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REVERSIBLE C-H INSERTION/REDUCTIVE ELIMINATION IN (n5-PENTAMETHYLCTCIOPENTADIENYL) (TRIMETHYLPHOSPHINE) IRIDIUM COMPLEXES. USE IN EFFECTING SELECTIVE PRIMARY FUNCTIONALIZATION, DETERMINING RELATIVE METAL-CARBON BOND ENERGIES, AND THERMALLY ACTIVATING...

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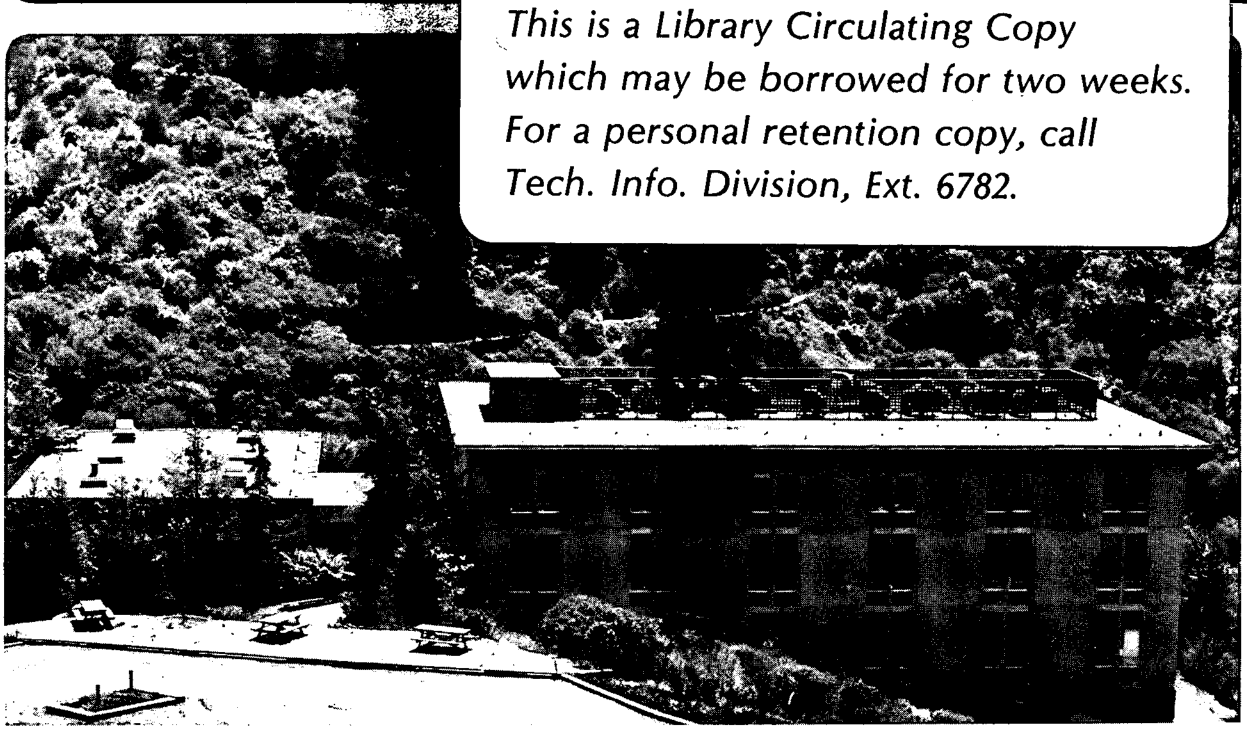
M.J. Wax, J.M. Stryker, J.M. Buchanan, C.A. Kovac,
and R.G. Bergman

August 1983



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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Reversible C-H Insertion/Reductive Elimination in (η^5-Pentamethylcyclopentadienyl)(trimethylphosphine)iridium Complexes. Use in Effecting Selective Primary Functionalization, Determining Relative Metal-Carbon Bond Energies, and Thermally Activating Methane.

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Contribution from the Materials and Molecular Research Division,
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Heating causes reductive elimination of alkane from (η^5-pentamethylcyclopentadienyl)(trimethylphosphine)(hydridoalkyl)iridium complexes, leading to an intermediate capable of undergoing oxidative addition to the C-H bonds in other alkanes.[1] We have used this property to achieve three goals in the C-H activation field which we wish to report: (a) conversion of a linear hydrocarbon into a hydridoalkyl complex in which only the primary carbon has been metallated; (b) establishment of reversible equilibrium between a pair of alkanes and hydridoalkyl complexes, allowing measurement of the equilibrium constant for this process and providing a method for determining relative metal-carbon bond energies, and (c) the first solution phase thermal oxidative addition of methane[2] leading directly to a stable hydridoalkylmetal complex.

The equilibration studies began with the mixture of dihydride (1) and alkyl hydrides (2 - 5) formed on irradiation of 1 in n-pentane.[1] As illustrated in Scheme 1, heating this mixture to 110° in n-pentane caused disappearance of all the resonances in the ^{1}H NMR spectrum due to the secondary hydrides, and a corresponding increase in the signal due to the primary hydride. We judged from this observation that isomerization of secondary to primary hydridoalkyl complexes is possible by thermal activation at this temperature, and that (as expected[3]) the primary complex is thermodynamically more stable. Evidence that this isomerization occurs by intermolecular reductive elimination/oxidative addition was obtained by carrying out the reaction in cyclohexane, rather than pentane, solvent. In this case the amount of primary hydride remained constant, and the secondary hydrides were converted into hydridocyclohexyl complex **6** rather than primary hydridopentyl complex **2** (Scheme 1).

This experiment also suggests that the primary complex is stable to reductive elimination at 110°. In fact, heating to 140° is required to bring this material into the reductive elimination/oxidative addition equilibrium; under these conditions the primary hydride **2** and the cyclohexyl hydride **6** interconvert with one another and with the corresponding alkanes (eq. (1)). The equilibrium constant for this process (eq. (2)) is most conveniently measured by heating the primary complex **2** in a solvent mixture containing 92% cyclohexane and 8% n-pentane. After 120 hr at 140°, equilibrium is reached, and it contains[4] a 52:48 ratio of **6** to **2**. This allows calculation of an equilibrium constant of 10.6, which corresponds to a free energy change of -1.9 kcal/mole at 140°.

Obtaining an accurate relative metal-carbon bond energy measurement for complexes **2** and **6** requires temperature-dependence data for the equilibrium constant, and such measurements are planned. However, we can obtain a reasonable estimate of this difference in the following way. The entropy change for eq. (1) is probably small, which suggests that $\Delta G° \cong \Delta H°$ for the reaction. The difference in energy between **2** and **6** is given to a good approximation by $|H°|$ for eq. (1) (ca. 2 kcal/mole) minus the difference between the primary (98 kcal/mole) C-H bond energy in n-pentane and the secondary (94.5 kcal/mole) C-H bond energy in cyclohexane.[5] This gives a difference of 1.5 kcal/mole favoring the metal-carbon bond energy in primary complex **2** over that in **6**.

The similar type of bond energy change which controls the isomerization of secondary pentyl complexes **2** to primary complex **6** is somewhat more difficult to estimate, because there is no free hydrocarbon ratio in the equilibrium which can be changed to modify the equilibrium concentrations of the species involved in the isomerization. However, we believe it is larger than the 1.5 kcal/mole estimated for eq. (1), because: (a) statistical factors favor the secondary complexes, (b) no secondary isomers are detectable after heating the mixture shown in Scheme 1 at 110° (less than 5% would have been seen) and (c) the secondary pentyl complexes are kinetically much less stable than the analogous secondary cyclohexyl complex **6**, undergoing reductive elimination at 110° instead of 140°.

Attempted photolysis of dihydride **1** in perfluoroalkane solvents under 4 atm of CH_4 gave no detectable methane activation (in contrast to Graham's observations[2e] on the methane-activating photolysis of $CpIr(CO)_2$), perhaps because of the very low solubility of **1** in these solvents. Photolysis in cyclooctane, a "slow" substrate for C-H insertion of the presumed intermediate $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir$, under CH_4 gave only the previously observed[1] hydridocyclooctyl complex (**8**). However, we were able to achieve methane activation thermally and in high yield under reversible conditions by taking advantage of the presumption that the hydridomethyl complex **7** would be thermodynamically more stable even than primary alkyl complexes such as **2**. Thus, as shown in Scheme 2 heating hydridocyclohexyl complex **6** in cyclooctane solvent in a sealed vessel under 20 atm of CH_4 at temperatures between 140° and 150° led to an 88% yield (^1H NMR) of hydridomethyl complex **7**. This structure was indicated by the ^1H NMR spectrum of the new material (δ 1.87 (dd, J=2.0, 0.7, C_5Me_5), 1.22 (d, J=9.8, PMe_3), 0.71 (d, J=5.8, IrMe), -17.22 (d, J=35.9, IrH)). Attempted isolation of the hydridomethyl complex by crystallization or chromatography proved difficult, as it has in other cases[1], and so the material was treated with $CHCl_3$, converting it to the corresponding chloromethyl complex **9**, which could be purified and characterized by conventional means. The isolated yield of **9** from starting hydridocyclohexyl complex **2** was 25%. Confirmation of these structural assignments was obtained by independent synthesis: chloromethyl complex **8** was prepared by ligand interchange involving the corresponding dichloro and dimethyl complexes (Scheme 2); it was then converted to hydridomethyl complex **7** by treatment with $LiBH_4$ in diethyl ether.

In the methane experiment, we assume that the hydridocyclohexyl complex **6** and hydridocyclooctyl complex **8** are formed reversibly, but do not build up due to their thermodynamic instability relative to the hydridomethyl complex **7**; i.e., **7** is the "thermodynamic sink" for the system. The ability to functionalize methane thermally, and convert it quantitatively to a metallated species, are essential steps in the development of possible catalytic functionalization schemes for this molecule; work along these lines is continuing. Efforts are also under way aimed at developing ways to convert selectively metallated linear alkanes into oxygenated organic molecules, and at applying our method for determining relative metal-carbon bond energies to additional pairs of alkyliridium complexes.

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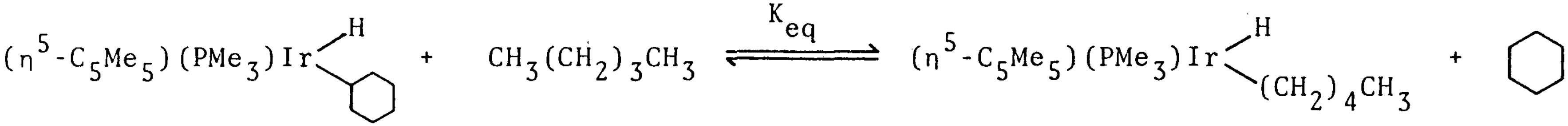
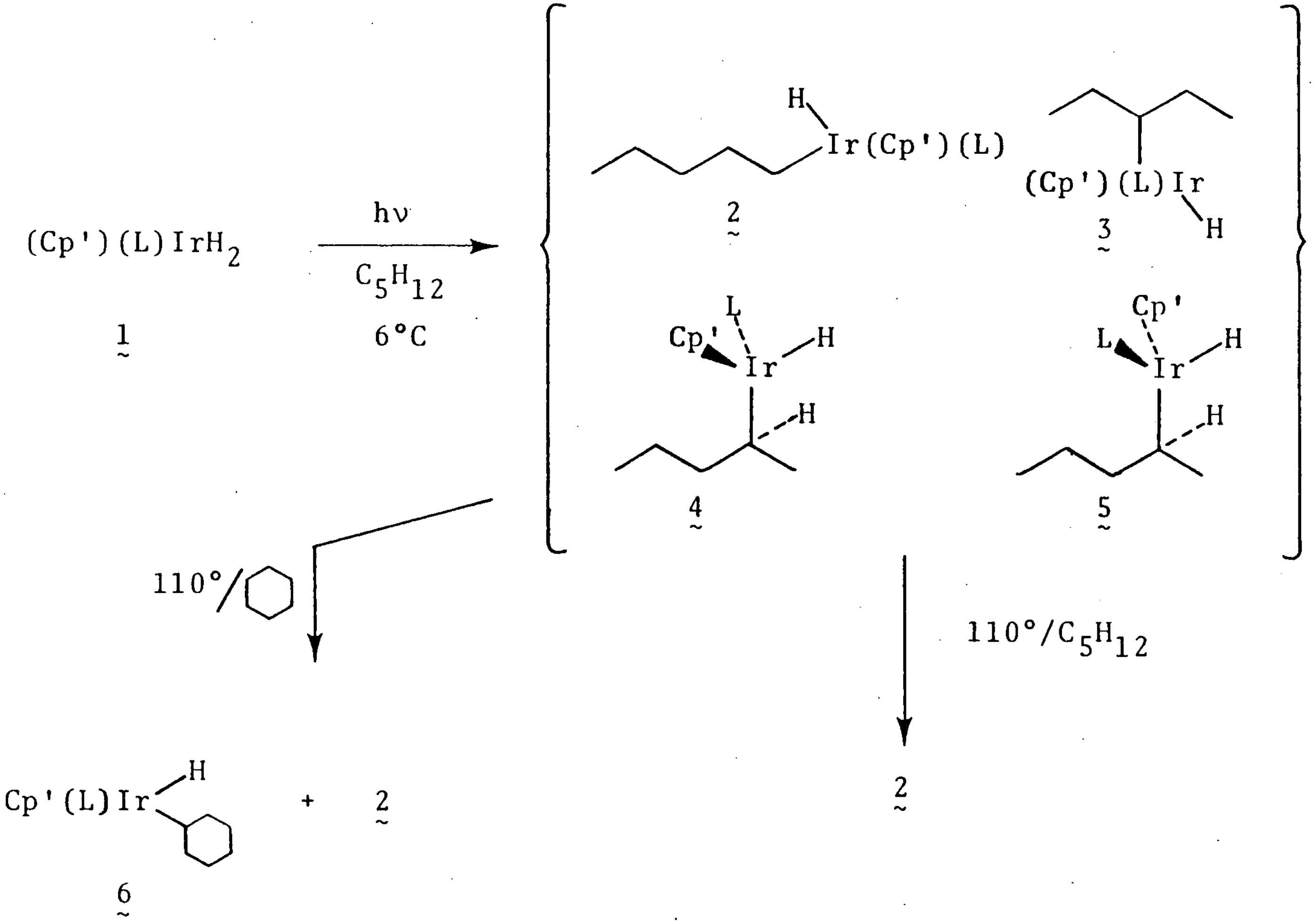
2. For discussions and examples of transition-metal based methane activation see: (a) Goldschleger, M. B.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. Zh. Fiz. Khim. **1969**, 43, 2174; (b) Webster, D. E. Adv. Organomet. Chem. **1977**, 15, 147; (c) Shilov, A. E.; Shteinman, A. A. Coord. Chem. Rev. **1977**, 24, 97; (d) Lavrushko, V. V.; Lermontov, S. A.; Shilov, A. E. React Kinet. Catal. Lett. **1980**, 15, 269; Watson, P. L. J. Am. Chem. Soc., submitted for publication; (e) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G., Ibid., submitted for publication; (f) Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A. J. Am. Chem. Soc. **1981**, 103, 1574; (g) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. Organometallics **1982**, 1, 963; (h) Remick, R. J.; Asunta, T. A.; Skell, P. S. J. Am. Chem. Soc. **1979**, 101, 1320.
3. Slow decomposition of the hydridoalkylmetal complexes takes place under these conditions; however, the isomerization is rapid enough that the equilibrium concentrations of **2** and **6** are not significantly perturbed.
4. (a) Halpern, J. Accts. Chem. Res. **1982**, 15, 238; (b) Schwartz, J.; Labinger, J. A. Angew. Chem. Int. Ed. (Engl.) **1976**, 15, 333.
5. Benson, S. W. "Thermochemical Kinetics", John Wiley and Sons, N. Y., 1976.
6. Data on chloromethyliridium complex **8**: ^{1}H NMR (C_6D_6) δ 1.47 (d, J=1.9, C_5Me_5), 1.17 (d, J=10.3, PMe_3), 1.08 (d, J=7.0, IrMe).



6 2 (1)

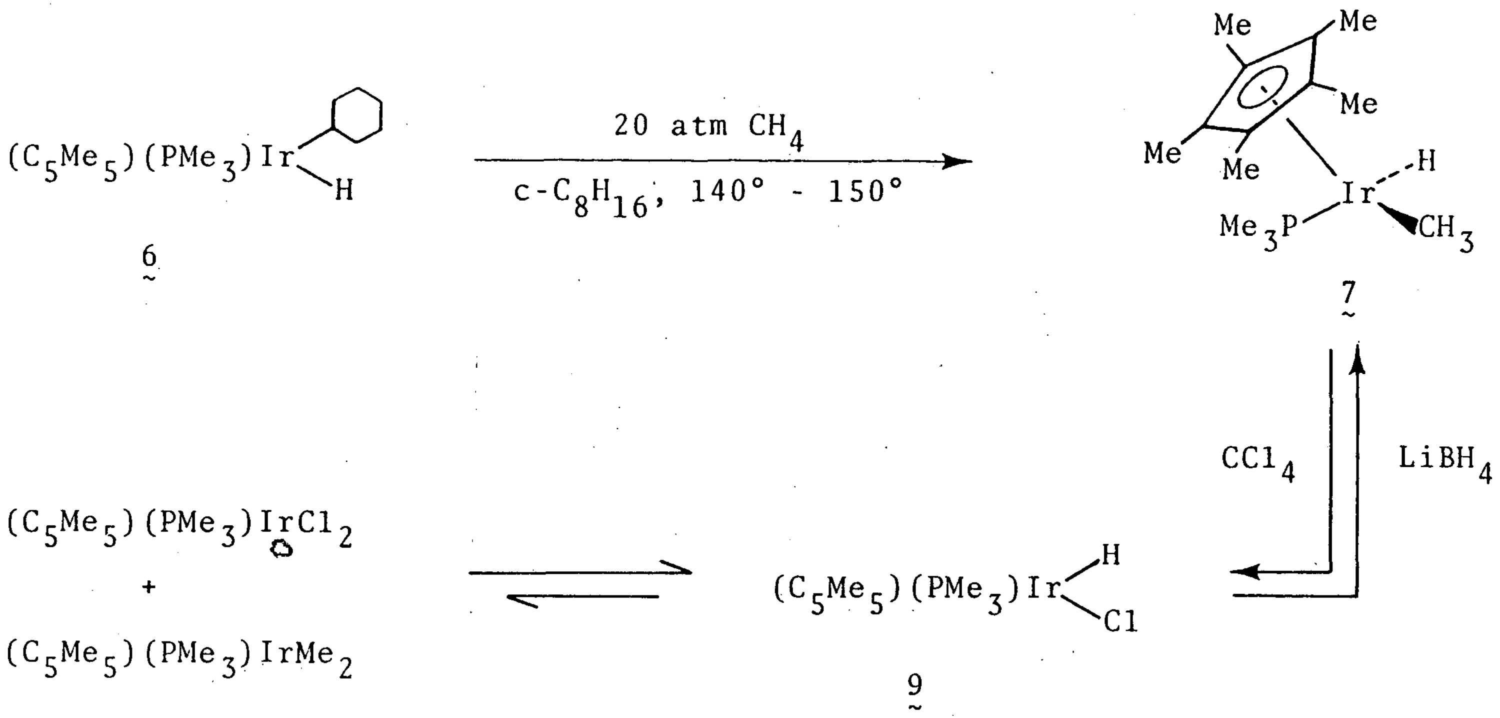
$$K_{eq} = \frac{[\underset{\sim}{2}][\text{Cyclohexane}]}{[\underset{\sim}{6}][\text{n-pentane}]} \qquad (2)$$

SCHEME 1



[Cp' ≡ η^5-C_5Me_5; L = PMe_3]

SCHEME 2


(C5Me5)(PMe3)Ir
H
6
20 atm CH4
c-C8H16, 140° - 150°
Me
Me
Me
Me
Me
Ir
H
Me3P
CH3
7
CCl4
LiBH4
(C5Me5)(PMe3)IrCl2
+
(C5Me5)(PMe3)IrMe2
(C5Me5)(PMe3)Ir
H
Cl
9

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