Title

C-H ACTIVATION IN COMPLETELY SATURATED HYDROCARBONS: DIRECT OBSERVATION OF M + R-H -> M(R)(H)

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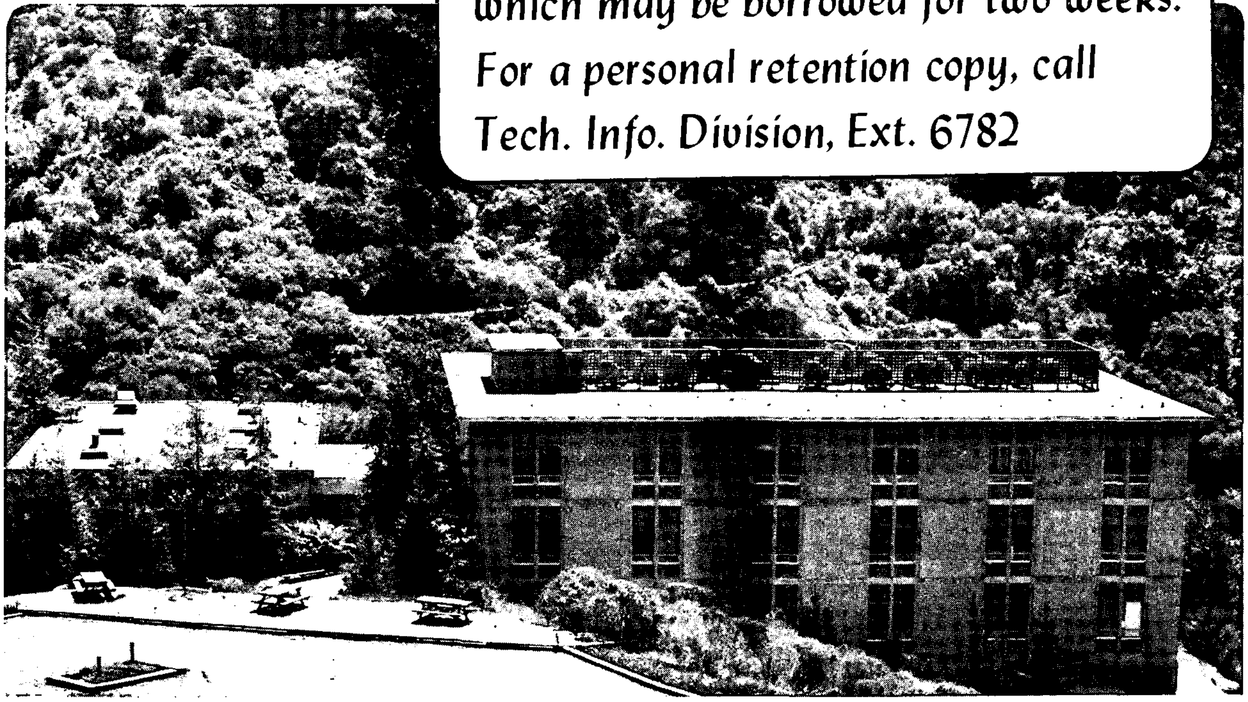

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C-H ACTIVATION IN COMPLETELY SATURATED HYDROCARBONS: DIRECT OBSERVATION OF M + R-H ⟶ M(R)(H)

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Abstract

This paper reports 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. (η^5-pentamethylcyclopentadienyl)(trimethylphosphine)-dihydridoiridium (**2**), prepared in a straightforward way from the known dimer $[(Me_5C_5)IrCl_2]_2$ (**1**), loses H_2 on irradition. This presumably leads to the coordinatively unsaturated transient intermediate $(\eta^5\text{-}Me_5C_5)(PMe_3)Ir$. In benzene, the metal center in this species inserts into a benzene C-H bond, which is a precedented process. However, in cyclohexane the unsaturated intermediate also reacts directly with solvent, leading to (η^5-pentamethylcyclopentadienyl)(trimethylphosphine)(cyclohexyl)hyridoiridium (**7**) in 90% yield at 74% conversion. In neopentane, C-H oxidative addition also occurs, leading to the corresponding hydridoalkyl complex **8** in 98% yield at 83% conversion. These products were isolated by chromatography under air-free conditions, and characterized by spectroscopic techniques. Treatment with mild oxidizing or electrophilic reagents causes reductive elimination of the hydrocarbon, and reaction with bromoform converts **7** and **8** to the corresponding bromoalkyl complexes **9** and **10**.

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

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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 cytochrome P-450 models.[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 now known involving intramolecular oxidative addition to unactivated C-H bonds.[5] However, most of these systems steadfastly resist reaction with C-H bonds not present in the same molecule as the metal center. In important 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 report

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

the discovery of an organotransition metal system capable of <u>intermolecular oxidative addition to single C-H bonds in saturated hydrocarbons</u>, leading to hydridometalalkyl complexes in quantitative yield at room temperature in homogeneous solution.

Our investigations began with the preparation of the dihydridoiridium(III) complex **2** shown in Scheme 1, which can be obtained in 42% yield by treatment of dimer[8] **1** with triphenylphosphine followed by lithium triethylborohydride. Irradiation ($\lambda_{max} \geq 275$ nm; high pressure Hg lamp, pyrex filter) of this material in benzene resulted in extrusion of dihydrogen,[7a,b;9] leading to the hydridophenyl complex **3** and the ortho-metallated complex **4** (47:53 ratio), presumably via the coordinatively unsaturated complex $(Me_5C_5)(Ph_3P)Ir$. Irradiation in other solvents (e.g., acetonitrile, cyclohexane) gave either all or mostly (see below) ortho-metallation. As indicated above, irradiative loss of H_2 and formation of **3** and **4** in these reactions has considerable precedent in related systems.

In an effort to make ortho-metallation less favorable, we decided to prepare 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 the appropriate phosphine, followed by $LiEt_3BH$, gave **5** in 43% yield.

Irradiation in benzene resulted in clean loss of H_2 and attack on solvent, leading to hydridophenyliridium complex **6**. However, when the irradiation was carried out in cyclohexane, a new material was formed (90% yield at 74% conversion of starting material after 5.5 hr irradiation) in which both the Me_3P and pentamethylcyclopentadienyl ligands were clearly intact.[10] Although thermally stable at room temperature, it was very sensitive both to air and chromatography supports (eliminating cyclohexane in certain cases; see below). 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)(hydrido)cyclohexyliridium(III) (**7**, Scheme 2) on the basis of spectral data and chemical conversion to the more sparingly soluble bromocyclohexyl complex **9** (see below). For **7**: ^1H-NMR(C_6D_6): δ1.87 (dd, J = 19.07 Hz, Me_5C_5), 1.25 (d, J = 9.5 Hz, PMe_3), 0.80, 1.50-2.30 (br, C_6H_{11}), -18.67 (d, J = 36.7 Hz, Ir-H). ^{13}C-NMR (C_6D_6): δ 92.36 (d, J = 3.4 Hz, $\underline{C}_5(CH_3)_5$), 19.69 (d, J = 35.7 Hz, $P(CH_3)_3$)), 10.75 (s, $C_5(\underline{C}H_3)_5$), 44.58 (d, J = 4Hz, C_6H_{11}(β-C)), 43.96 (d, J = 2 Hz, C_6H_{11}(β-C)), 32.92 (s, C_6H_{11} (γ-C)), 32.85 (s, C_6H_{11} (γ-C)), 28.33 (s, C_6H_{11} (δ-C)), 3.27 (d, J = 7.1 Hz, C_6H_{11} (α-C)). MS (m/e) = 488, 486.

The intermediate formed on irradiation of **5**, presumably $(MeC_5)(Me_3P)Ir$, also reacts with neopentane. Irradiation of **5** in neopentane solvent gives, after 5.3 hr irradiation time (98% NMR yield after 83% conversion), a new complex once again seen by NMR to contain alkyl and hydride ligands, and intact Me_5C_5 and Me_3P groups. Its structure is assigned as **8**, the hydridoalkyl complex analogous to **7**, on the basis of spectral data and conversion to the corresponding bromoneopentyl complex **10**. Data for **8**: ^1H-

NMR(C_6D_6): δ 1.82 (dd, J = 1.7, 0.7 Hz, Me_5C_5), 1.21 (d, J = 9.6 Hz, PMe_3), 1.28 (s, $C\underline{H}_3)_3$); 1.5 (complex mult., $C\underline{H}_2$), -17.67 (d, J = 36.5 Hz, IrH). ^{13}C-NMR (C_6D_6): δ 92.00 (d, J = 3.4 Hz, $\underline{C}_5(CH_3)_5$), 19.68 (d, J = 36.7 Hz, $P(CH_3)_3$), 10.62 (s, $C_5(\underline{C}H_3)_5$), 33.83 (s, $(CH_3)_3$), 35.71 (s, $\underline{C}(CH_3)_3$), 6.20 (d, J = 7.1 Hz, CH_2). Treatment of **7** and **8** with almost any oxidizing or electrophilic reagent (e. g. $ZnBr_2$, H_2O_2, Br_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** with Al_2O_3 in benzene solution for one hr generates cyclohexane (95% yield) and the hydridophenyl complex **6**; neopentane is similarly formed in 98% yield from **8**.

Following the observations summarized immediately above, we re-examined the irradiation of the triphenylphosphine complex **2** in cyclohexane. As stated earlier, the predominant product of this reaction is the ortho-metallated complex **4**. However, a significant amount (ca. 30%) of a second hydride is also formed in this reaction. Preliminary NMR data suggest this material is the intermolecular C-H activation product analogous to 7, having PPh_3 in place of the PMe_3 ligand. Thus even in the presence of a proximate aromatic group, intermolecular reaction appears to be possible for the iridium center.

We are now in the process of seeking reagents which will allow conversion of the alkyl groups in **7** and **8** into functionalized organic compounds. In addition, we are carrying out experiments aimed at probing the mechanism of the oxidative addition more deeply. Perhaps most important, however, is the issue of selectivity.[1] Clearly the intermediate generated on irradiation of **5** has already achieved the first, and perhaps most crucial type of selectivity--it reacts more readily with C-H bonds in other molecules, even hydrocarbons, than it does with those present in its own ligands. It is now important to determine how effectively the unsaturated intermediate discriminates in reactivity between different types of C-H bonds in reactant molecules and, if this type of "external" selectivity is low, whether analogs of 5 can be prepared in which it is increased. Experiments directed at these goals are underway.

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References

1) (a) Parshall, G. W. Catalysis, **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; N. Y., 1980; p. 179ff; (d) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry," University Science Books, Mill Valley, CA, 1980; p. 222ff.

2) Shilov, A. E. Pure Appl. Chem. **1978**, 50, 725.

3) (a) Groves, J. T. Adv. Inorg. Biochem. **1979**, 1, 119; (b) Groves, J. T.; Nemo, T. E.; Myers, R. S. J. Am. Chem. Soc. **1979**, 101, 1032; (c) Groves, J. T.; Van Der Puy, M. J. Am. Chem. Soc. **1976**, 98, 5290; (d) Chang, C. K.; Kuo, M.-S., J. Am. Chem. Soc. **1979**, 101, 3413; (e) Groves, J. T.; Kruper, W. J., Jr. J. Am. Chem. Soc. **1979**, 101, 7613; (f) Hill, C. L.; Schardt, B. C. J. Am. Chem. Soc. **1980**, 102, 6374.

4) We note some examples of C-H activation involving metal atoms in low-temperature matrices and in the gas phase: see, e.g., (a) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. J. Am. Chem. Soc. **1981**, 103, 962; (b) Allison, J.; Freas, R. B.; Ridge, D. P. J. Am. Chem. Soc. **1979**, 101, 1332; (c) Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A. J. Am. Chem. Soc. **1981**, 102, 1574.

5) For examples, see (a) Foley, P.; Whitesides, G. M. J. Am. Chem. Soc. **1979**, 101, 2732; (b) Clark, H. C.; Goel, A. B.; Goel, S. Inorg. Chem. **1979**, 18, 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) Bennett, C. R.; Bradley, D. C. J. Chem. Soc. Chem. Commun. **1979**, 29; (g) Andersen, R. A.; Jones, R. A.; Wilkinson, J. Chem. Soc. Dalton Trans. **1978**, 446; (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.

6) (a) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. J. Am. Chem. Soc. **1979**, 101, 7738; (b) Crabtree, R. H.; Mellea, M. F., Mihelcic, J. M.; Quirk, J. M. J. Am. Chem. Soc., in press; (c) Baudry, D.; Ephritikine, M.; Felkin, H. J. Chem. Soc. Chem. Commun. **1980**, 1243.

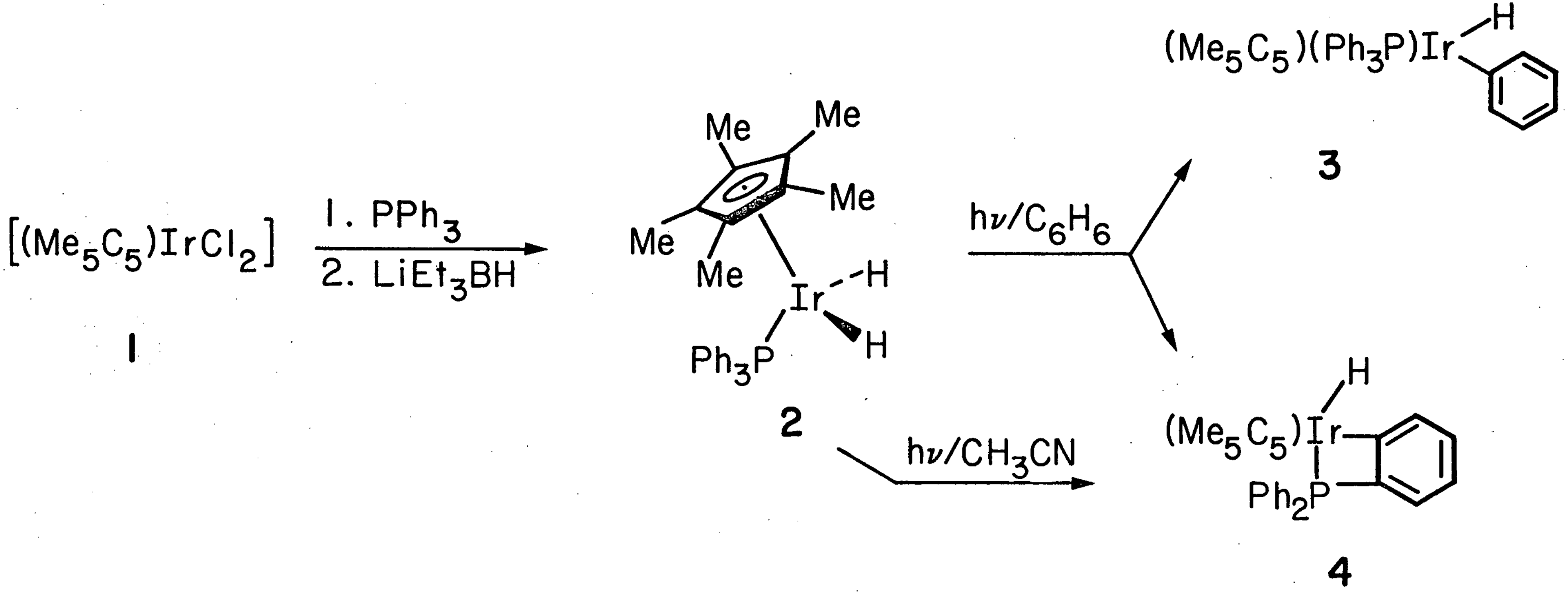
7) Examples: (a) Berry, M.; Elmitt, K.; Green, M. L. H., J. Chem. Soc. Dalton Trans. **1979**, 1950; (b) Green, M. L. H.; Berry, M.; Couldwell, C.; Prout, K. Nouv. J. Chim. **1977**, 1, 187; (c) Ittel, S. D.; Tolman, C. A.; Krusic, P. J.; English, A. D.; Jesson, P. J. Inorg. Chem. **1978**, 17, 3432; (d) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, P. J. Am. Chem. Soc. **1976**, 98, 6073; **1978**, 100, 7577; Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. J. Am. Chem. Soc. **1981**, 103, 379.

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

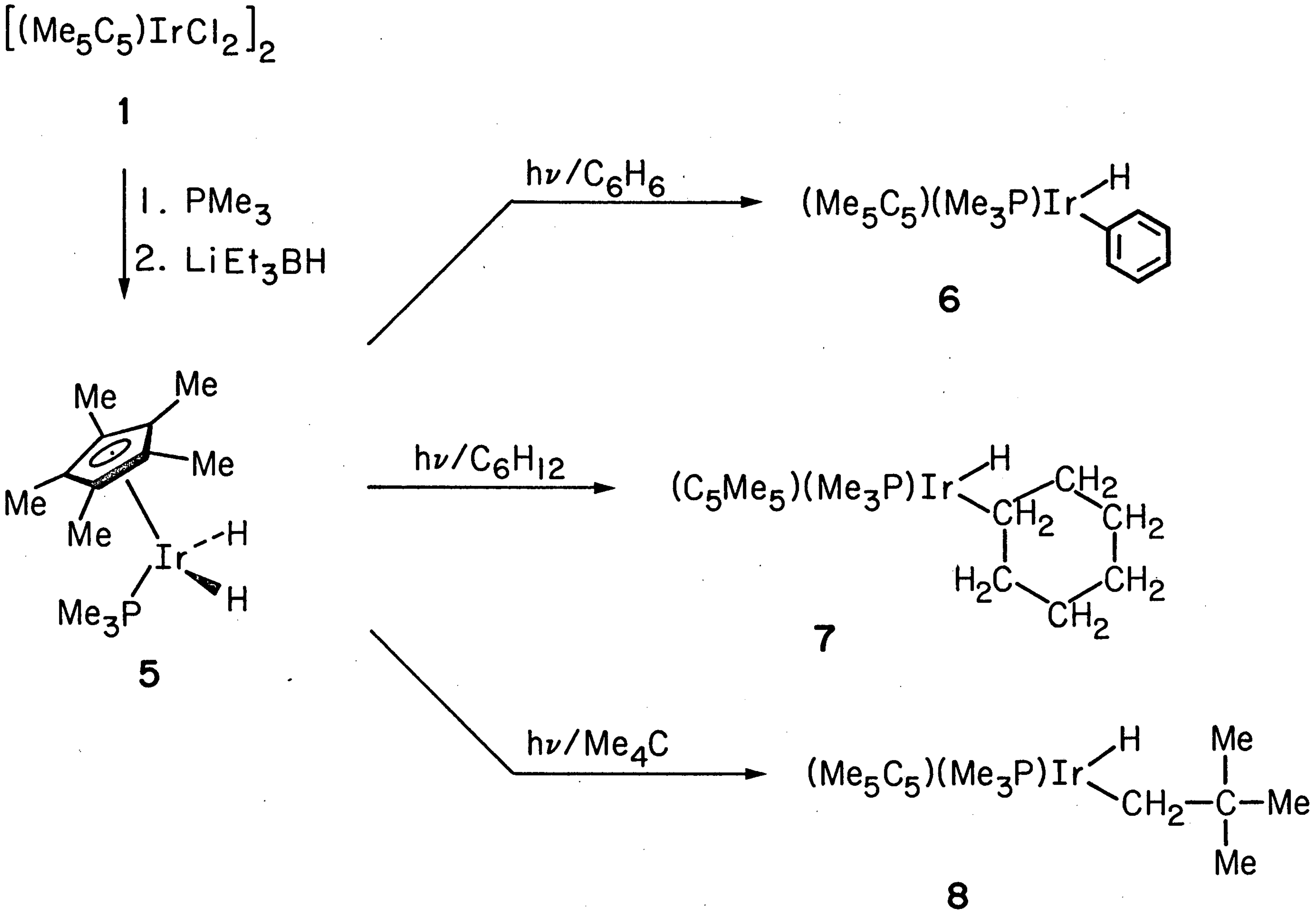
9) (a) Geoffrey, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979; (b) Pierantozzi, R.; Geoffreoy, G. L. *Inorg. Chem.* **1980**, *19*, 1821 and references cited here.

10) Although this system seems to avoid it, intramolecular C–H activation in coordinated Me$_3$P ligands is known; see, for example, (a) Chiu, K. W.; Wong, W.-K.; Wilkinson, G. *J. Chem. Soc. Chem. Commun.* **1981**, *451*; (b) Karsch, H. H.; Klein, H.-F.; Kreiter, C. G.; Schmidbaur, H. *Chem. Ber.* **1974**, *107*, 3692; (c) Al-Jibori, S.; Crocker, C.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc. Dalton Trans* **1981**, *1572* and references cited there.

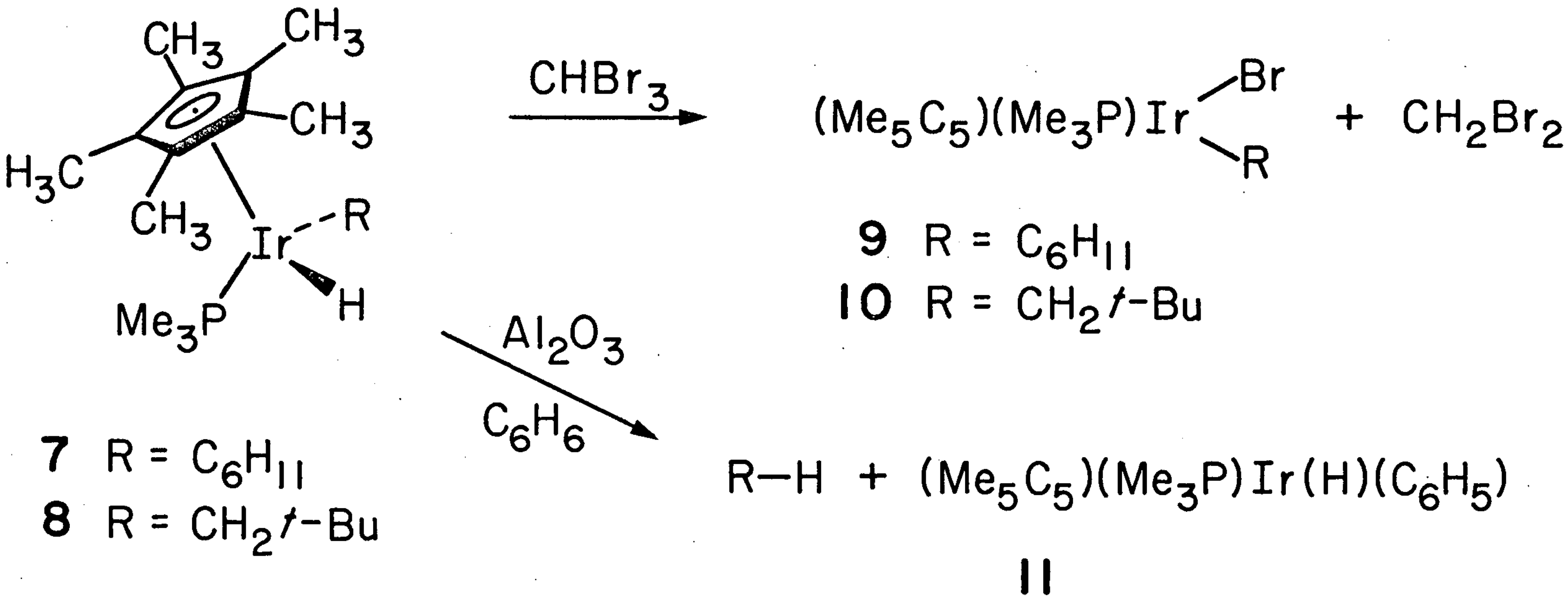
Scheme I


$[(Me_5C_5)IrCl_2]$
1
1. PPh_3
2. $LiEt_3BH$
Me
Me
Me
Me
Me
Ir
H
H
Ph_3P
2
$h\nu/C_6H_6$
$h\nu/CH_3CN$
$(Me_5C_5)(Ph_3P)Ir$
H
3
$(Me_5C_5)Ir$
H
Ph_2P
4

Scheme 2


[(Me$_5$C$_5$)IrCl$_2$]$_2$
1
1. PMe$_3$
2. LiEt$_3$BH
Me
Me
Me
Me
Me
Ir
H
H
Me$_3$P
5
hν/C$_6$H$_6$
(Me$_5$C$_5$)(Me$_3$P)Ir
H
6
hν/C$_6$H$_{12}$
(C$_5$Me$_5$)(Me$_3$P)Ir
H
CH$_2$
CH$_2$
CH$_2$
H$_2$C
CH$_2$
CH$_2$
7
hν/Me$_4$C
(Me$_5$C$_5$)(Me$_3$P)Ir
H
CH$_2$
C
Me
Me
Me
8

Scheme 3



9 R = C_6H_{11}
10 R = CH_2*t*-Bu

7 R = C_6H_{11}
8 R = CH_2*t*-Bu

11

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