J. Am. Chem. Soc. **1983**, *105*, 3929–3939

sealed at −196 °C. In preparation for each run, the tube was warmed to −78 °C in a CO_2/2-propanol bath with shaking to assure the complete formation of **5a**. The tube was then warmed to room temperature and placed in the probe of an NMR spectrometer maintained at 28.0 ± 0.5 °C. Data sets were collected over 3 half-lives of the reaction. A typical data set consisted of 12 acquisitions at 201.947 MHz with a SW = ±1113.58 Hz, a pulse width of 20°, and a 5-s delay between pulses. The progress of the reaction was monitored by integrating the Cp resonances of **5a** and **6e** at δ 5.4 and 5.15, respectively, vs. the ferrocene resonance at δ 4.1.

Acknowledgment. We are grateful for support of this work from National Institutes of Health, Grant No. GM-25459. We also wish to thank Dr. Peter Hoffmann for providing us with the results of his calculations prior to publication. R.G.B. acknowledges a Research Professorship from the Miller Institute for Basic Research in Science at U. C. Berkeley, 1982–1983.

Registry No. 3, 51862-20-5; **4**, 78305-62-1; **5a**, 78305-63-2; **6a**, 78305-64-3; **6b**, 78305-65-4; **6c**, 85454-60-0; **6d**, 85454-61-1; **6e**, 85454-62-2; **8a**, 85454-63-3; CH_3I, 74-88-4; CH_3CH_2I, 75-03-6; PPh_3, 603-35-0; PEt_3, 554-70-1; $(\eta^5\text{-}MeC_5H_4)Co(CO)_2$, 75297-02-8; $CH_3C_5H_5$, 26519-91-5; $Co_2(CO)_8$, 10210-68-1; $CpCo(CO)_2$, 12078-25-0; NO, 10102-43-9; $[MeCpCo(NO)]_2$, 85454-64-4; Na[MeCpCoNO], 85454-65-5; PPNCl, 21050-13-5; PPN-**4**, 85454-66-6; PPN[MeCpCoNO], 85454-68-8; $LiAlH_4$, 16853-85-3; methyl *p*-toluenesulfonate, 80-48-8; isopropyl iodide, 75-30-9; *p*-methylbenzyl bromide, 104-81-4; Co, 7440-48-4.

Activation of C–H Bonds in Saturated Hydrocarbons on Photolysis of $(\eta^5\text{-}C_5Me_5)(PMe_3)IrH_2$. Relative Rates of Reaction of the Intermediate with Different Types of C–H Bonds and Functionalization of the Metal-Bound Alkyl Groups

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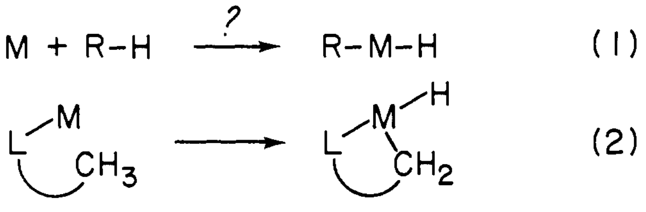
Received October 20, 1982

Abstract: The full details of experiments on a homogeneous system which successfully converts completely saturated alkanes into hydridoalkylmetal complexes (M + RH → R–M–H) are reported. Irradiation of $(\eta^5\text{-}C_5Me_5)(PMe_3)IrH_2$ (**5**) in saturated hydrocarbons (R–H) using a 500-W Oriel focused-beam mercury lamp leads to extrusion of H_2 and production of the hydrido alkyl complexes $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(R)(H)$. Competition experiments have allowed measurement of the relative rates at which the intermediate formed on H_2 loss (presumably the coordinatively unsaturated complex $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir$) reacts with different types of C–H bonds. Relative to cyclohexane (1.0), these are as follows: benzene (4.0), cyclopropane (2.65), cyclopentane (1.6), neopentane (1.14), cyclodecane (0.23), and cyclooctane (0.09). Reductive elimination of hydrocarbon occurs at elevated temperature, regenerating $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir$, which may then react with another hydrocarbon acting as solvent; thus the C–H activation process can also be induced thermally. C–H bonds having high bond energies react relatively rapidly; this fact, along with crossover experiments, suggests that radical intermediates are not involved in the C–H activation reaction. Treatment of the hydrido neopentyl complex **8** with $CHBr_3$ converts it to the corresponding bromo neopentyl complex **10**. This material reacts with $HgCl_2$ to give neopentylmercuric chloride, which forms neopentyl bromide on reaction with Br_2. Thus overall stoichiometric conversion of hydrocarbons to functionalized organic molecules is feasible in this system. The factors which have been presumed to influence the rates of reaction of transition-metal complexes with saturated C–H bonds–notably the need for electron-rich metals and close proximity of reacting centers—are discussed in detail.

One of the most intriguing—and yet elusive—goals of organometallic chemistry has been the use of transition-metal complexes to "activate" carbon–hydrogen bonds in completely saturated organic compounds.[1] One impetus for research in this area is that saturated hydrocarbons are among the most ubiquitous, and chemically stable, of all organic materials, due to the high values of their C–H and C–C bond energies. It is important to learn the chemical requirements for causing such stable substances to react and, if such reactions are found, to understand their mechanisms. On a more practical level, understanding C–H activation should help to develop methods for converting saturated hydrocarbons, such as those found in petroleum and formed in Fischer–Tropsch reactions, into functionalized compounds more easily utilized in chemical conversions.

Scheme I



Saturated hydrocarbons are of course not completely unreactive, and as a result they have a long history of activation by nonmetallic reagents and methods. Hydrocarbon thermal reactions and combustion have been studied by both chemists and chemical engineers, and there are well-known free radical reactions (e.g.,

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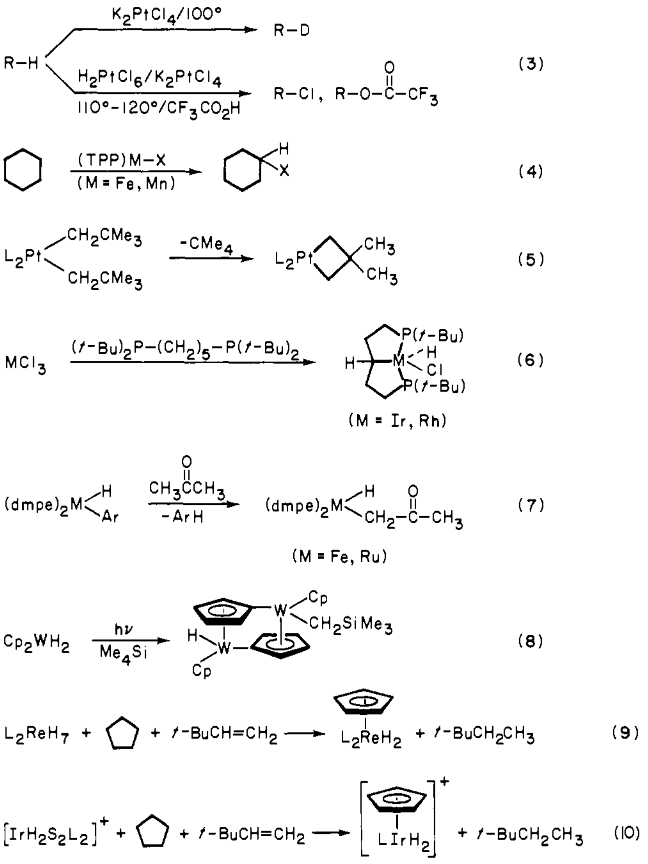
[1] (a) Parshall, G. W. *Catalysis* (*London*) **1977**, *1*, 335. (b) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97. (c) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147. (d) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; p 179 ff. (e) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980, p 222 ff. (f) Halpern, J. *Discuss. Faraday Soc.* **1968**, *46*, 7.

0002-7863/83/1505-3929$01.50/0

Scheme II

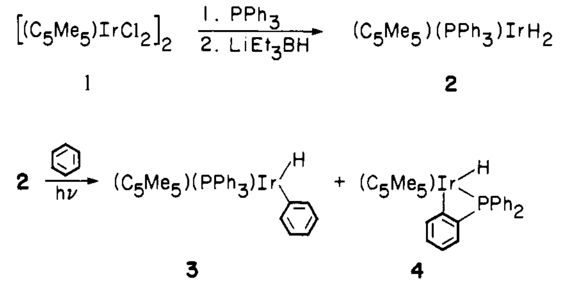


autoxidation, photochlorination) which can serve to functionalize these materials.[2] More recently, reagents such as ozone, superacids, fluorine, and H_2O_2 have been used to activate hydrocarbons.[3]

The reactions summarized above often require large amounts of energy (either light, heat, or chemical) and are usually very unselective. The hope of carrying out C–H activation with higher selectivity has been one of the major incentives to organometallic research in this area. Much work has been done over the past 10 or 15 years, and while certain types of C–H activation have been achieved, the direct intermolecular insertion (oxidative addition) of a metal center into a C–H bond, leading to a stable hydrido alkyl complex (reaction 1 in Scheme I), has eluded discovery.

A few examples of C–H activation reactions which were known when this work was initiated are shown in Scheme II. In the late 1960s and early 1970s it was demonstrated that certain platinum salts, in the presence of acid, could be used to effect H–D exchange (eq 3), first in aromatic compounds and then in alkanes.[4] Many studies have also been done in which alkane oxidations have been mediated by metals.[5] Although there is a possibility that some of these reactions are initiated by oxidative addition of a metal center to a C–H bond, many clearly involve free radical mechanisms, and some may even be heterogeneous processes. More recent studies of alkane activation utilizing porphyrin complexes (e.g., reaction 4), stimulated by the importance of biological alkane hydroxylation, have been clearly shown to proceed by free radical pathways.[6]

Scheme III



The search for direct intermolecular oxidative addition has been less rewarding. It has been made even more frustrating by the facility of certain C–H oxidative additions which appear to proceed easily in intramolecular situations (eq 2 in Scheme I) but apparently cannot be extended to the intermolecular case. The insertion of a metal into the C–H bond of a ligand already attached to it at some other point (such as a phosphorus atom) is a ubiquitous process when aromatic or otherwise activated C–H bonds are involved, but cases are now known in which metals undergo intramolecular insertion into C–H bonds not activated (i.e., lowered in bond energy or increased in acidity) by adjacent organic functional groups.[7] As illustrated in the examples shown in eq 5 and 6, this latter process has been developed as a useful method for synthesizing metallacycles.[7a,d,e] It appears, however, that the metal centers in these systems resist reaction with C–H bonds not present in the same molecule as the metal center.

Intermolecular metal/hydrocarbon reactions have been achieved with certain very reactive metal fragments, such as metal atoms in matrices and metal ions in the gas phase.[8] In solution, a few relatively electron-rich complexes have been demonstrated to undergo insertion into C–H bonds activated by adjacent functional groups (e.g., eq 7 and 8), but the metal centers in these molecules apparently react with C–H bonds in their own ligands more rapidly than with saturated hydrocarbons.[9]

Recently, the two very interesting and unique intermolecular C–H activation reactions shown in eq 9 and 10 were reported.[10,11]

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(2) (a) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957. (b) Huyser, E. S. "Free Radical Chain Reactions"; Wiley: New York, 1970. (c) Pryor, W. A. "Free Radicals"; McGraw-Hill: New York, 1966.

(3) (a) Beckwith, A. L. J.; Duong, T. *J. Chem. Soc. Chem. Commun.* **1978**, 413. (b) Cohen, Z.; Keinan, E.; Mazur, Y.; Haim Varkony, T. *J. Org. Chem.* **1975**, *40*, 2141 and references cited there. (c) Deno, N. C.; Jedziniak, E. J.; Messer, L. A.; Meyer, M. D.; Stroud, S. G.; Tomezsko, E. S. *Tetrahedron* **1977**, *33*, 2503. (d) Rozen, S.; Gal, C.; Faust, Y. *J. Am. Chem. Soc.* **1980**, *102*, 6861 and references cited there. (e) Olah, G. A.; Parker, D. G.; Yoneda, N. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 909.

(4) (a) Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1969**, *43*, 2174. (b) Hodges, R. J.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Chem. Commun.* **1971**, 462.

(5) (a) Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: 1973; Vol. II, Chapter 11. (b) Howard, J. A. In "Free Radicals"; Kochi, J. K. Ed., Wiley-Interscience: New York, 1973; Vol. II, Chapter 12.

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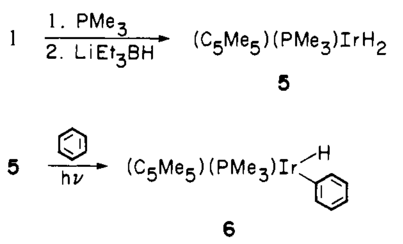
(7) For examples, see: (a) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732. (b) Clark, H. C.; Geol, A. B.; Geol, S. *Inorg. Chem.* **1979**, *188*, 2803. (c) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7728. (d) Empsall, H. D.; Hyde, E. M.; Markham, R.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589. (e) Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans* **1980**, 59 and references cited there. (f) Andersen, R. A.; Jones, R. A.; Wilkinson, *Ibid.* **1978**, 446. (g) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991. (h) Chappell, S. D.; Cole-Hamilton, D. *J. Chem. Soc., Chem. Commun.* **1980**, 238. (i) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448. (j) Adams, R. D.; Selegue, J. P. *Inorg. Chem.* **1980**, *19*, 1795. (k) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *209*, C60.

(8) (a) Hale, L. F.; Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 962. (b) Allison, J.; Feas, R. B.; Ridge, D. P. *Ibid.* **1979**, *101*, 1332. (c) Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A. **1981**, *102*, 1574. (d) Breckenridge, W. H.; Renlund, A. M. *J. Phys. Chem.* **1679**, *83*, 303. (e) Remick, R. J.; Asunta, T. A.; Skell, P. S. *J. Am. Chem. Soc.* **1979**, *101*, 1320.

(9) (a) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113. (b) Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1950. (c) Green, M. L. H.; Berry, M.; Couldwell, C.; Prout, K. *Nouv. J. Chim.* **1977**, *1*, 187. (d) Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1971**, 1508. (e) Ittel, S. D.; Tolman, C. A.; Krusic, P. J.; English, A. D.; Jesson, J. P. *Inorg. Chem.* **1978**, *17*, 3432. (f) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 6073; **1978**, *100*, 7577. (g) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *Ibid.* **1981**, *103*, 379. (h) Rausch, M. D.; Gastinger R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *Ibid.* **1977**, *99*, 7870.

Scheme IV



These may be initiated by C–H insertion, but it has so far been difficult to determine this conclusively, because the reactions are quite complicated. They involve multiple hydrogen loss in the saturated hydrocarbon reactants and require an added alkene as a hydrogen acceptor. A most unusual aspect of the iridium reaction is that it is carried out in methylene chloride. Thus C–H activation takes place in preference to reaction with the normally much more labile C–Cl bonds of the solvent.

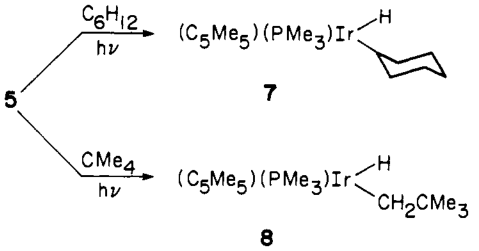
Despite this extensive work in the C–H activation area, when the discovery discussed in this paper was made, no intermolecular example of the reaction shown in eq 1 was known for organo-transition–metal complexes and completely saturated hydrocarbons in homogeneous solution. Early in 1982 we reported such a reaction in a new iridium complex.[12] The details of this work, along with additional information on the chemistry and selectivity of the iridium system, are described here.

Results and Discussion

Synthesis and Reactions of (η^5-C_5Me_5)Ir(PPh_3)H_2 (2). Our initial experiments centered around the previously unknown dihydridoiridium complex **2**. As shown in Scheme III, **2** was prepared in 42% yield by treatment of the dichloride dimer **1**[13] with PPh_3, followed by 2 equiv of $LiEt_3BH$. Irradiation of this material through Pyrex in benzene solution resulted in extrusion of dihydrogen. The loss of H_2 upon photolysis of transition-metal di- and polyhydrides is a well-documented process.[9b,c,14] The resulting organometallic products were the hydrido phenyl complex **3** and the ortho-metalated complex **4** in a ratio of 47:53, respectively.

These materials were formed presumably via the coordinatively unsaturated intermediate Cp′IrPPh$_3$ (Cp′ = η^5-C_5Me_5). Hydrido phenyl 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 oxidative addition. 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-metalated product **4**. However, in the case of cyclohexane, a significant amount (30%) of a new hydride was detected by NMR spectroscopy in the crude reaction mixture. Its ^{1}H 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 δ 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). These NMR data suggested that this material might be the intermolecular C–H activation product, Cp′Ir(PPh_3)(H)(C_6H_{11}). This new material could not be separated successfully from the ortho-metalated complex. We therefore decided to prepare and examine the photolysis of the corresponding PMe_3 dihydride, in hopes of making ortho-metalation less favorable.

Scheme V



Scheme VI

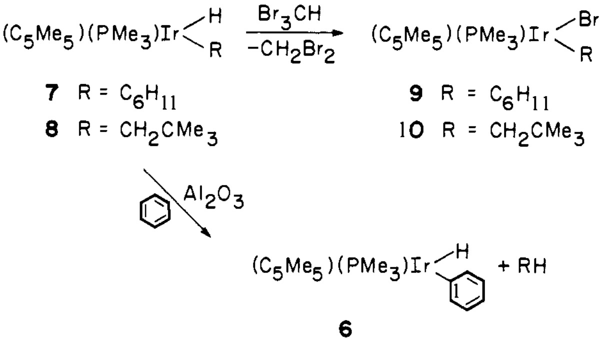


Table I. ^{1}H and ^{13}C NMR Spectra of (η^5-C_5Me_5)Ir(PMe_3)(C_6H_{11})H (7) and (η^5-C_5Me_5)Ir(PMe_3)(CH_2CMe_3)H (8)[a]

	7	8
	^{1}H Spectra	
C_5Me_5	1.87 (dd, J = 1.8, 0.7)	1.82 (dd, J = 1.7, 0.7)
PMe_3	1.24 (d, J = 9.5)	1.21 (d, J = 9.6)
Ir-H	−18.67 (d, J = 37.0)	−17.67 (d, J = 37.1)
Ir-R	1.50–2.30 (br)	1.28 (s, CMe_3)
		1.5 (m, CH_2)
	^{13}C Spectra	
C_5Me_5	92.36 (d, J = 3.4)	92.00 (d, J = 3.4)
$C_5(\mathit{C}H_3)_5$	10.75 (s)	10.62 (s)
P(CH_3)	19.69 (d, J = 35.7)	19.68 (d, J = 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, C($\mathit{C}H_3$)$_3$)
	43.96 (d, 2, β-C)	35.71 (s, 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 in δ; coupling constants in Hz.

Synthesis and Reactions of (η^5-C_5Me_5)Ir(PMe_3)H_2 (5). As in the synthesis of triphenylphosphine dihydride **2**, treatment of dichloride dimer **1** with trimethylphosphine, followed by $LiEt_3BH$, gave **5** in 76% yield (Scheme IV).[15] Irradiation of **5** in benzene resulted in loss of H_2 and attack on the solvent, leading to the hydridophenyliridium complex **6**. We detected only the intermolecular product; no evidence for any intramolecular reaction was found.[16] When 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-h irradiation) in which both the PMe_3 and C_5Me_5 ligands were clearly intact.[17] Although thermally stable

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(10) (a) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738. (b) Crabtee, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *Ibid.* **1982**, *104*, 107. (c) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic; J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *Ibid.* **1982**, *104*, 6994.

(11) (a) Baudry, D.; Ephritikine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243. (b) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *Ibid.* **1982**, 1235.

(12) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.

(13) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

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(15) Following submission of the preliminary communication, an alternative preparation of complex **5** was reported: Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003.

(16) Although this system seems to avoid it, intramolecular C–H activation in coordinated Me_3P ligands is known; see, for example: (a) Chiu, K. W.; Wong, W.-K.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1981**, *451*. (b) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272. (c) Al-Jibori, S.; Crocker, C.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1981**, 1572 and references cited there.

Table II. ^1H NMR Shifts (δ) for the Alkyl Hydrides Produced upon Irradiation of 5 in "Nonsaturated Hydrocarbon" Organic Solvents[a]

substrate	C_5Me_5 $(J)^b$	PMe_3 $(J)^c$	IrH $(J)^d$
acetonitrile	1.72 (1.3)[e]	1.22 (10.1)	−17.23 (36.5)
tetramethylsilane[f]	1.80 (1.9)[e]	1.17 (9.8)	−17.08 (38.4)
tetrahydrofuran	1.80[g]	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 constants in Hz. [c] Doublet, coupling constants in Hz. [d] Doublet, coupling constants in Hz. [e] Unable to detect the smaller coupling. [f] Trimethylsilyl resonance is a singlet at δ 0.35. [g] Overlapping peaks prevent the assignment of all the C_5Me_5 resonances and accurate measurement of the coupling constants.

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 (η^5-pentamethylcyclopentadienyl)(trimethylphosphine)hydridocyclohexyliridium(III) (**7**, Scheme V) on the basis of spectral data (Table I) and chemical conversion to the more sparingly soluble bromocyclohexyl complex **9** (Scheme VI). Thus, the intermediate formed on irradiation of dihydride **5**, presumably $Cp'Ir(PMe_3)$, reacts cleanly with unactivated C–H bonds.

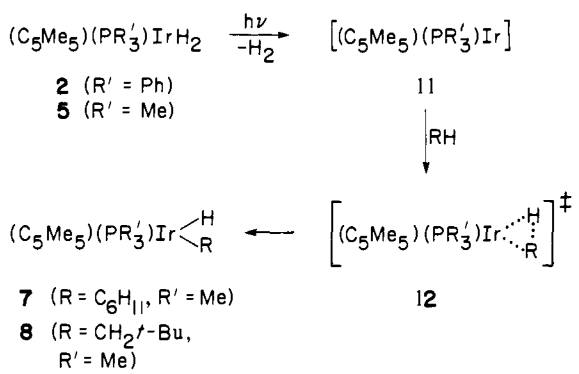
An interesting feature of these alkyl hydrides can be seen in examining the ^{13}C NMR spectrum of cyclohexyl complex **7**. The iridium atom, having four different substituents, is a chiral center. Thus, the β and γ carbon atoms form pairs of diastereomeric carbon atoms, and two signals appear for each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

Irradiation of dihydride **5** in neopentane solvent gives, after 5.3-h irradiation time (64% NMR yield after 83% conversion), a new complex once again seen by NMR spectroscopy 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 hydrido alkyl complex analogous to **7** (Scheme V)), on the basis of spectral data (Table I) and conversion to the corresponding bromo neopentyl complex **10** (Scheme VI).

Treatment of hydrido alkyl complexes **7** and **8** with reagents such as $ZnBr_2$, H_2O_2, Br_2, HBF_4, or O_2 resulted 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 1 h generates the hydrido phenyl complex **6** and cyclohexane (95% yield) or neopentane (98% yield), respectively (Scheme VI).

Photochemical reaction of dihydride **5** with a few other organic compounds was investigated briefly by NMR spectroscopy. A single hydride product was formed in the presence of both acetonitrile and tetramethylsilane. In the case of tetrahydrofuran, four new hydride resonances were detected by NMR spectroscopy. We assume these are products formed by attack at both the 2- and 3-positions, yielding two pairs of diastereomers. The ^1H NMR chemical shifts of the products formed in these experiments are summarized in Table II.

Scheme VII



Scheme VIII

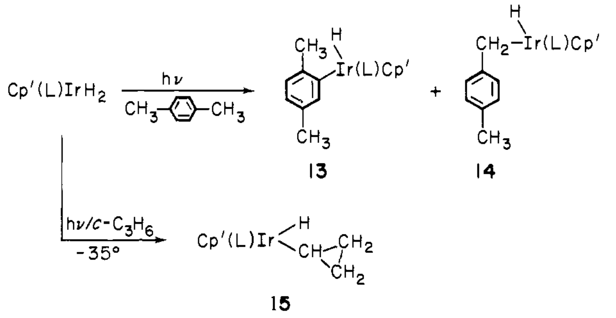
(A)

$$\mathrm{Cp'(L)IrH_2 \xrightarrow{h\nu} Cp'(L)IrH + H\cdot}$$
$$\mathrm{H\cdot + RH \longrightarrow H_2 + R\cdot}$$
$$\mathrm{Cp'(L)IrH + R\cdot \longrightarrow Cp'(L)Ir(R)(H)}$$

(B)

$$\mathrm{Cp'(L)IrH_2 \xrightarrow{h\nu} Cp'L(Ir) + H_2}$$
$$\mathrm{Cp'(L)Ir + RH \longrightarrow Cp'(L)IrH + R\cdot}$$
$$\mathrm{Cp'(L)IrH + R\cdot \longrightarrow Cp'(L)Ir(R)(H)}$$

Scheme IX



Mechanism of the C–H Oxidative Addition Reaction. The most straightforward mechanism for the oxidative addition reaction is that shown in Scheme VII. We assume, based on extensive precedent,[9b,c,14] that irradiation of the trimethylphosphine dihydride complex **5** leads to an elctronically excited state which rapidly loses H_2, forming coordinatively unsaturated complex **11** as a transient intermediate. The reactive 16-electron metal center in this intermediate then undergoes oxidative addition to the C–H bond of a solvent molecule, presumably via a three-center transition state such as **12**.

Given the difficulties which have arisen in elucidating the mechanisms of certain other oxidative addition reactions,[18] before concluding that Scheme VII is the most likely pathway for our reactions, we felt some care should be taken in ruling out other possibilities, especially those involving free radicals. Two possible radical mechanisms are shown in Scheme VIII. The first one (mechanism A) suggests that irradiation might generate an excited state in which only one M–H bond is cleaved, leading to a paramagnetic intermediate Cp'IrLH (Cp' = Me_5C_5) and a hydrogen atom. The latter should be sufficiently reactive to abstract a hydrogen atom from an ordinary alkane, leading to H_2 and akyl radicals. These would then recombine with the iridium fragment, leading to the hydrido alkyl product. In the second

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(17) The qualitative behavior of these photolytic reactions is reproducible, but they are relatively inefficient, and the buildup of small amounts of unidentified absorbing materials tends to make the rates decrease as the reaction proceeds. This has prevented us from carrying several of them to completion and has also discouraged attempts to measure quantum yields. As a result of these factors, the C–H activation reactions require a relatively intense light source and in some cases extended reaction times (these typically ranged from 5 to 25 h, depending on the substrate). Photolyses were carried out by irradiating carefully degassed solutions of the air-sensitive dihydride in sealed or tightly capped Pyrex NMR tubes, using a focused-beam Oriel photolysis apparatus equipped with a 450-Watt mercury lamp. Careful adjustment of the beam was required to achieve subtantial conversion of the dihydride to product.

(18) See, for example: (a) Labinger, J. A.; Braus, R. J.; Dolphin, D.; Osborn, J. A. *J. Chem. Soc., Chem. Comm.* **1970**, 612. (b) Jensen, F. R.; Knickel, B. *J. Am. Chem. Soc.* **1971**, *93*, 6339. (c) Pearson, R. G.; Muir, W. R. *Ibid. Chem. Soc.* **1970**, *92*, 5519. (d) Lau, K. S. Y.; Fries, R. W.; Stille, J. K. *Ibid.* **1974**, *96*, 4983. (e) Labinger, J. A.; Osborn, J. A. *Inorg. Chem.* **1980**, *198*, 3230.

mechanism, H_2 is lost in the first step. If, for some reason, the intermediate **11** were to abstract a hydrogen atom rather than undergo insertion, this would generate Cp′(L)IrH and an alkyl radical, and these could then recombine to give the final product.

The first mechanism is rather easy to rule out, since it predicts that one of the hydrogens in the starting dihydride remains in the final product. We therefore carried out the reaction of dihydride **5** in perdeuteriocyclohexane. Only $Cp'(PMe_3)Ir(C_6D_{11})D$ and H_2 were formed in this reaction.[19]

One type of evidence which may be used to test mechanism B in Scheme VIII utilizes the assumption that because the second step in this mechanism generates alkyl radicals, the rate of the reaction should be relatively fast when stable radicals are generated but slower when less stable radicals are formed. Put another way, weak C–H bonds should be abstracted most readily, as they are in other hydrocarbon radical processes such as autoxidation and chlorination. We have examined this prediction by carrying out some simple relative rate studies using competition techniques. The general question of selectivity is discussed in the next section, but two experiments relevant to the radical–reaction problem are summarized in Scheme IX. As illustrated, irradiation of dihydride **5** in *p*-xylene provides the unsaturated intermediate **11** with an opportunity to choose between attack on the aromatic ring and abstraction of the relatively weak benzylic C–H bond. It is well established that radicals preferentially choose the latter;[20] our iridium intermediate, in contrast, reacts 3.7 times more rapidly with the aromatic ring (ratio corrected for the number of hydrogens available in each path), giving a preponderance of **13** over **14** (a further discussion of this reaction in the following section details the method of analysis of this reaction mixture). Even more striking is the reaction with cyclopropane. This organic molecule has relatively weak C–C bonds due to strain but very strong C–H bonds (106 kcal/mol)[21] due to the large amount of s character in these bonds. As a result, alkyl radicals abstract hydrogen only very slowly from cyclopropane. Even if radical reactivity were not a problem, one might expect the iridium intermediate **11** to insert into the C–C bonds of cyclopropane, rather than abstract a hydrogen. As shown in Scheme IX, however, this does not occur—the exclusive product of the reaction is the hydrido cyclopropyl complex **15** formed by C–H insertion. Following this experiment, we irradiated dihydride **5** in a mixture of cyclopropane and cyclohexane. This demonstrated that the $Cp'Ir(PMe_3)$ intermediate actually reacts *faster* with the C–H bonds of the smaller ring (rate constant ratio 2.6 after statistical correction), again in sharp contrast to the result which would be predicted for a radical-like species.

Another test of the second radical mechanism in Scheme VIII, as well as any other process which might place the R and H groups from the reacting hydrocarbon on different metal centers in the final product, involves a crossover experiment.[22] In a mixture of deuterated and undeuterated hydrocarbons such as cyclohexane-d_{12} and cyclohexane-d_0, direct insertion (Scheme VII) should lead only to d_0 and d_{12} products. However, to the extent that the radicals in the second mechanism in Scheme VIII escape their solvent cage, some d_1 and d_{11} products should be generated. Any other so-called "intermolecular" mechanism which separates R and H before they become attached to the metal will have a similar result.

We were unable to carry out this experiment with labeled and unlabeled cyclohexane, because the sensitive hydrido alkyl complexes decomposed during analysis by conventional electron-impact mass spectroscopy. Although good molecular ion peaks could be obtained by using field desorption mass spectroscopy, the FDMS peak intensities were not reproducible enough to provide trustworthy estimates of the amount of crossover products which might be present in our reaction mixtures. As an alternative, therefore, we decided to take advantage of the very different chemical shifts in the hydride region of the ^1H NMR spectrum of cyclohexyl and neopentyl hydride complexes **7** and **8**. The results which would be expected from concerted and "crossover" mechanisms are illustrated in Scheme X. To make sure the two hydrocarbons had similar reactivities, dihydride **5** was irradiated in a 1:1 mixture of neopentane and cyclohexane. Figure 1a shows the Me_5C_5 and

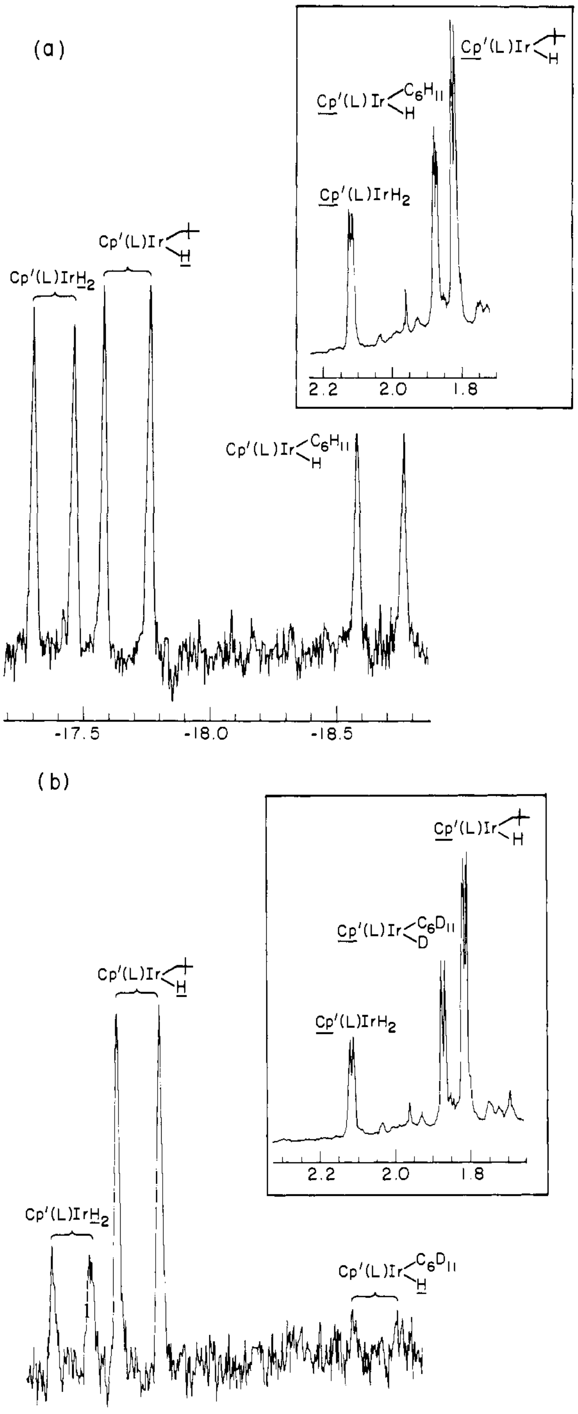

Figure 1. (a) ^1H NMR spectrum (200 MHz) of mixture obtained upon photolysis of dihydride **5** in a 1:1 mixture of neopentane and cyclohexane. (b) ^1H NMR spectrum of mixture obtained upon photolysis of dihydride **5** in 1:1 mixture of neopentane and cyclohexane-d_{12}. In each case, the lower part of the drawing illustrates the hydride region; inset shows C_5Me_5 region of the spectrum. Peak assignments are indicated on the drawing.

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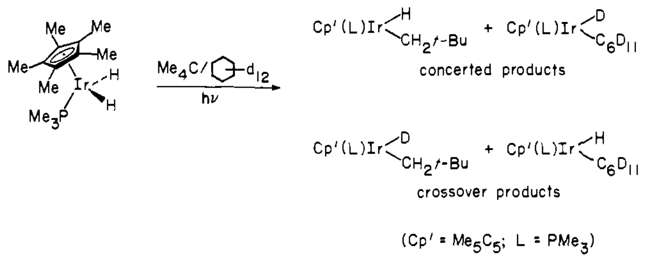
[19] This was established by carrying out the photolysis to low conversion (approximately 40 min; ca. 10% conversion), so that the isotopic labeling in the primary product of the reaction could be clearly identified. After prolonged photolysis (5 h), some HD and D_2 begin to appear in the reaction mixture, presumably due to secondary photoreactions of the product.

[20] Pryor, W. A.; Tang, F. Y.; Tang, R. H.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 2885 and references cited there.

[21] Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 2838.

[22] Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113.

Scheme X



hydride regions of the NMR spectrum of the solution obtained in this irradiation; integration demonstrated that the cyclohexyl (**7**) and neopentyl (**8**) complexes were formed in a ratio of 0.88. After irradiation of dihydride **5** in a 1:1 mixture of neopentane and cyclohexane-d_{12}, inspection of the C_5Me_5 region of the NMR spectrum (Figure 1b) assured us that the two hydrocarbons still had comparable reactivity, although the deuterated cyclohexane reacted a bit more slowly than its undeuterated counterpart—the **7**/**8** ratio was now 0.64. The hydride region of the spectrum, however, is substantially different. The neopentyl hydride appears as a strong peak, but the resonance due to hydrido cyclohexyl complex **8** has almost completely disappeared. It appears that some (7–8%) cyclohexyl-d_{11} hydride was formed; however, we can conservatively estimate that at least 90% of the reaction proceeds by a pathway which does not produce crossover. A similar percentage of **7**-d_{11} was found when **5** was irradiated in a 1:5 mixture of neopentane and cyclohexane-d_{12}.

We do not know the source of the small amount of crossover product. It is clearly not due to secondary thermal hydrogen exchange; at room temperature, over a span of 2 months, there is no measurable exchange of hydride and deuteride between oxidative addition products **7**-d_{12} and **8**. It is difficult to conclusively rule out a photochemical hydride exchange, because the photolysis slows considerably during the reaction, presumably because of the generation of small amounts of highly absorbing materials; in any case, to the extent that we can measure it, continued photolysis does not increase the amount of crossover observed. An indication that some type of secondary reaction is possible comes from the irradiation (discussed above) of dihydride **5** in cyclohexane-d_{12}. Although only H_2 is detected early in this reaction (40 min), after longer photolysis (24 h), detectable amounts of HD and D_2 are produced. This results in a decrease in the isotopic purity of the cyclohexane-d_{12}, which may account for at least some of the d_{11} product observed in our crossover experiment.

Another interesting piece of information available from the crossover experiment is the isotope effect on C–H insertion. Dividing the cyclohexane/neopentane product (rate) ratio by the cyclohexane-d_{12}/neopentane ratio gives $k_H/k_D = 1.38$ for insertion of Cp′(L)Ir into the six-membered ring substrate. Although in the normal direction, this is relatively small for a primary isotope effect. Unfortunately, very little isotope effect data on R–H oxidative additions are available for comparison with this result. Chock and Halpern measured the isotope effect for oxidative addition of dihydrogen to Vaska's complex,[23] interestingly, it is also small and normal ($k_H/k_D = 1.22$). A rationalization for this is provided by the prediction of one theoretical calculation that the H_2 addition has a transition state which lies at a very early point (i.e., structurally closer to starting materials than products) along the reaction coordinate.[24] If this is also the explanation in our case, reductive elimination may have a somewhat larger isotope effect. Again, data are scarce, but Halpern's measure of 3.3 in the reductive elimination of methane from *cis*-$(PPh_3)_2Pt(H)(CH_3)$ seems to support this.[25] One dihydrogen reductive elimination isotope effect is lower, however (1.51),[26] and one appears to be inverse.[27] Clearly more isotope effect information needs to be accumulated on such systems before they will be fully understood.

Table III. Relative Rates of Reaction of $(C_5Me_5)Ir(PMe_3)$ with Hydrocarbons[a]

hydrocarbon	rel rate	hydrocarbon	rel rate
benzene	4.0	cyclohexane	1.0
cyclopropane	2.65	cyclodecane	0.23
cyclopentane	1.6	cyclooctane	0.09
neopentane	1.14		

[a] In each case, mixtures of two hydrocarbons were used as solvent, as described in the text. Relative rates listed are ratios of the two products, corrected for the number of hydrogens available in each hydrocarbon.

In summary, we cannot yet rule out conclusively the possibility that a mechanism such as B in Scheme VIII is operating with (for some unknown reason) very little escape of radicals from the solvent cage. However, two things militate against this: (1) most conventional radical processes show substantial cage/escape rate ratios, and (2) the benzyl/aromatic and cyclopropane/cyclohexane hydrogen insertion ratios are quite different from those one would predict for a radical process. At present, therefore, our results seem to be most consistent with the concerted C–H oxidative addition pathway shown in Scheme VII.

Selectivity of the C–H Activation Reaction. Having reasonable confidence that the C–H activation reaction operates by a concerted three-center oxidative addition mechanism, we decided to examine the selectivity of the process. Irradiation of $Cp'(PMe_3)IrH_2$ (**5**) in the presence of solvents having different types of C–H bonds allowed the reactive intermediate $Cp'(PMe_3)Ir$ to compete for those bonds. With the assumption that the products of the insertions are themally and photochemically stable at low conversion,[28] the ratio of the products formed in such an experiment is then directly equal to the ratio of rate constants for insertion into each type of C–H bond. Two types of selectivity experiments were carried out: those involving competition of the intermediate for C–H bonds in different molecules ("intermolecular selectivity") and competition for different types of C–H bonds located in the same molecule ("intramolecular selectivity").

Intermolecular selectivities can be established most readily, because each of the individual oxidative addition products can be independently generated. Each selectivity experiment was carried out by using mixtures of two liquid hydrocarbons as solvent. First the dihydride **5** was irradiated in each pure solvent, and the NMR spectrum of the product recorded (due to the difficulty of isolating these materials, isolation was not attempted except in the case of cyclohexane and neopentane, as described earlier). Then the irradiation was carried out in a mixture (usually 1:1) of the two solvents, and the ratio of products measured, usually by repetitive integration of the hydride resonances in the high-field region of the spectrum. The rate ratio was calculated by correcting the product ratio for the number of hydrogens available in each molecule. In this way, the neopentane/cyclohexane rate ratio of 1.14 and cyclopropane/cyclohexane ratio of 2.6, mentioned in the previous section, were obtained. Similarly, we were able to determine the relative rates of attack by $Cp'Ir(PMe_3)$ on one C–H

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[23] Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511.

[24] (a) Kitaura, K.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1981**, *103*, 2891. See also: (b) Noell, J. O.; Hay, P. J. *Ibid.* **1982**, *104*, 4578.

[25] Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.

[26] Mays, M. J.; Simpson, R. N. F.; Stefanini, F. P. *J. Chem. Soc. A* **1970**, 3000.

[27] Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1982**, 745.

[28] Isolation of the hydrido alkyl complexes and resubjection to irradiation shows that they do in fact undergo photoinduced reductive elimination. However, if this were occurring to a significant extent during the irradiation of dihydride **5**, dependence of the product distribution on the extent of conversion should be observed, because at early conversion the dihydride is present in sufficient concentration to absorb most of the incident light, and this becomes less true as reaction proceeds. However, the ratio of products formed, as measured by integration of their hydride resonances in the NMR spectrum, does not change substantially throughout the irradiation. It appears that the absorbing impurity referred to in ref 17, which retards the decomposition of dihydride **5** as the reaction proceeds, apparently also serves to prevent photochemical decomposition of the hydrido alkyl products.

Table IV. ^1H NMR Chemical Shifts in Metal Hydride Region for Hydrido Alkyl Products Formed in C-H Activation Reactions[a]

hydrocarbon	chem shift, ppm	coupling const, Hz
cyclopropane	−18.16	34.4
cyclopentane	−18.16	33.9
cyclohexane	−18.67	37.0
cyclooctane	−18.64	36.6
cyclodecane	−18.50	37.2
neopentane	−17.67	37.1
p-Xylene benzyl	−17.56	38.6
aryl	−16.68	39.0
benzene	−17.04	36.8
propane primary	−17.81	37.0
secondary	−18.51	36.5
n-pentane primary	−17.96	38.0
secondary	−18.50	39.5
	−18.54	38.0
	−18.61	38.9

[a] Chemical shifts are recorded relative to tetramethylsilane, in C_6D_6 solvent.

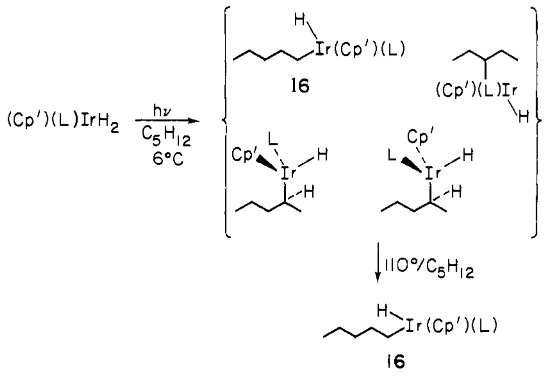
bond in each of the molecules in Table III, compared to cyclohexane as 1.0. It appears that in rings smaller than cyclohexane the C–H bonds are a bit more accessible sterically; medium-sized rings show a decrease in reactivity reminiscent of that sometimes seen in organic reactions involving these materials. A competition experiment using a cyclohexane/benzene mixture demonstrated the aromatic C–H bonds to be 4.0 times more reactive than the cyclohexyl.

Intramolecular selectivities presented a more difficult problem. Here we were faced with determining both the identities and relative amounts of products which could not be generated independently. In general the hydridoalkyl complexes are so nonpolar, and so similar to one another in chromatographic properties (including instability in many cases), that preparative separation was not feasible. A possible solution to this problem became apparent during the intermolecular selectivity studies summarized above. As shown in Tables I and IV, the ^1H NMR hydride resonances of the hydrido alkyl products formed from each of the cyclic hydrocarbons appeared at very similar chemical shifts, ranging from δ −18.16 for the metal-bound hydride in the hydrido cyclopropyl complex to δ −18.67 for the hydrido cyclohexyl complex. The location of this narrow range differed substantially from the position of the hydride resonance observed for the hydrido neopentyl complex **8**, which appeared at δ −17.67. Insertion into the C–H bond of benzene gave a complex which exhibited a hydride resonance at even lower field (−17.04 ppm). It seems that for some fortunate (but not well-understood) reason, the hydride chemical shift appears to be determined by the type of substitution at the carbon atom of the alkyl fragment directly attached to the metal. Thus (in the absence of heteroatoms which provide an added perturbation; cf. Table II) products formed by insertion into secondary C–H bonds may be distinguished from products formed by insertion into primary C–H bonds and aryl C–H bonds by the characteristic chemical shifts of the metal-bound hydride resonances in the hydrido alkyl products.

This judgment was reinforced by the results of our first intramolecular selectivity experiments, carried out on *p*-xylene as summarized in the preceding section and illustrated in Scheme IX. Irradiation of dihydride **5** in *p*-xylene gave two products, as judged by the appearance of only two new doublets in the high-field region of the NMR spectrum. One of these, assigned to benzylic complex **14**, appeared at −17.56 ppm, very close to that observed for the neopentyl complex **8** (i.e., in the "primary hydride" region). The other, due to aryl complex **13**, appeared at the lower field position of −16.68 ppm (the aryl hydride region). The fact that the primary insertion product is benzylic, and the aryl insertion product has an *o*-alkyl substituent, apparently does not greatly perturb the relative positions of these resonances.

In acyclic hydrocarbons, the chemical shift patterns also appear to hold up. Thus, irradiation of dihydride **5** in propane gives a mixture which exhibits two new hydride doublets in the NMR spectrum, one in the primary region at −17.81 ppm, and the other in the secondary region at −18.51 ppm; integration and statistical correction gives a primary/secondary rate ratio of 1.51. The situation with higher acyclic hydrocarbons is more complicated. In the case of *n*-pentane, four new hydride doublets are detected. There is a unique lowest field hydride signal; although this appears at −17.96 ppm, somewhat higher than that in propane, we assign it to the primary insertion product **16** (Scheme XI). The three other resonances appear at −18.50, −18.54, and −18.61 ppm, consistent with their assignment as secondary insertion products. We presume the formation of three complexes is due to the fact that insertion into the hydrogen at C-2 in pentane is capable of generating two diasteromers due to the fact that the iridium is a chiral center, as shown in Scheme XI. Although we cannot assign the identity of each of these very similar complexes, summation of the secondary integrations and correcting for statistics gives a primary/secondary attack ratio of 2.7.

Scheme XI



Unfortunately, in repetitive experiments with *n*-pentane the measured primary/secondary insertion product ratio was somewhat variable. In preliminary experiments with more highly branched hydrocarbons, we have as yet observed no hydride resonances which could be attributed to attack on tertiary C–H bonds. Heating the mixture of four products formed from *n*-pentane to 110 °C for 17 h converted them completely into the primary product **16**, as determined by NMR analysis and shown in Scheme XI. This is an extremely interesting result from a practical point of view, because it suggests that a combination of photolysis followed by thermal equilibration will allow exclusive primary functionalization of linear alkanes. We assume the thermal equilibration occurs by reductive elimination/readdition, rather than reversible β elimination as seen with, e.g., alkylzirconium complexes,[29] since our complexes are coordinatively saturated and PMe_3 dissociation is probably very slow. Thus it is clear that the complex formed by insertion into the primary C–H bond is thermodynamically more stable than the corresponding secondary insertion products. In view of the fact that reductive elimination of these very sensitive hydrido alkyl complexes can be induced by a wide range of oxidizing agents and Lewis acids (vide infra), it seems quite possible that some secondary insertion products, and perhaps all tertiary insertion products, might not be stable to our reaction conditions. Therefore, although we feel reasonably confident about the kinetic primary/secondary selectivity in our intermolecular cases and *n*-propane, some concern should be expressed about the *n*-pentane value, and no quantitative judgment should be made at this time as to the relative rates of insertion into the different types of C–H bonds in larger, more highly branched hydrocarbons. However, given the fact that primary insertion appears to be prefered over secondary on both a kinetic and thermodynamic basis (presumably at least partially because of the severe steric requirements of the iridium center), it is our guess that the rate of insertion of $Cp'Ir(PMe_3)$ into tertiary hydrogen is in fact relatively low.

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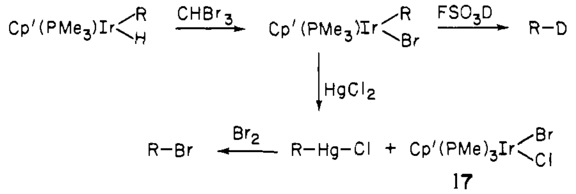
(29) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333.

Scheme XII



Thermal, Photochemical, and Functionalization Reactions of the Hydrido Alkyl Insertion Products. We next sought a method for conversion of the C–H activation products Cp'(PMe$_3$)Ir(H)(R) into functionalized organic molecules. Our first attempts to reach this goal centered around reactions of the hydrido alkyls with various reagents. As mentioned previously, treatment of cyclohexyl complex **7** or neopentyl **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.[28] 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 h yielded the corresponding deuteriophenyl deuteride (**6**-d_6) or *n*-pentyl hydride (**16**), respectively. This suggests that one forms the same unsaturated iridium intermediate in the thermal and photochemical experiments.

Upon treatment of neopentyl complex **8** with carbon monoxide (0.73 atm) at 60 °C for 4 h, one begins to see the formation of what is believed to be (η^5-C$_5$Me$_5$)Ir(CO)PMe$_3$ (by IR and NMR spectroscopy) and neopentane. Upon further reaction with CO, this complex disappears and (η^5-C$_5$Me$_5$)Ir(CO)$_2$[30] forms. Carbon dioxide (4.3 atm), on the other hand, is inert toward **8** up to 110 °C, where the thermal reaction with solvent occurs.

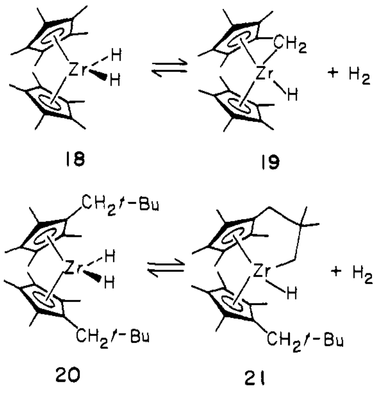
We decided that a possible solution to the functionalization problem might be available by replacement of the hydride ligand with halogen. Bromoform was found to react with the hydrido pentyl complex to produce (η^5-C$_5$Me$_5$)Ir(PMe$_3$)(*n*-pentyl)Br, and treatment of this material with deuterated fluorosulfonic acid gave 1-deuteriopentane. Treatment of bromo cyclohexyl complex **9** with Br$_2$ in a variety of solvents (benzene, pentane, CCl$_4$) gave less than 2% 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.

As shown in Scheme XII, treatment of neopentyl complex **8** with mercuric chloride in benzene was more successful. By ^{1}H NMR spectroscopy, we observed the clean exchange of the neopentyl group for a Cl atom. This resulted in the formation of a new material, assigned on the basis of its NMR spectrum as neopentylmercuric chloride (δ 1.12 (2 H), 0.57 (9 H)). Also formed was a precipitate, presumably bromo chloro complex **17**. The reaction mixture containing the neopentylmercuric chloride was subsequently treated with Br$_2$ to give neopentyl bromide in >98% NMR yield.[31] This demonstrates that the saturated hydrocarbon neopentane can be converted in high yield to a metal complex and then to a functionalized organic molecule.

Conclusions and Further Questions

We have succeeded in uncovering the first soluble organotransition-metal complex which is capable of undergoing direct oxidative addition to the C–H bonds of saturated hydrocarbons, leading to alkyliridium hydrides in high yield as 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$_5$Me$_5$)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 three-center transition state such as that shown in Scheme VII. Selectivity studies, demonstrating that insertion into primary and small-ring C–H bonds is preferred, are inconsistent with relative rates expected for radical reactions. It is the most sterically accessible C–H bonds that are most prone to react.

Scheme XIII



Despite these advances, our understanding of why (η^5-C$_5$Me$_5$)Ir(PMe$_3$) (**11**) undergoes this reaction is far from complete. We wish to consider two important questions raised by our results.

The first concnerns the need for an electron-rich metal center in oxidative addition reactions of this type. Conventional wisdom has spurred some recent searches for C–H activation systems in this direction; one example is the oxidative additions to weakly activated C–H bonds discovered at Du Pont. These reactions employ metal centers such as iron and ruthenium carrying the powerfully electron-donating bis(dimethylphosphino)ethane (dmpe) group.[9a,e] Clearly our system also fulfills this criterion—both the cyclopentadienyl ring and phosphorus atom in **11** carry electron-donating methyl groups. However, we cannot yet determine the stringency of the requirement for these groups. An indication that less electron-rich systems might function well in this reaction has been provided recently by Graham and Hoyano, who found that Cp'Ir(CO), generated photochemically from the corresponding dicarbonyl, also undergoes insertion into the C–H bonds of saturated hydrocarbons.[30] We should also keep in mind Crabtree's system, referred to in the introduction to this paper, which utilizes a (presumably relatively electrophilic) iridium center carrying a positive charge.[10a] It may be that some of these systems operate by different mechanisms, but clearly we have much to learn about the relationship between C–H oxidative addition and electron density at the reacting metal center.

The second perplexing question raised by our observations concerns the relationship between the rates of intra- and intermolecular C–H insertion. It is generally understood that when chemically similar intra- and intermolecular reactions are compared, the intramolecular process will proceed at a more rapid rate. Just how much more rapid is a question of some controversy and one which has been debated in systems ranging from organometallic to enzymatic.[32] However, the primary contributor to the rate acceleration associated with intramolecular processes is the entropy gained by preassociation of the reacting fragments. It seems reasonable to account for the relatively large number of intramolecular C–H activation systems which are known on the basis of this favorable entropic situation.

Several organic systems have been studied which provide comparisons of the rates of chemically comparable intra- and intermolecular reactions.[33] In contrast, the literature contains surprisingly few reports of studies in which the intermolecular analogue of a known intramolecular C–H activation reaction has

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[30] Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723.

[31] Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York, 1968. Makarova, L. G.; Nesmeyanov, A. N. "The Organic Compounds of Mercury"; North-Holland Publishing Co.: Amsterdam, 1967.

[32] See, for example: Page, M. I.; Jencks, W. P. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 1678.

[33] For an excellent discussion of the factors which control the relative rates of chemically similar intra- and intermolecular reactions, see: Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95.

been explicitly sought, so that clear-cut rate comparisons can be made. Perhaps some intramolecular C–H activation systems have been examined carefully for small amounts of intermolecular products, and unsuccessful results have simply not been reported.

One system in which a qualitative comparison of intra- and intermolecular C–H activation has been made[34] is that shown in Scheme XIII. Treatment of bis(pentamethylcyclopentadienyl)zirconium dihydride (**18**) with deuterium gas results in exchange of all available hydrogens in **18** for deuterium. Evidence has been obtained that **18** is in equilibrium with the intramolecular C–H insertion product **19**. Reduction of the substituted analogue bis(neopentyltetramethylcyclopentadienyl)zirconium dichloride gives complex **21**, presumably formed by insertion of the metal center in the reduced zirconocene intermediate into one of the (unactivated) C–H bonds of the neopentyl group attached to the five-membered ring. This material also reacts reversibly with hydrogen gas, leading to dihydride **20**. As in the case of the **18** $\rightleftharpoons$ **19** system, exposure of **20** $\rightleftharpoons$ **21** to deuterium gas causes exchange of deuterium with all available hydrogens in the molecule.

Exchange of the *tert*-butyl hydrogens in **20** $\rightleftharpoons$ **21** with deuterium gas is rapid: after exposure to 4 atm of deuterium gas for 1 h at 70 °C, the hydrogen atoms in both *tert*-butyl groups were 96% exchanged. A comparison of this qualitative rate with an intermolecular case was obtained by exposing the bis(pentamethylcyclopentadienyl) system **18** $\rightleftharpoons$ **19** to 4 atm of H_2 in toluene-d_8. After 1 week at 70 °C, the toluene-d_8 showed 54% exchange of its aromatic hydrogens and 71% exchange of its methyl hydrogens. These two experiments were done by using different molecules and different temperatures, and precise rate and activation energy data are not available. It is therefore difficult to use this information to obtain a quantitative estimate of the difference between the inter- and intramolecular exchange rates. However, by estimating the half-lives for exchange in the two experiments and making some crude assumptions about reaction order and entropies of activation, we estimate that the intramolecular/intermolecular C–H activation rate constant ratio must be at least 10^6 for the zirconium system.

This result is in the conventionally expected direction. However, it is rather large considering that intramolecular/intermolecular rate ratios for simple organic systems (so-called "effective molarities", as discussed by Illuminati and Mandolini[33]) are more often in the 10^3–10^5 range. Whatever the exact rate ratio, however, the zirconium system emphasizes how unusual the iridium system is. In the iridium case intermolecular reaction with saturated hydrocarbons occurs at a rate comparable to that of ortho-metalation of triphenylphosphine, a reaction which often outstrips other processes available to an unaturated metal center. Thus when the triphenylphosphine ligand is replaced by the slower metalating trimethylphosphine, we have been unable to observe any intramolecular oxidative addition at all. Similarly, the methyl groups attached to the Cp ring, which are reactive in the zirconium system, remain uninvolved relative to intermolecular C–H activation in the iridium system. Clearly there are very significant factors besides entropic ones which control these relative reactivities, and our understanding of these factors is quite minimal at present. Extensive further study of this unique system is an essential prerequisite to obtaining such understanding.

Experimental Section

General Data. All manipulations of oxygen- or water-sensitive materials were conducted under a prescrubbed recirculating atmosphere of nitrogen in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or with use of standard Schlenk or vacuum line techniques. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-390 90 MHz spectrometer or a 200- 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 (UC 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 by using a Varian 90P gas chromatograph using a 10 ft × 0.25 in. 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 UC Berkeley analytical facility. Ultraviolet spectra were recorded on a Hewlett-Packard 8450A UV/vis spectrophotometer using 1-cm path length quartz cells.

Preparative column chromatography was performed on neutral alumina (III) that was degassed before being taken into the drybox. All columns were packed and chromatograms run under air-free conditions. Photolyses were conducted with an Oriel 500-W high-pressure mercury lamp powered by an Oriel Corp. (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 purified before use by distillation or vacuum transfer from sodium/benzophenone ketyl. Olefin-free hexane was distilled from *n*-butyllithium. Methylene chloride and CD_2Cl_2 were distilled from calcium hydride under nitrogen. Chloroform and $CDCl_3$, carbon tetrachloride, cyclohexane (spectral grade), cyclohexane-d_{12}, pentane (spectral grade), *p*-xylene, cyclopentane, and cyclooctane were vacuum transferred from molecular sieves and stored 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 8 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**,[13] $(\eta^5\text{-}C_5Me_5)Ir(PPh_3)Cl_2$,[36] and $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)Cl_2$[15] 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 drybox. After the tube was capped it was removed from the drybox, 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 spectrum; in others, the analysis was performed after irradiation for 5 h. After irradiation, the reaction mixture was taken back into the drybox 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 drybox. The tube was capped with a vacuum stopcock and taken from the drybox 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 5 h. After photolysis, the tube was broken open in the drybox, 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.

$(\eta^5\text{-}C_5Me_5)(PMe_3)IrH_2$ (5). $(C_5Me_5)(PMe_3)IrCl_2$[13] (0.39 g, 0.81 mmol) was slurried in diethyl ether (15 mL) in the drybox. Dropwise addition of $LiEt_3BH$ (2.42 mL, 2.42 mmol) to the stirring slurry resulted in a gradual clearing of the reaction mixture. The solution was stirred 3 h and then filtered through alumina III packed into a 15-mL fritted funnel. The alumina was washed with diethyl ether and the resulting filtrate concentrated under vacuum. The resulting crude product was chromatographed in the drybox on silica with hexane followed by ether. The ethereal fractions containing product were identified by the clou-

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[34] Bercaw, J. E.; Erwin, D. K., private communication. Erwin, D. K. Ph. D. Thesis, California Institute of Technology, 1979.

[35] Evidence that the corresponding rhodium system will also insert into the C–H bonds of saturated hydrocarbons has been obtained recently: (a) Jones W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562. (b) Periana-Pillai, R. A.; Bergman, R. G., unpublished results.

[36] Booth, B. L.; Haszeldine, R. N.; Hill, M. *J. Organomet. Chem.* **1969**, *16*, 491.

diness imparted to the solution; removal of solvent from the combined fractions gave pure **5** as a pale yellow oil (0.25 g, 0.62 mmol, 76%) which occasionally crystallized (mp 43–44 °C) on standing: ^{1}H 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, C_5Me_5), 11.69 (s, C_5Me_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 × 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 alumina (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: mp 171 °C; ^{1}H NMR δ 1.90 (br 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 mm (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 the reaction mixture was removed from the drybox, it was cooled to −196 °C and evacuated on the vacuum line. The solution was irradiated for 8.5 h. 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 drybox 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: mp 215 °C; ^{1}H NMR (C_6D_6) δ 1.60 (dd, J = 1.8, 0.8 Hz, 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 Hz, IrH); IR (C_6D_6) 2110 cm^{-1} (ν_{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** [^{1}H NMR (C_6D_6) δ 1.84 (d, J = 1.8 Hz, C_5Me_5), 6.72, 7.06, 7.53, 7.98 (m, 1 H each, C_6H_4), 6.97, 7.28 (m, 6 H and 4 H each, PPh_2), −13.09 (d, J = 26.7 Hz, IrH)] decomposed on the column.

Irradiation of 5 in Cyclohexane. (η^5-C_5Me_5)Ir(PMe_3)(C_6H_{11})H (**7**) was prepared following the procedure described for the preparation of **3** but 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 h. After the irradiation, the cyclohexane was removed in vacuo, and the residue was taken up in cyclohexane and chromatographed on alumina (III) in the drybox 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 successfully. The cyclohexyliridium hydride was isolated in 39% yield and was pure by NMR spectrocopy: for ^{1}H and ^{13}C NMR spectra, see Table I; IR (C_6H_{12}) 2100 cm^{-1} (ν_{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 drybox. The two necks were topped with a vacuum stopcock and a septum. The flask was removed from the drybox, 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 mp 159 °C; ^{1}H 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 (br, 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 obtain 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 5 h, the cyclohexane was removed in vacuo, and the reaction mixture was taken up in benzene-d_6; by NMR spectroscopy, 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 2 h, 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 the solvent was removed in vacuo, the orange solid was recrystallized from toluene/ether to give (η^5-C_5Me_5)Ir(PMe_3)Br_2: mp 214 °C; ^{1}H 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 drybox. Benzene-d_6 (0.5 mL) was added, and a septum was used to cap the tube. After the tube was removed from the drybox, Br_2 (1.0 μL, 1.9 × 10^{-5} mol) was added by syringe. By ^{1}H 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 drybox. 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 ^{1}H NMR spectroscopy, cyclohexane (δ 1.40) 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 drybox. Benzene-d_6 (0.5 mL) was added, and after the tube was removed from the drybox, H_2O_2 (30%, 10 μL) was added. By ^{1}H NMR spectroscopy, cyclohexane (δ 1.39) 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 drybox. Benzene-d_6 (0.5 mL) and the $HBF_4 \cdot OEt_2$ (1.0 mL) were added, respectively. By ^{1}H NMR spectroscopy, cyclohexane (δ 1.39) was the major organic product.

(e) Irradiation. **7** (3.0 mg, 6.1 × 10^{-6} mol) was added to an NMR tube in the drybox. 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 h. The tube was returned to the drybox, 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 × 10^{-6} mol) was added to an NMR tube fused to a ground glass joint in the drybox. Benzene-d_6 (0.6 mL) was added, and the tube was subsequently topped with a vacuum stopcock. The tube was removed from the drybox, immersed in liquid nitrogen, evacuated and sealed. After 43 h at 60 °C, no reaction occurred, but after 22 h 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 the solution was heated in a sealed tube at 110 °C for 52 h, the tube was broken open in the drybox, the solvent was removed and the residue was taken up in benzene-d_6. By NMR analysis, the only new product was **16** (88% yield).

Irradiation of 5 in Neopentane. (η^5-C_5Me_5)Ir(PMe_3)(CH_2CMe_3)H (**8**) was prepared as described for **7** using a glass bomb for a vessel. Column chromatography on alumina (III) resulted only in decomposition. A second preparation was attempted by using the same procedure with **5** (127 mg, 3.13 × 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 ^{1}H and ^{13}C NMR spectra, see Table I; 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 5 h 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 analysis 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 2 h, 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 of **10**. It was obtained in 46% overall yield (75% yield, corrected for unreacted **5**): mp 163 °C; ^{1}H 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** (20.3 mg, 5.00 × 10^{-5} mol) was irradiated following the procedures for a photochemical experiment in an NMR tube in pentane (0.51 mL). After the mixture was irradiated for 5 h, the solvent was removed in vacuo and the residue was taken up in benzene-d_6. As indicated in the text, the major product was the primary hydride **16**; in most cases ca. 30% of secondary hydrides were also observed by ^{1}H NMR spectroscopy: IR (pentane) 2101 cm^{-1} (ν_{Ir-H}). Bromoform (10 μL, 1.16 × 10^{-4} mol) was added to the solution by syringe. After 2 h, the solution was chromatographed on a small alumina (III) column with benzene/ether eluent. The first fraction was collected, te solvent was removed in vacuo, and the solid was recrystallized twice from hexamethyldisiloxane giving 9.0 mg of (η^5-C_5Me_5)(PMe_3)Ir(*n*-C_5H_{11})Br. It was obtained as yellow/orange crystals in 38% overall yield (76% yield, corrected for unreacted **5**): mp 127 °C; ^{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 (br, *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, 1.2×10^{-5} mol) and bromoform (15 μL, 1.7×10^{-4} mol) in benzene-d_6 (0.5 mL)) was removed from the drybox, and bromine (15 μL, 2.9×10^{-4} mol) was added by syringe. By NMR analysis, very little information, except for the resonances for $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir(PMe}_3)\text{Br}_2$, 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 analysis.

(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 h. The solvent was removed in vacuo and replaced with benzene-d_6. Bromoform (3.0 μL) was added by syringe. To this solution was added DSO_3F by syringe. The volatiles were vacuum transferred, and an NMR analysis revealed the pentane to be $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{D}$ (integration: $\text{CH}_3/\text{CH}_2 = 0.86$).

(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 (presumably $(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{IrBrCl}$) started to form within 1 min. After 2 h, the NMR tube was removed from the drybox and centrifuged. The ^{1}H NMR spectrum showed two new resonances at δ 1.12 (2 H) and 0.57 (9 H) for neopentylmercuric chloride (as compared to an authentic sample). Br_2 (3 μL) was added to the reaction mixture. After 24 h, the resonances for neopentylmercuric chloride had disappeared, and new resonances for neopentyl bromide (as compared to an authentic sample) at δ 0.79 (9 H) and 2.87 (2 H) had grown in (yield >98%). This assignment was corroborated by a comparison of GC retention time of the organic product with that of neopentyl bromide.

Competition Experiments. To gather ^{1}H NMR data for the cycloalkylhydridoiridium complexes, the irradiation of **5** in the appropriate cycloalkane was carried out. In a typical experiment, **5** (7.9 mg, 1.95×10^{-5} mol) was added to an NMR tube in the drybox. Cyclopentane (0.60 mL) was added by syringe. The tube was capped, removed from the drybox, and sealed with parafilm. The reaction mixture was irradiated for 5 h, the solvent was removed in vacuo, and the remaining residue was taken up in benzene-d_6 (0.55 mL) for ^{1}H NMR analysis. For NMR data, see Table IV.

The other cycloalkane irradiations were carried out in similar fashion: amounts of reagents and exceptions to the general procedure are given below: cyclooctane (**5**, 8.2 mg, 2.02×10^{-5} mol; cyclooctane, 0.50 mL); cyclopropane (**5**, 12.5 mg, 3.08×10^{-5} mol; cyclopropane, 3.0 mL) using a glass bomb as a reaction vessel. In the cyclooctane reaction, we observe a second hydride (doublet at δ −17.88 (J = 37.2 Hz)) which is unidentified.

A representative competition experiment was carried out as follows: **5** (11.1 mg, 2.74×10^{-5} mol) was added to an NMR tube in the drybox. Cyclohexane (240 μL, 2.22×10^{-3} mol) and then cyclopentane (250 μL, 2.66×10^{-3} mol) were added by syringe. The tube was capped, removed from the drybox, and sealed with parafilm. The reaction mixture was irradiated for 5 h. 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 ^{1}H NMR analysis.

Crossover Experiments. **5** (11.0 mg, 2.71×10^{-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, 2.44×10^{-3} mol) and then neopentane (401.5 torr, 3.05×10^{-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 h. Afterwards, the tube was taken back into the drybox, 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 ^{1}H NMR spectroscopy by examining the hydride region of the spectrum. The crossover product accounted for 7% of the product hydrides and deuterides. When the C_5Me_5 region of the spectrum was examined the ratio of **8** to all the isotopic isomers of **7** was 1.56.

In the photolysis of **5** (11.0 mg, 2.71×10^{-5} mol) in cyclohexane (320.2 torr, 2.45×10^{-3} mol) and neopentane (400.2 torr, 3.04×10^{-3} mol) carried out under the same conditions and with the same procedures as above, the ratio of **8** to **7** was 1.14. Therefore, the isotope effect k_H/k_D is 1.38.

A second crossover experiment was run under the same conditions as above but with **5** (10.5 mg, 2.59×10^{-5} mol), cyclohexane-d_{12} (160.9 torr, 4.47×10^{-3} mol), and neopentane (32.2 torr, 8.95×10^{-4} mol) using a 516-mL bulb. In this case, the crossover product **7**-d_{11} accounted for 8% of the hydride and deuteride products.

5 (14.8 mg, 3.64×10^{-5} mol) and cyclohexane-d_{12} (1.0 mL) were added to a glass bomb in the drybox. After the bomb was removed from the drybox, 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, 3.25×10^{-5} mol) in cyclohexane-d_{12} (0.8 mL) for 24 h led to some exchanged hydrogen by mass spectral analysis, and 20% of the hydrogen gas was HD and 1.7% D_2.

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Registry No. **2**, 80145-87-5; **3**, 80146-08-3; **4**, 80145-86-4; **5**, 80146-01-6; **6**, 80146-02-7; **7**, 80145-83-1; **8**, 80145-84-2; **9**, 80145-85-3; **10**, 80160-32-3; **16**, 85453-02-7; **17**, 85453-03-8; $(\text{C}_5\text{Me})(\text{PMe}_3)\text{IrCl}_2$, 80298-81-3; $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir(PMe}_3)\text{Br}_2$, 85453-01-6; cyclopropane, 75-19-4; cyclopentane, 287-92-3; cyclohexane, 110-82-7; cyclooctane, 292-64-8; cyclodecane, 293-96-9; neopentane, 463-82-1; *p*-xylene, 106-42-3; benzene, 71-43-2; propane, 74-98-6; *n*-pentane, 109-66-0.