance to **16a**, the product of attack at the primary C-H bonds of the ethyl group. The other two resonances were assigned to diastereomers **16b** and **16c**, the products of attack at the primary C-H bonds of the isopropyl group. (Scheme VI). As predicted, corrected for the number of hydrogens, attack at the ethyl group C-H bond favored attack at the isopropyl group by a factor of 1.3. Thus, more product is formed at the more sterically accessible C-H bonds.

In order to study the reactivity of secondary C-H bonds, we turned to the cycloalkanes: cyclopentane, cyclohexane, cyclooctane and cyclopropane. Photolysis of 5 with each of the cylcoalkanes yielded a single new hydride (Table 5). As expected for secondary hydrides, the ^{1}H NMR high field resonances for all these secondary systems were upfield of those for 5 by 0.8 to 1.3 ppm. One might have expected some C-C bond activation in the photolysis of 5 with cyclopropane to yield a metallacylobutane,[14] but only reaction at the C-H bond was observed.

Using the ^{1}H NMR data from the individual cycloalkyl hydrides, competition experiments were run with pairs of different substrates competing for the unsaturated iridium intermediate. We first examined the relative rates of attack at primary and cycloalkyl secondary C-H bonds. After irradiation of 5 in a 1:1 mixture of pentane and cyclohexane, integration of the respective hydride resonances demonstrated that attack at the

Table 5. ^{1}H NMR shifts for the cycloalkyl hydrides.[a]

Cycloalkane	$C_5Me_5(J)$[b]	$PMe_3(J)$[c]	IrH(J)[d]
cyclopropane	1.87(1.8,0.8)	1.30(9.9)	−18.16(34.4)
cyclopentane	1.86(1.8,0.6)	1.22(9.6)	−18.16(33.9)
cyclohexane	1.87(1.8,0.7)	1.24(9.5)	−18.67(37.0)
cyclooctane	1.87[e]	1.14(8.8)	−18.64(36.6)

[a] C_6D_6. [b] doublet of doublets, coupling in Hz. [c] doublets, coupling in Hz. [d] doublets, coupling in Hz. [e] unable to reliably measure coupling constants.

primary C–H bonds in pentane was only slightly favored over activation of the secondary C–H bonds in cyclohexane (a factor of 2.7, corrected for the number of available hydrogens). In the photolysis of 5 in a mixture of pentane and cyclopentane, again the primary C–H bonds were favored, but in this case by a factor of 1.6 (corrected for the number of available hydrogens). These results bring up three points. First, in all cases attack at primary C–H bonds is preferred over secondary C–H bonds. Second, the secondary C–H bonds in cyclohexane and cyclopentane react much more rapidly than the secondary C–H bonds in n-pentane; thus, they must be different from one another in some significant way. Perhaps this is again due to the accessibility of a C–H bond to the incoming iridium complex. The secondary C–H bonds in cyclopentane should be less sterically encumbered due to the tying-back of the rest of the molecule compared to secondary C–H bonds in pentane. However, it is difficult to explain the surprising difference in reactivity between the secondary C–H bonds in pentane and those in cyclohexane. It has been widely accepted that the C–H bonds in cyclohexane are "normal" secondary C–H bonds since cyclohexane is considered an unstrained cycloalkane.[13] Third, the cyclopentane/cyclohexane ratio of 1.6, verified by the irradiation of 5 in a 1:1 cyclopentane/cyclohexane mixture, is consistent with a greater "tying back" of the molecule in cyclopentane, making the cyclopentyl C–H bonds more accessible.

If this accessibility argument is general, one would expect the C–H bonds of a cycloalkane such as cyclooctane to be less reactive due to H-H interactions. The result of the selectivity experiment between cyclohexane and cyclooctane is consistent with this prediction; cyclohexyl C-H bonds are favored by a factor of eleven (Table 6).

We next examined molecules containing both primary and reactive cyclic secondary C-H bonds. After photolysis of 5 in 1,1-dimethylcyclohexane, four major products were detected by ^{1}H NMR. Three of these were assigned as cyclohexyl ring substituted products by the similarity of their hydride chemical shifts (δ -18.62, -18.66 and -18.75) to that of cyclohexyl hydride 7. The fourth product was assigned as a methyl substituted product, on the basis of its "primary" hydride chemical shift at δ -17.70. The ring products were tentatively assigned as two diastereomers resulting from attack at the 3- position and one from attack at the 4- position. The primary/secondary reactivity ratio was 1.7 (corrected for the number of hydrogens), again favoring the activation of primary C-H bonds.

The mixture formed on photolysis of 5 in methylcyclohexane was even more complex, and we could not determine the exact number of hydride products due to overlap in all areas of the ^{1}H NMR spectrum. We were able, however, to assign the hydride resonance at δ -17.60 to the primary product resulting from attack at the methyl group. In the secondary alkyl hydride region of the spectrum, a very broad doublet centered at δ -18.64, due to several overlapping resonances, was found. By integration we determined that the primary product was favored

Table 6. Relative rates determined in the competition experiments.[a]

Hydrocarbons	Relative Rates
pentane[b]	2.7
cyclopentane	1.6
cyclohexane	1.0
cyclooctane	0.09

[a] corrected for the number of hydrogens. [b] rates determined for the primary C-H bonds in pentane.

over the secondary products by a factor of 3.5 (corrected for the number of available hydrogens). This result is consistent with the accessiblity prediction. One would expect the primary/secondary ratio to be greater in methylcyclohexane, due to the greater steric congestion at the "neopentyl-type" methyl groups in 1,1-dimethylcyclohexane.

Referring back to the photolysis of 5 in pentane, we considered the possibility that there might be some type of intramolecular process by which secondary products rearrange to primary products under the reaction conditions. Rearrangement could be going through some sort of β-elimination, olefin insertion mechanism such as that in hydrozirconation.[15] Although not rigorously ruled out, this possibility is deemed unlikely by the fact that we are working here with coordinatively saturated complexes, and by the fact that both ring- and methyl- sbstituted products are formed from methylcyclohexane.[16] In addition, the primary/secondary ratios are internally consistent among all of the selectivity experiments.

Finally, the photolysis of 5 in methylcyclopentane also yielded products formed from attack at both methyl and ring positions. By the same method of comparing the product hydride resonances, we detected one methyl- and four ring- C-H activation products. We believe the ring products correspond to the two possible sets of diastereomers. The primary/secondary product ratio shows that primary C-H attack is favored by a factor of 1.7 (corrected for the number of hydrogens). This result is again consistent with all the previous selectivities and the notion of

C-H bond accessibility.

Functionalization. The facile conversion of unreactive materials such as saturated hydrocarbons into functionalized organic molecules is a goal sought by many. Our attempts to reach this goal centered around reactions of $(\eta^5-C_5Me_5)IrPMe_3(H)R$ with various reagents. As mentioned previously, treatment of 7 or 8 with oxidizing or electrophilic reagents resulted in reductive elimination of the hydrocarbon RH. The photolysis of 7 in benzene or neopentane also led to the formation of cyclohexane and 6 or 8, respectively. Reductive elimination and subsequent C-H activation can also be induced thermally. Heating 7 in benzene-d_6 or pentane in a sealed tube at 110°C for 24 hrs, yielded the corresponding deuterophenyl deuteride (6-d_6) or n-pentyl hydride (13), respectively. Thus, only primary C-H attack is observed in pentane thermally as well as photochemically. These experiments suggest that one forms the same unsaturated iridium intermediate in the thermal and photochemical experiments.

Upon treatment of 8 with carbon monoxide (0.73 atm) at 60°C for four hrs, one begins to see the formation of what is believed to be $(\eta^5-C_5Me_5)Ir(CO)PMe_3$ (17) (by IR and NMR) and neopentane. Upon further reaction with CO, 17 disappears and $(\eta^5-C_5Me_5)$-$Ir(CO)_2$ (18) forms. Carbon dioxide (4.3 atm), on the other hand, is inert towards 8 up to 110°, where the thermal reaction with the solvent occurs.

We decided that a possible solution to the functionalization problem might be available by replacement of the hydride ligand with halogen. Bromoform was found to react with the alkyl hydrides to produce $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(R)Br$ and dibromomethane in quantitative yield (Scheme IV). The alkyliridium bromides turn out to be quite easy to handle and crystallize. Therefore, our attempts at functionalization turned to these alkyliridium bromide complexes. Treatment of $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(n\text{-pentyl})Br$ (**14**) with deuterated flourosulfonic acid gave 1-deuteropentane. Although this does not introduce a new functional group, it is a technique by which we can confirm our judgments about which C-H bonds are activated.

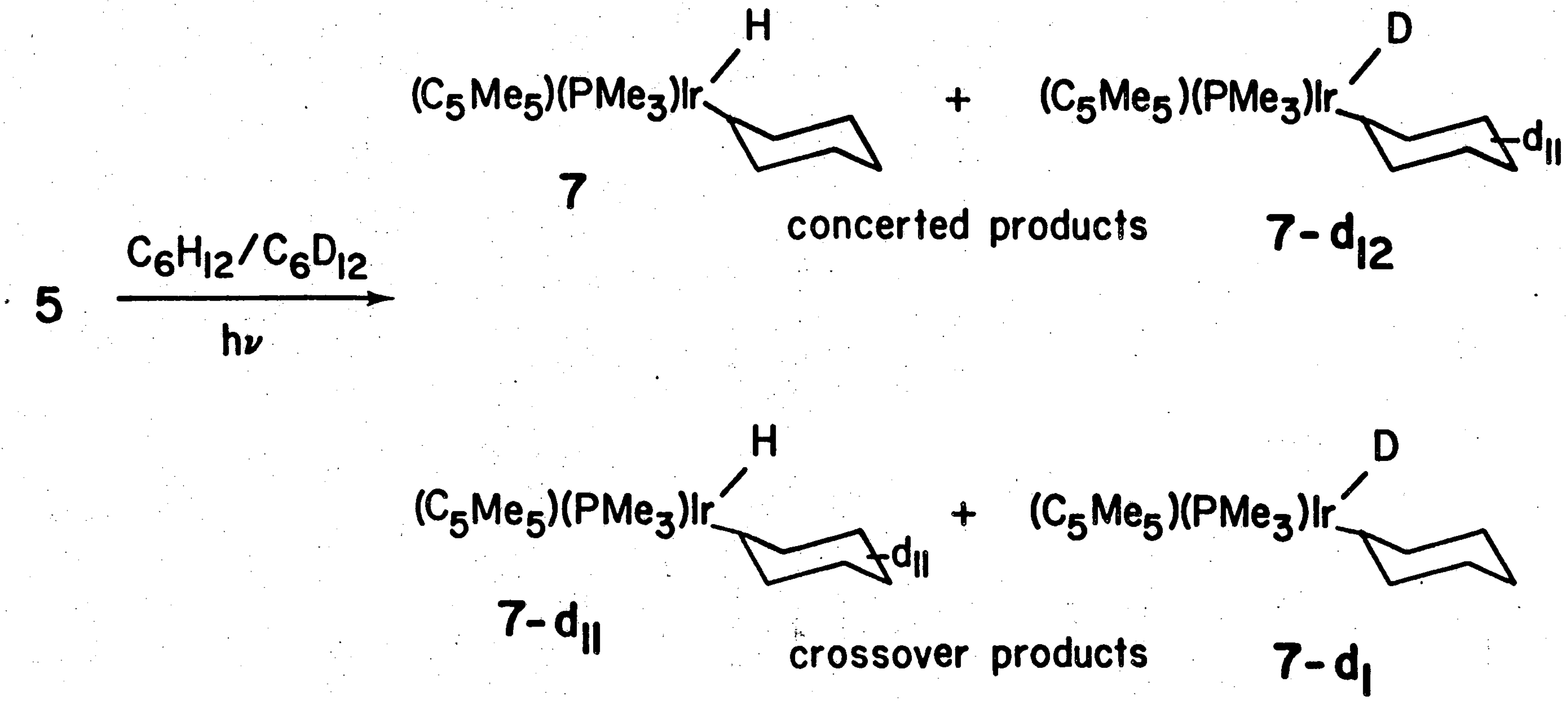
Treatment of **9** with Br_2 in a variety of solvents (benzene, pentane, CCl_4) gave less than 2% of cyclohexyl bromide. By gas chromatographic analysis, using retention times, the major organic products seemed to be cyclohexane and/or cyclohexene and a higher molecular weight material (perhaps cyclohexylcyclohexane). These results indicate that some sort of free radical reaction is occurring.

Treatment of **8** with mercuric chloride in benzene was more successful. By ^1H NMR, we observed the clean exchange of the neopentyl group for a Cl atom. This resulted in the formation of neopentylmercuric chloride (δ 1.12 (2H), 0.57 (9H)) and presumably a monobromide derivative of **11** which precipitated from the solution, perhaps the driving force of the reaction. The reaction mixture containing the neopentylmercuric chloride was subsequently treated with Br_2 to give neopentylbromide in >98% NMR yield.[18] Thus, we have started with neopentane and finished with neopentyl bromide, our functionalized hydrocarbon. Studies are continuing to check the generality of this reaction sequence.

Crossover experiments. In order to probe the mechanism of the C–H activation reaction more closely, we irradiated **5** in a 1:1 mixture of cyclohexane and deuterocyclohexane. Here we hoped to determine the relative amounts of products formed by intramolecular reaction (presumably concerted insertion), **7** and **7**-d_{12} and those formed by intermolecular processes leading to scrambled or crossover products **7**-d_1 and **7**-d_{11} (Scheme VII). Crossover products could be formed either by a free radical pathway via initial Ir–H bond homolysis or by secondary H–D exchange process between the products or starting material. Unfortunately, we were unable to quantitatively analyze the ratio of products from this experiment because decomposition occurred on mass spectroscopy of these alkyl hydrides. We have also been unsuccessful in obtaining accurately reproducible peak intensities by field desorption mass spectrometry.

As an alternative, therefore, we decided to take advantage of the very different chemical shifts in the hydride region of the ^{1}H NMR of **7** and **8**. To make sure the two hydrocarbons had similar reactivities, **5** was irradiated in a 1:1 mixture of neopentane and cyclohexane; **7** and **8** were formed in a ratio of 0.88. After the irradiation of **5** in a 1:1 mixture of neopentane and cyclohexane-d_{12}, inspection of the C_5Me_5 region of the NMR spectrum showed that **7**-d_{12} and **8** were the major products, formed in a ratio of 0.64. From these data, the isotope effect

Scheme VII



7

$7-d_{12}$

concerted products

$7-d_{11}$

$7-d_1$

crossover products

on insertion of the iridium intermediate into the C-H or C-D bond of the appropriate cyclohexane was determined to be $k_h/k_d = 1.38$. In the hydride region of the spectrum, while some cyclohexyl-d_{11} hydride (7-8%) was formed, it appears this crossover is due to a secondary process and not the initial pathway. The initial process occurring upon the photolysis of 5 is the loss of H_2, not homolytic cleavage of the Ir-H bond, as shown in the exclusive production of H_2 in the presence of deuterated solvent (see below). At room temperature, over the span of two months, there is no measurable exchange between 7-d_{12} and 8. A similar percentage of 7-d_{11} was found when 5 was irradiated in a 1:5 mixture of neopentane and cyclohexane-d_{12}. The interaction of the iridium fragment with a C-H bond is, therefore, at least >92% intramolecular. That is, concerted oxidative addition across the C-H bond rather than a radical abstraction process appears to be the major reaction pathway.

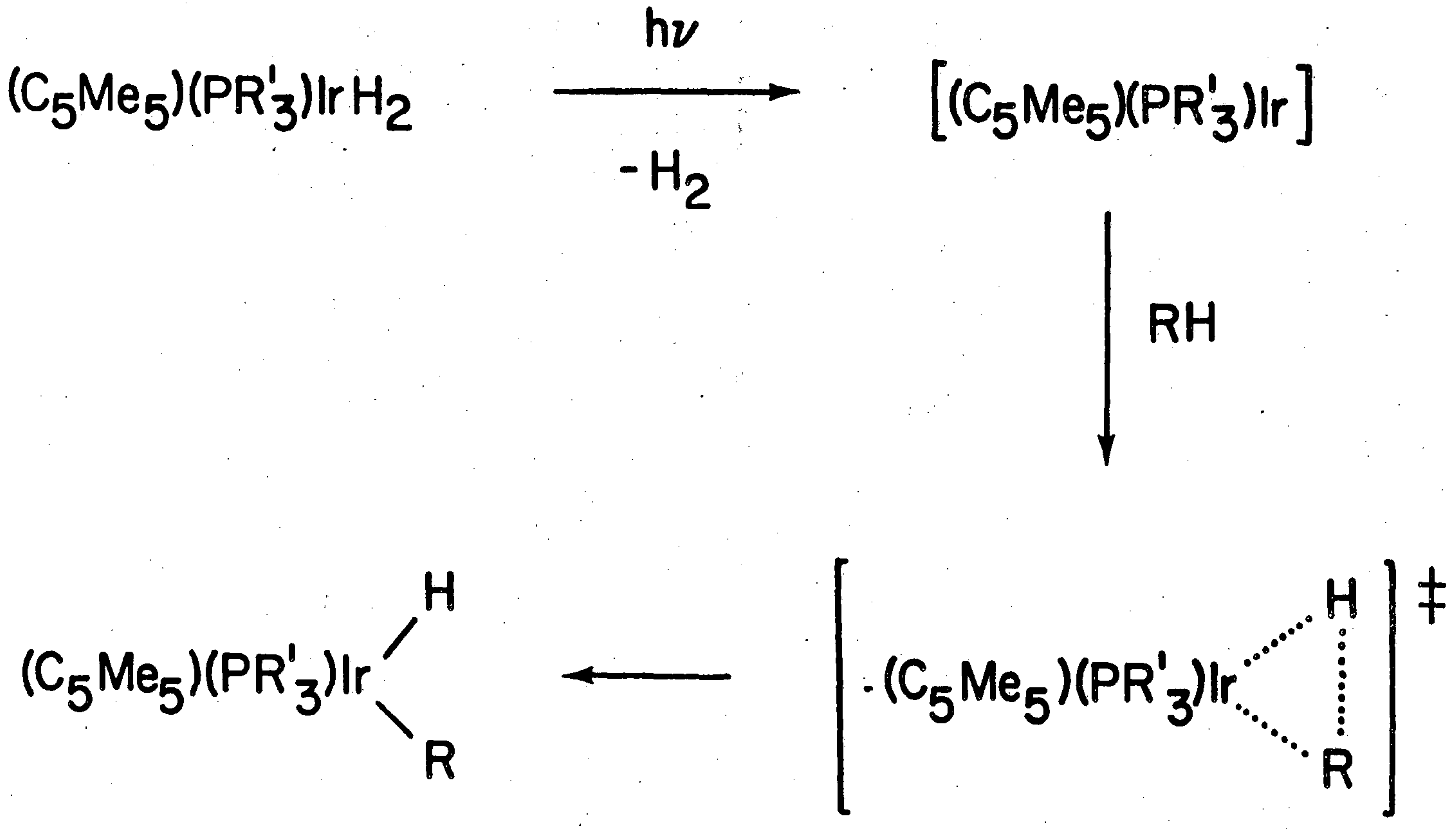
Irradiation of 5 in cyclohexane-d_{12} for 40 min gave only H_2 and 7-d_{12}, supporting the judgment that the first step in the reaction involves concerted loss of hydrogen. Upon prolonged photolysis (24 hr), however, a significant amount of HD (20%) and some D_2 (1.7%) are produced. This secondary process could be accounting for the small amount of crossover product we detect, since the isotopic purity of our cyclohexane would be adversely affected throughout the reaction.

Conclusion

We have succeeded in designing the first system capable of activating the C-H bonds of saturated hydrocarbons which leads directly to alkyliridium hydrides in high yield at room temperature. The mechanism of the photolysis of dihydrides 2 and 5 and subsequent reaction with saturated hydrocarbons is believed to occur via (1) the concerted loss of hydrogen to form (η^5-C_5Me_5)Ir(PR_3) and (2) oxidative addition across the C-H bond of the hydrocarbon. This oxidative addition seems to proceed in a concerted fashion via a triangular type of transition state 19 (Scheme VIII).[19,7b] Selectivity studies, demonstrating that insertion into primary C-H bonds is preferred, are inconsistent with relative rates expected for radical reactions. It is the most sterically accessable C-H bonds that are most prone to react.

Why does (η^5-C_5Me_5)Ir(PMe_3) insert into C-H bonds? This type of electron-rich 16-electron species is expected to interact with a C-H bond by dispersing the negative charge from the metal to the alkyl and hydride ligands.[7b,d] The complex has shown the ability to undergo intermolecular reaction with unactivated C-H bonds (completely when PR_3 is PMe_3 and partially when PR_3 is PPh_3). It is surprising that even with a PPh_3 group, orthometallation is not the sole process occurring. This ability to undergo intermolecular reactions is the key to the C-H activation. Just why this system selectively undergoes intermolecular reactions is not clear at this time. That the C-H bonds this system does react with seem to be the most accessible suggests that the intermediate is in a geometrical configuration

Scheme VIII



19

that makes its own C-H bonds inaccessible. Hoyano and Graham[20] have found that $(\eta^5\text{-}C_5Me_5)IrCO$, generated photochemically from the corresponding dicarbonyl, undergoes the same type of C-H activation reaction. $(\eta^5\text{-}C_5H_5)IrCO$, however, reacts with the C-H bonds of benzene[7f] but seems to form clusters in hydrocarbons.[21] The alkyl hydrides in the C_5H_5 system are probably thermally unstable at room temperature; thus, the added electron density afforded by the C_5Me_5 ligand seems to be an important factor. One also cannot rule out the favorable steric effects of the more bulky ligand. Further modifications of the system are being studied in the hope of clarifying the situation.

Finally, we have succeeded in cleanly functionalizing saturated hydrocarbons. Although we were unable to obtain functionalized organic compounds directly from the alkyl hydrides, conversion to the alkyliridium bromides led to a functionalizable species. Upon reaction with mercuric chloride, an alkyl group is transferred to the mercury which can be easily converted to an alkyl halide upon treatment with the appropriate halogen. Thus, we have met our goal of inducing the clean reaction of saturated hydrocarbons with a transition metal system and subsequently transforming them to functionalized organic materials.

Experimental Section

General. All manipulations of oxygen or water sensitive materials were conducted under a pre-scrubbed recirculating atmosphere of nitrogen in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or using standard Schlenk or vacuum line techniques.

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian EM-390 90 MHz spectrometer or a 200 MHz or 250 MHz high field Fourier Transform instrument. Each high field system consisted of a Cryomagnets Inc. magnet, Nicolet Model 1180 data collection system and electronics assembled by Mr. Rudi Nunlist (U. C. Berkeley). All chemical shifts are reported relative to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer using NaCl solution cells.

Gas-liquid chromatography (GC) analyses were performed using a Varian 90P gas chromatograph using a 10' x 1/4" glass column packed with 15% Apiezon L on acid washed Chromosorb W at 150°C.

Mass spectroscopic (MS) analyses were conducted on an AEI MS-1 spectrometer interfaced with a Finnegan 2300 Data System. Elemental analyses were performed by the U. C. Berkeley analytical facility. Ultraviolet spectra were recorded on a Hewlett-Packard 8450A UV/Vis spectrophotometer using 1 cm pathlength quartz cells.

Preparative column chromatography was performed on neutral alumina (III) that was degassed before being taken into the dry box. All columns were packed and chromatograms run under air-free conditions.

Photolyses were conducted with an Oriel 500W high pressure mercury lamp powered by an Oriel Corporation (model 6128) Universal Lamp Power Supply and mounted in an Oriel focused beam lamp housing. The reaction samples were immersed in a quartz water or methanol bath that was cooled by a copper coil heat exchanger containing a circulating -10°C ethylene glycol/water mixture. With the heat that was generated by the lamp, the cooling bath was approximately 6°C.

Benzene-h_6 and -d_6, tetrahydrofuran-h_8 and -d_8, diethyl ether and toluene were purifed before use by distillation or vacuum transfer from sodium-benzophenone ketyl. Prior to distillation from n-butyl lithium in hexane, the hexane used was purified by shaking two times with 5% nitric acid in sulfuric acid, washed in sequence with distilled water, saturated sodium carbonate solution and distilled water and dried over calcium chloride. Methylene chloride-h_2 and -d_2 was distilled from calcium hydride under nitrogen. Chloroform-h_1 and -d_1, carbon tetrachloride, cyclohexane (spectral grade), cyclohexane-d_{12}, pentane (spectral grade), methanol, tetramethylsilane, p-xylene, neohexane, isopentane, methylcyclohexane, 1,1-dimethylcyclohexane, methylcyclopentane, cyclopentane and cyclooctane were vacuum transferred from molecular sieves under nitrogen. Acetonitrile was dried over molecular sieves and distilled under nitrogen from P_2O_5. Neopentane and cyclopropane were used as received.

$LiEt_3BH$ (1 M in THF), H_2O_2 (30%), Br_2, $HBF_4 \cdot OEt_2$, and DSO_3F were used as received. $HgCl_2$ was recrystallized from water and $ZnBr_2$ was heated at 150°C for eight hours under high vacuum before use. Bromoform was vacuum transferred from molecular sieves. PPh_3 was recrystallized from hexane, and PMe_3 was vacuum transferred before use. 1,[9] $(\eta^5\text{-}C_5Me_5)Ir(PPh_3)Cl_2$ (18),[22] and $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)Cl_2$ (11)[23] were prepared by literature methods.

Photochemical Experiments. A typical analytical photolysis was carried out as follows. Dihydride 5 (10.0 mg, 2.47×10^{-5} mol) and the substrate (usually a liquid saturated hydrocarbon used as a solvent (0.60 mL)) were added to a 5 mm NMR tube in the dry box. After capping the tube, it was removed from the dry box, and the cap was secured with parafilm. The tube was immersed in a water-filled quartz dewar in front of the focused photolysis beam. In some cases the reaction was monitored periodically by examining the hydride region in the NMR; in others, the analysis was performed after irradiation for five hrs. After irradiation, the reaction mixture was taken back into the dry box where the solvent was removed in vacuo. The residue was taken up in benzene-d_6 and added to a new NMR tube to record the NMR spectrum.

Exceptions to this general scheme occurred when the hydrocarbon was gaseous at room temperature (cyclopropane and neopentane), and when larger-scale preparative experiments were performed. For example, the NMR tube scale reaction with neopentane was carried out utilizing an NMR tube fused to a 14/20 ground glass joint, which was loaded with 5 in the dry box. The tube was capped with a vacuum stopcock and taken from the dry box to a vacuum line where the dihydride was degassed and neopentane added by vacuum transfer at −196°C. The tube was sealed and irradiated for five hours. After photolysis, the tube was broken open in the dry box, and the same procedures for removing the solvent and preparing the sample in benzene-d_6 were followed.

With cyclopropane and other large scale preparative reactions, glass bombs equipped with built-in vacuum stopcocks were used as the reaction vessels. After irradiation, the hydrocarbons were removed by vacuum transfer before attempting to isolate the products. Isolation procedures for larger-scale experiments are described below.

$(\eta^5\text{-}C_5Me_5)Ir(PMe_3)H_2$ (5). Dichloride 11 (1.455 g, 3.07 mmol) and THF (100 mL) were added to a 250 mL round bottomed flask equipped with a stir bar in the dry box. $LiEt_3BH$ (6.2 mL of a 1 M THF solution) was added dropwise to the stirring slurry, which was subsequently stirred for two hours. The solvent was removed in vacuo, and the residue was taken up in benzene and filtered through neutral alumina (III). The alumina was washed with benzene and the resulting filtrate concentrated in vacuo to approximately five mL. This residue was chromatographed on neutral alumina (III) with benzene eluent. After discarding the first column volume of eluent, the next fraction collected contained pure 5. The solvent was removed in vacuo leaving analytically pure 5 as a pale yellow oil that occasionally solidified (m.p. 43-44) upon standing (668 mg, 54%). ^1H NMR (C_6D_6): δ 2.12 (dt J_{P-H}=1.9 Hz, J_{H-H}=0.7 Hz, C_5Me_5), 1.33 (d J=10.0 Hz, PMe_3), -17.38 (d J=32.2 Hz, IrH_2). ^{13}C NMR (C_6D_6): δ 91.26 (d J=2.4 Hz, $\underline{C}_5Me_5$), 11.69 (s, $C_5\underline{Me}_5$), 24.00 (d J=37.8 Hz, PMe_3). IR (C_6H_{12}): 2099 cm^{-1} (ν_{Ir-H}). MS: m/e 406, 404 (parent isotope and M-H_2), 402 (M-H_2). UV (C_6H_{12}): λ_{max}=259 (ε=1.6 x 10^3). Anal. Calcd for $C_{13}H_{26}IrP$: C, 38.50; H, 6.46. Found: C, 38.50; H, 6.37.

(η^5-C_5Me_5)Ir(PPh_3)H_2 (2). Dihydride 2 was prepared in a similar manner. After column chromatography on alimina (III) with benzene eluent, the solvent was removed in vacuo and 2 was recrystallized once from ether. It was obtained in 42% yield as an air-sensitive pale tan solid, m.p. 171. ^{1}H NMR: δ 1.90 (broad d J=1.00 Hz, C_5Me_5), 7.04 and 7.70 (m, PPh_3), −16.47 (d J=31.7 Hz, IrH_2). IR (C_6H_6): 2110 cm^{-1} (ν_{Ir-H}). UV (C_6H_{12}): λ_{max}=288 (ε=750). Anal. Calcd for $C_{28}H_{32}IrP$: C, 56.83; H, 5.45. Found: C, 56.44; H, 5.43.

(η^5-C_5Me_5)Ir(PPh_3)(C_6H_5)H (3). Dihydride 2 (120 mg, 0.0203 mmol) and benzene (10 mL) were placed in a glass bomb that contained a stir bar. After removing the reaction mixture from the dry box, it was cooled to −196°C and evacuated on the vacuum line. The solution was irradiated for 8.5 hr. The solvent was removed in vacuo, and the residue was taken up in benzene-d_6. NMR analysis showed that the two organometallic products were 3 and 4 in a 47:53 ratio. The benzene-d_6 was removed in vacuo, and the residue was taken back up in a minimal amount of benzene and chromatographed on alumina (III) in the dry box with benzene eluent. The benzene was removed from the first fraction in vacuo and the solid was recrystallized once from ether to give 38 mg (28% yield) of a colorless solid, m.p. 215. ^{1}H NMR (C_6D_6): δ 1.60 (dd J=1.8, 0.8, C_5Me_5), 7.00 (m, PPh_3 m- and p- H), 7.47 (m,

PPh_3 o- H), 6.92 (m, Ph m- and p- H), 7.61 (m, Ph o- H), −16.36 (d J=36.7, IrH). IR (C_6D_6): 2110 cm^{-1} (v_{Ir-H}). Anal: Calcd for $C_{34}H_{36}IrP$: C, 61.15; H, 5.43. Found: C, 60.86; H, 5.36. Product 4 [^1H NMR (C_6D_6): δ 1.84 (d J=1.8 Hz, C_5Me_5), 6.72, 7.06, 7.53, 7.98 (m, 1H each, C_6H_4), 6.97, 7.28 (m, 6H and 4H each, PPh_2), −13.09 (d J=26.7 Hz, IrH)] decomposed on the column.

Irradiation of 5 in cyclohexane. $(\eta^5-C_5Me_5)Ir(PMe_3)(C_6H_{11})H$ **(7)** was prepared following the procedure described for the preparation of 3, with 5 (177 mg, 3.63×10^{-4} mol) and cyclohexane (5.0 mL) using a glass bomb for a vessel. The solution was irradiated for 58 hr. After the irradiation, the cyclohexane was removed in vacuo, and the residue was taken up in cyclohexane and chromatographed on alumina (III) in the dry box with 4% THF/cyclohexane eluent. The solution was forced through quickly with pressure from a hand held bulb. The first fraction was collected, and the solvent was removed in vacuo leaving an oily pale yellow/brown material, which could not be recrystallized successfullly. The cyclohexyliridium hydride was isolated in 39% yield and was pure by NMR. For ^1H and ^{13}C NMR spectra, see Table 1. IR (C_6H_{12}): 2100 cm^{-1} (v_{Ir-H}). Electron impact mass spectrometry gave only a very small parent ion due to reductive elimination. FDMS: 488, 486. Anal. Calcd for $C_{19}H_{36}IrP$: C, 46.79; H, 7.44. Found: C, 47.58; H, 7.67.

To obtain complete characterization, the compound was converted to the corresponding bromide derivative 9. Cyclohexyl hydride 7 (22 mg, 4.5×10^{-5} mol) was taken up in pentane (2 mL) in a two necked 5 mL pear shaped flask in the dry box. The two necks were topped with a vacuum stopcock and a septum. The flask was removed from the dry box, and $CHBr_3$ (5.0 µL, 5.78×10^{-5} mol) was added by syringe. The solvent was removed in vacuo, and the solid was recrystallized once from toluene/pentane, giving 23 mg (90% yield) of yellow/orange crystals, m.p. 159. ^1H NMR (C_6D_6): δ 1.52 (d J=1.9 Hz, C_5Me_5), 1.23 (d J=9.9 Hz, PMe_3), 3.32, 2.70, 1.96, 1.84, 1.63 (broad, C_6H_{11}). Anal. Calcd for $C_{19}H_{35}IrPBr$: C, 40.28; H, 6.31. Found: C, 40.61; H, 5.98.

To get an overall yield for the direct formation of 9 from 5, dihydride 5 (30.2 mg, 7.45×10^{-5} mol) was irradiated in cyclohexane (0.72 mL) following the aforementioned procedure for a photochemical experiment in an NMR tube. After five hr, the cyclohexane was removed in vacuo, and the reaction mixture was taken up in benzene-d_6; by NMR, 53% of 5 was converted to cyclohexyl hydride 7. Bromoform (10 µL, 1.16×10^{-4} mol) was added to the reaction solution by syringe. After two hours, the solution was chromatographed on a small alumina column with benzene/ether eluent. The first fraction was collected, the solvent was removed in vacuo and the remaining solid was recrystallized once from toluene/hexane giving 16.1 mg of 9. It was obtained in 44% overall yield (83% yield, corrected for unreacted 5).

The remaining orange band was washed off the column with THF. After removing the solvent in vacuo, the orange solid was recrystallized from toluene/ether to give $(\eta^5-C_5Me_5)Ir(PMe_3)Br_2$ (21), m.p. 214. ^1H NMR (C_6D_6): δ 1.39 (d J=2.2 Hz, C_5Me_5), 1.41

(d J=10.9 Hz, PMe_3). Anal. Calcd for $C_{13}H_{24}IrPBr$: C, 27.72; H, 4.29. Found: C, 27.97; H, 4.38.

Reactions of 7.

a) **With Bromine.** 7 (5.0 mg, 1.0×10^{-5} mol) was added to an NMR tube in the dry box. Benzene-d_6 (0.5 mL) was added, and a septum was used to cap the tube. After removing the tube from the dry box, Br_2 (1.0 μL, 1.9×10^{-5} mol) was added by syringe. By ^1H NMR, cyclohexane (δ 1.39 ppm) was the major organic product.

b) **With Zinc Bromide.** 7 (5.0 mg, 1.0×10^{-5} mol) was added to an NMR tube in the dry box. CD_2Cl_2 (0.5 mL) and $ZnBr_2$ (2.0 mg, 8.9×10^{-6} mol) were added to the tube, and an instant color change from pale yellow to dark yellow occurred. By ^1H NMR, cyclohexane (δ 1.40 ppm) was the major organic product.

c) **With Hydrogen Peroxide.** 7 (5.0 mg, 1.0×10^{-5} mol) was added to an NMR tube in the dry box. Benzene-d_6 (0.5 mL) was added, and after removing the tube from the dry box, H_2O_2 (30%, 10 μL) was added. By ^1H NMR, cyclohexane (δ 1.39 ppm) was the major organic product.

d) **With Tetrafluoroboric Acid.** 7 (3.0 mg, 6.1×10^{-6} mol) was added to an NMR tube in the dry box. Benzene-d_6 (0.5 mL) and the $HBF_4 \cdot OEt_2$ (1.0 mL) were added, respectively. By ^1H NMR, cyclohexane (δ 1.39 ppm) was the major organic product.

e) **Irradiation.** 7 (3.0 mg, 6.1×10^{-6} mol) was added to an NMR tube in the dry box. Benzene (0.6 mL) was added to the tube, after which the tube was capped and sealed with parafilm. The reaction mixture was photolyzed for 12 hrs. The tube was returned to the dry box and the solvent was removed in vacuo. The residue was taken up in benzene-d_6; NMR analysis showed the product to be 6.

f) Thermal decomposition. 1) Benzene-d_6. 7 (3.0 mg, 6.1 x 10^{-6} mol) was added to an NMR tube fused to a ground glass joint in the dry box. Benzene-d_6 (0.6 mL) was added, and the tube was subsequently topped with a vacuum stopcock. After removing the tube from the dry box, it was immersed in liquid nitrogen, evacuated and sealed. After 43 hrs at 60°C, no reaction occurred, but after 22 hrs at 110°C, NMR analysis showed that 44% of 7 had been converted to 6-d_6 and cyclohexane.

2) Pentane. The same procedure as with benzene-d_6 was carried out with pentane (0.55 mL). After heating the solution in a sealed tube at 110°C for 52 hrs, the tube was broken open in the dry box, the solvent was removed and the residue was taken up in benzene-d_6. By NMR, the only new products were 17 (88% yield) and cyclohexane.

Irradiation of 5 in neopentane. $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(CH_2CMe_3)$ (8) was prepared as described for 7 using a glass bomb for a vessel. Upon column chromatography on alumina (III), only decomposition occurred. A second preparation was attempted using the same procedure with 5 (127 mg, 3.13 x 10^{-4} mol) and neopentane (5.0 mL). After the NMR spectrum was taken, the benzene-d_6 was removed in vacuo and the residue was taken up in pentane. The solution was cooled to -40°C and filtered. The filtrate was collected, the solvent was removed in vacuo and the resulting yellow oil was collected. We have been unable to crystallize the compound. For ^1H and ^{13}C NMR spectra, see Table 1. IR (C_6H_{12}): 2106 cm^{-1} (ν_{Ir-H}).

To obtain complete characterization, the compound was converted to the corresponding bromide derivative (10). In a third experiment, 5 (26.5 mg, 6.53×10^{-5} mol) and neopentane (0.71 mL) were irradiated for five hr in a sealed NMR tube. Following the same procedures as for the synthesis of 9, the reaction mixture was taken up in benzene-d_6; by NMR, 61% of 5 was converted to neopentyl hydride 8. Bromoform (10 µL, 1.16×10^{-4} mol) was added to the solution by syringe. After two hr, the solution was chromatographed on a small alumina (III) column with benzene/ether eluent. The first fraction was collected, the solvent was removed in vacuo and the orange solid was recrystallized once from toluene/hexane giving 14.1 mg 10. It was obtained in 46% overall yield (75% yield, corrected for unreacted 5), m.p. 163. ^1H NMR (C_6D_6): δ 1.42 (d J=1.9 Hz, C_5Me_5), 1.26 (d J=10.2 Hz, Pme_3), 1.46 (s, CMe_3), 2.20 and 1.52 (d J=12.2 Hz, CH_2). Anal. Calcd for $C_{18}H_{35}IrPBr$: C, 38.98; H, 6.36. Found: C, 38.79; H, 6.23.

Irradiation of 5 in pentane. Dihydride 5 (8.5 mg, 2.10×10^{-5} mol) was irradiated following the procedures for a photochemical experiment in an NMR tube in pentane (0.59 mL). After irradiating for 5.2 hr, the solvent was removed in vacuo and the residue was taken up in benzene-d_6. By NMR, 77% of 5 was converted to 13. For NMR data, see Table 3. IR (pentane): 2101 cm^{-1} (ν_{Ir-H}).

To obtain complete characterization, 13 was converted to the corresponding bromide derivative (17). Dihydride 5 (20.3 mg, 5.00 x 10^{-5} mol) was irradiated following the procedures for a photochemical experiment in an NMR tube in pentane (0.51 mL). After five hr, the solvent was removed in vacuo and the reaction mixture was taken up in benzene-d_6. By ^{1}H NMR, 50% of 5 was converted to the alkyl hydride 13. Bromoform (10 µL, 1.16 x 10^{-4} mol) was added to the solution by syringe. After two hr, the solution was chromatographed on a small alumina (III) column with benzene/ether eluent. The first fraction was collected, the solvent was removed in vacuo and the solid was recrystallized twice from hexamethyldisiloxane giving 9.0 mg of 17. It was obtained as yellow/orange crystals in 38% over-all yield (76% yield, corrected for unreacted 5), m.p. 127. ^{1}H NMR (C_6D_6): δ 1.52 (d J=1.9 Hz, C_5Me_5), 1.29 (d J=10.1 Hz, PMe_3), 2.62, 1.20-1.85 (broad, n-pentyl). Anal. Calcd for $C_{18}H_{35}IrPBr$: C, 38.98; H, 6.36. Found: C, 39.34; H, 5.98.

Reactions of Alkyliridium Bromides.

a) With Bromine. The NMR tube solution of 9 (prepared in situ by the reaction of 7 (5.0 mg, 1.2 x 10^{-5} mol) and bromoform (15 µL, 1.7 x 10^{-4} mol) in benzene-d_6 (0.5 mL)) was removed from the dry box and bromine (15 µL, 2.9 x 10^{-4} mol) was added by syringe. By NMR, very little information, except for the resonances for (η^5-C_5Me_5)Ir(PMe_3)Br_2 (21), could be gathered due to spectrum broadening. The volatile products were vacuum transferred into a 5 mL pear shaped flask from which they were sampled by GC. By retention times, only a trace (<2%) of cyclohexyl bromide was detected. Similar results were obtained in CCl_4 and pentane, except that in pentane a higher molecular weight product was detected by GC.

b) With DSO_3F. A solution containing 5 (8.5 mg, 2.1×10^{-5} mol) and pentane (0.59 mL) was photolyzed in an NMR tube for 5.2 hr. The solvent was removed in vacuo and replaced with benzene-d_6. Bromoform (3.0 µL) was added by syringe. To this solution of 17, DSO_3F was added by syringe. The volatiles were vacuum transferred, and an NMR analysis revealed the pentane to be $CH_3(CH_2)_2CH_2D$ (integration: $CH_3/CH_2 = 0.86$).

c) With $HgCl_2$. 10 (5.0 mg, 1.2×10^{-5} mol) and benzene-d_6 (0.55 mL) were added to an NMR tube. $HgCl_2$ (10.2 mg, 3.76×10^{-5} mol) and toluene (6.0 µL) as an internal standard were added. A yellow precipitate started to form within one min. After two hrs, the NMR tube was removed from the dry box and centrifuged. The ^1H NMR spectrum showed two new resonances at δ 1.12 (2H) and 0.57 (9H) for neopentylmercuric chloride (as compared to an authentic sample). The resonances for the iridium monobromide derivative of 11 had disappeared due to its insolubility in benzene. Br_2 (3 µL) was added to the reaction mixture. After 24 hrs, the resonances for neopentylmercuric chloride had disappeared, and new resonances for neopentylbromide (as compared to an authentic sample) at δ 0.79 (9H) and 2.87 (2H) have grown in (yield > 98%). This assignment was corroborated by a comparison of retention times of the organic product with neopentyl bromide.

Competition Experiments. To gather ^1H NMR data for the cycloalkyl hydrides, the irradiation of 5 in the corresponding alkane was carried out. A typical experiment is as follows: 5 (7.9 mg, 1.95 x 10^{-5} mol) was added to an NMR tube in the dry box. Cyclopentane (0.60 mL) was added by syringe. The tube was capped, removed from the dry box and sealed with parafilm. The reaction mixture was irradiated for five hours, the solvent was removed in vacuo and the remaining residue was taken up in benzene-d_6 (0.55 mL) for ^1H NMR analysis. For NMR data, see Table 5.

The other cycloalkane irradiations were carried out in an identical fashion with the following amounts of reagents and exceptions: cyclooctane (5, 8.2 mg, 2.02 x 10^{-5} mol; cyclooctane, 0.50 mL); cyclopropane (5, 12.5 mg, 3.08 x 10^{-5} mol; cyclopropane, 3.0 mL) using a glass bomb as a reaction vessel. In the cyclooctane reaction, we observe a second hydride resonance doublet at δ -17.88 which is unexplained. In the primary alkyl hydride resonance region, this may be a primary C-H bond containing impurity in the cyclooctane which reacts much faster than cyclooctane itself.

A representative competition experiment was carried out as follows: 5 (11.1 mg, 2.74 x 10^{-5} mol) was added to a NMR tube in the dry box. Cyclohexane (240 µL, 2.22 x 10^{-3} mol) and then cyclopentane (250 µL, 2.66 x 10^{-3} mol) were added by syringe. The tube was capped, removed from the dry box and sealed with parafilm. The reaction mixture was photolyzed for five hrs. The solvent was then removed from the reaction mixture in vacuo and the remaining residue was taken up in benzene-d_6 (0.55 mL) for ^1H NMR analysis.

The other selectivities were carried out in an identical manner with the following amounts of reagents: pentane/cyclohexane (5, 5.7 mg, 1.4 x 10^{-5} mol; pentane, 275 µL, 2.39 x 10^{-3} mol; cyclohexane, 258 µL, 2.39 x 10^{-3} mol); pentane/cyclopentane (5, 11.0 mg, 2.71 x 10^{-5} mol; pentane, 255 µL, 2.21 x 10^{-3} mol; cyclopentane, 250 µL, 2.66 x 10^{-3} mol); cyclohexane/cyclooctane (5, 10.7 mg, 2.64 x 10^{-5} mol; cyclohexane, 250 µL, 2.31 x 10^{-3} mol; cyclooctane, 233 µL, 1.73 x 10^{-3} mol). The results are summarized in Table 6. All relative rates are corrected for the number of available hydrogen atoms.

Crossover Experiments. 5 (11.0 mg, 2.71 x 10^{-5} mol) was loaded into an NMR tube fused to a ground glass joint and topped with a vacuum stopcock. Using a bulb with known volume (141 mL), cyclohexane-d_{12} (321.5 torr, 2.44 x 10^{-3} mol) and then neopentane (401.5 torr, 3.05 x 10^{-3} mol) were expanded into the evacuated bulb and subsequently condensed in the NMR tube. The tube was sealed, and the reaction mixture was photolyzed for 5 hrs. Afterwards, the tube was taken back into the dry box, the solvent was removed in vacuo and the residue was taken up in benzene-d_6 (0.55 mL). The amount of crossover product (7-d_{11}) was then determined by ^1H NMR by examining the hydride region of the spectrum. The crossover product accounted for seven percent of the product hydrides and deuterides. Upon examining the C_5Me_5

region of the spectrum, the ratio of 8 to all the isotopic isomers of 7 was 1.56.

In the photolysis of 5 (11.0 mg, 2.71 x 10^{-5} mol) in cyclohexane (320.2 torr, 2.45 x 10^{-3} mol) and neopentane (400.2 torr, 3.04 x 10^{-3} mol) carried out under the same conditions and with the same procedures as above, the ratio of 8 to 7 was 1.41. Therefore, the isotopic effect is k_H/k_D = 1.38.

A second crossover experiment was run under the same conditions as above but with 5 (10.5 mg, 2.59 x 10^{-5} mol), cyclohexane-d_{12} (160.9 torr, 4.47 x 10^{-3} mol) and neopentane (32.2 torr, 8.95 x 10^{-4} mol) using a 516 mL bulb. In this case, the crossover product 7-d_{11} accounted for eight percent of the hydride and deuteride products.

5 (14.8 mg, 3.64 x 10^{-5} mol) and cyclohexane-d_{12} (1.0 mL) were added to a glass bomb in the dry box. After removing the bomb from the dry box, the reaction mixture was put through three freeze/pump/thaw cycles and then photolyzed for 40 min. The hydrogen evolved was collected by Toepler pumping through two liquid nitrogen traps. A mass spectral analysis showed >99.9% of the hydrogen was H_2.

A similar photolysis of 5 (13.2 mg, 3.25 x 10^{-5} mol) in cyclohexane-d_{12} (0.8 mL) for 24 hrs led to some exchanged hydrogen by mass spectral analysis. 20% of the hydrogen gas was HD and 1.7% D_2.

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23) The PMe_3 complex was prepared in an analogous fashion to the PPh_3 complex (Ref. 9). Since that time, it has been prepared by other workers (Ref. 11).

Epilogue

Throughout the last three and a half years, I performed many experiments, not all of which are included in my thesis. What has been included are those experiments that, when taken together, tell a coherent story. Sometimes the logic behind the examining of a particular reaction becomes lost, so I will recount historically how all of my projects evolved.

After joining the Bob Bergman group, I chose a project proposed by Bob that looked at the mechanism of the hydrogenolysis of $CpCo(PPh_3)Me_2$ (A). I have always been interested in mechanisms and the reactions of small molecules. After looking at the reaction of A and H_2, I could not find any simple kinetic expression to explain my data. I thought that since I was running these reactions in an NMR tube, I was not getting good mixing of hydrogen with the solution. To alleviate this problem, I attempted to synthesize the dibenzyl cobalt analogue of A, a compound reported in the literature. In this case, I had hoped to follow the uptake of hydrogen gas by a change in gas volume, and not worry about diffusion of hydrogen into the solution or having a gaseous alkane as a product. To my dismay, I could not synthesize the dibenzyl cobalt complex in over one dozen attempts with varied conditions. In my frustration, I decided to synthesize the pentamethylcyclopentadienyl derivative of A (B). Naively, perhaps, I thought that I might have a chance to stabilize our proposed cobalt dihydride with more electron density. After confronting many difficulties in the synthesis of B, I wondered if this project had reached its end. Only the surprisingly successful synthesis of B via a Grignard reagent in acetonitrile solvent saved this project. I must admit that the preparation with acetonitrile was a last gasp attempt. It is difficult to put into words the feeling I experienced when I took the NMR spectrum of the reaction mixture of B and hydrogen. I was dutifully scanning the hydride region, as I had in all of my previous reactions, but this time it was not in vain — a hydride resonance appeared. The majority of the subsequent reactions were fruitful and were thus discussed in Chapter I.

During the course of this cobalt project, Prof. James Collman of Stanford proposed that d^8 CpML complexes were of high energy and not favorable intermediates. This was surprising to our group, since we had invoked this type of intermediate many times in our work. Bob, Henry Bryndza and I discussed this proposal and decided to take the product of my preliminary hydrogenolyses, $CpCo(PPh_3)_2$ (C), and show kinetically that $CpCoPPh_3$ was indeed a viable intermediate. We proceeded to show that phosphine substitution in C goes by a dissociative mechanism. This work was not included in my thesis because it has already appeared in the thesis of Henry Bryndza (1981). It has also been published previously in full paper form (Janowicz, A. H.; Bryndza, H. E.; Bergman, R. G. J. Am. Chem. Soc. 1981, 103, 1516).

At the close of my cobalt hydrogenolysis project, I was intrigued by the cobalt dihydride that I had synthesized. It easily lost dihydrogen, so I thought that by going down the periodial table to rhodium or iridium, I should be able to synthesize and isolate these dihydrides and study their chemistry. This turned out to be the case, as I was able to isolate both the rhodium and iridium analogues of the cobalt dihydride. After performing some reactions with both the rhodium and iridium dihydrides, I decided to concentrate on the iridium dihydride. As stated in Chapter II, other workers had shown that upon the photolysis of dihydrides, dihydrogen was extruded, which resulted in the formation of reactive intermediates. Initially, I had hoped that the reactive intermediate that I would be generating would react with cyclopropane to form a metallacyclobutane. To my surprise, the intermediate in the iridium case reacted with the benzene solvent as well as with one of its own ligands. As noted in Chapter II, I substituted PMe_3 for the PPh_3 ligand to alleviate the intramolecular reactions. At this point, I realized I had generated a <u>very</u> reactive intermediate and proceeded to react it with saturated hydrocarbons to see what the result would be. When cyclohexane reacted across the C-H bond to give the alkyl hydride, I was extremely excited (an understatement), since I realized this activation of a C-H bond in a saturated hydrocarbon had been sought after for many years. Not surprisingly, I had some difficulty convincing Bob of this reaction at first, but the rest is history.

The work on my system is not over now that I am leaving

Berkeley. Four new students are picking up where I left off and are expanding in the area. I am anxiously awaiting their further results.

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