Evidence for the Intervention of Different C−H Activating Intermediates in the Irradiation of (η^5-C_5Me_5)(PMe_3)IrH_2 and the Reaction of (η^5-C_5Me_5)(PMe_3)Ir(H)(Cl) with Strong Base. Detection and Spectroscopic Characterization of (η^5-C_5Me_5)(PMe_3)Ir(Li)(Cl), an Intermediate in the Dehydrohalogenation Reaction

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Abstract: Reaction of (η^5-C_5Me_5)(PMe_3)Ir(H)(X) (X = Cl, Br) with *tert*-butyllithium in hydrocarbon solvent results in dehydrohalogenation of the iridium center and subsequent C−H bond activation of solvent to give (η^5-C_5Me_5)(PMe_3)Ir(R)(H) (R = Ph, cyclohexyl, cyclooctyl). Low-temperature ^{1}H, ^{31}P, and ^{7}Li NMR studies indicate that the dehydrohalogenation reaction occurs via the formation of the intermediate (η^5-C_5Me_5)(PMe_3)-Ir(Li)(X). Competition experiments involving C−H bond activation in benzene−cyclohexane−cyclooctane mixtures have allowed for the determination of a relative intermolecular selectivity scale for these substrates. The selectivities (reported on a per hydrogen basis) for benzene, cyclooctane, and cyclohexane C−H bond activation were found to be 4.98:0.74:1, respectively, and are significantly different from those obtained via photoinduced dihydrogen elimination from (η^5-C_5Me_5)(PMe_3)IrH_2. Further, when Brønsted bases other than *tert*-butyllithium were employed, the intermolecular selectivities in the base-promoted dehydrohalogenation reaction were found to be dependent on the alkali metal, but *not* the counteranion, of the base, with benzene/cycloalkane selectivity increasing in the order K > Na > Li. These results provide strong evidence that the selectivity-determining steps in the C−H bond activations by dehydrohalogenation of (η^5-C_5Me_5)(PMe_3)Ir-(H)(X) and the photoinduced dihydrogen elimination in (η^5-C_5Me_5)(PMe_3)IrH_2 involve different reactive intermediates. In the base-induced reaction, we postulate that the eliminated salt remains coordinated to the iridium, primarily through the alkali metal, in the C−H activation transition state.

Introduction

While the activation of the C−H bonds of alkanes and arenes by photolysis and thermolysis of Cp*ML_n complexes (Cp* = C_5Me_5; M = Ir, Rh) has been known for over 15 years, unresolved mechanistic details continue to provide stimulus for further research. The species believed to be active in the oxidative additions of hydrocarbons is the coordinatively and electronically unsaturated Cp*ML fragment and/or the corresponding solvate or "alkane complex." Methods for generation of this highly reactive fragment include photoextrusion of H_2,[1−5] CO,[6−12] or C_2H_4[13−16] from dihydride, carbonyl, and ethylene complexes and thermal reductive elimination of alkanes,[17−19] alkenes,[20] and arenes[18,21] from alkyl, alkenyl, and aryl hydrides. The resulting alkyl hydrides are thermally unstable for the Cp*Ir-(CO) and Cp*Rh(PMe_3) systems, but can be isolated for the Cp*Ir(PMe_3) systems. The study of C−H activation by soluble, discrete transition metal complexes represents one area in which the direct observation of the key reactive entities is only just beginning to be realized, and the development of ultrafast laser techniques has led to a number of important observations regarding the nature of the C−H activating complex.[8−12]

(1) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.
(2) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.
(3) Janowicz, A. H.; Periana, R. A.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *Pure Appl. Chem.* **1984**, *56*, 13.
(4) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508.
(5) Bloyce, P. E.; Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1988**, 846.
(6) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723.
(7) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc* **1983**, *105*, 7190.
(8) Weiller, B. H.; Wasserman, E. P.; Bergman, R. G.; Moore, C. B.; Pimentel, G. C. *J. Am. Chem. Soc.* **1989**, *111*, 8288.
(9) Weiller, B. H.; Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 4326.
(10) Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *Science* **1992**, *255*, 315.
(11) Schultz, R. H.; Bengali, A. A.; Tauber, M. J.; Weiller, B. H.; Wasserman, E. P.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7369.
(12) Bengali, A. A.; Schultz, R. H.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 9585.
(13) Bell, T. W.; Haddleton, D. M.; McCamley, A.; Partridge, M. G.; Perutz, R. N.; Willner, H. *J. Am. Chem. Soc.* **1990**, *112*, 9212.
(14) Bell, T. W.; Brough, S.-A.; Partridge, M. G.; Perutz, R. N.; Rooney, A. D. *Organometallics* **1993**, *12*, 2933.
(15) Haddleton, D. M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1986**, 1734.
(16) Haddleton, D. M.; McCamley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 1810.
(17) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562.
(18) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.
(19) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.
(20) Stoutland, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732.
(21) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814.

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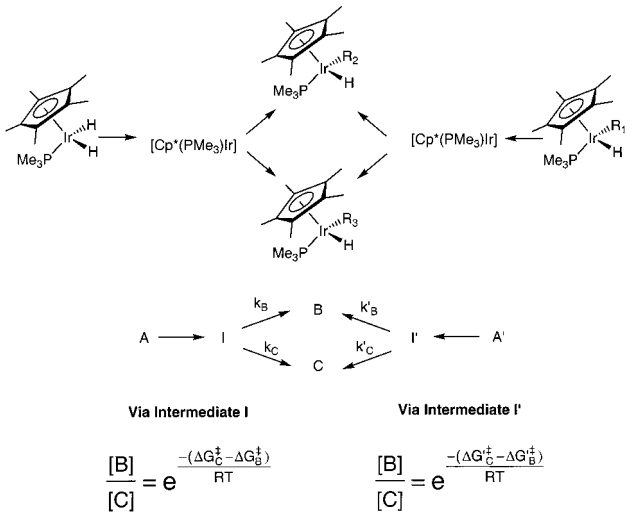


Figure 1. Analysis of energetic factors controlling product formation from two identical intermediates generated from different precursors.

Previously, we reported that the activation of hydrocarbons by the photolysis of $Cp^*(PMe_3)IrH_2$ or the thermolysis of compounds of the general formula $Cp^*(PMe_3)Ir(R)(H)$ (R = primary or secondary alkyl) both proceed via the same reactive intermediate, the putative 16-electron $Cp^*(PMe_3)Ir$ fragment or a solvate of this species.[19] This assertion was based upon the fact that the product ratios observed in competition experiments involving different hydrocarbon substrates were independent of the origin of the C−H activating intermediate. The competition method assumes that the ratio of two products formed in a reaction sequence is determined by the ratios of the respective rate constants in a product-forming step. By application of transition state theory, these rate constants can be related to the activation parameters for formation of the respective products. The product ratio can therefore be equated with the exponentiated differences between the activation free energies associated with two different reaction paths, as illustrated in Figure 1.

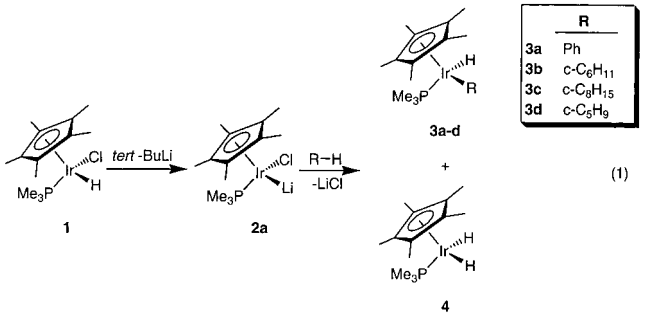
For two different chemical reactions to provide identical product ratios, the exponential terms containing the differences in activation free energies leading to those products must also be identical. Thus, barring an unlikely coincidence that the two reactions proceed via different intermediates which exhibit identical differences in free energy barriers for product formation, the reactions can be regarded as occurring via a common intermediate.

Previous mechanistic investigations of the C−H activation process have compared inter- and intramolecular selectivities of alkane and arene oxidative additions.[2,4,6,18−20,22−26] However, one difficulty associated with such experiments is the possibility that the observed products are derived from secondary reactions of an initially formed adduct and hence do not reflect the *intrinsic* selectivity of the reactive intermediate. We have found that the high temperatures often required to effect formation of "$Cp^*Ir(PMe_3)$" from the corresponding alkyl hydride complexes can sometimes promote intramolecular rearrangements in the derived activation products.[27] In these cases, the kinetic selectivity cannot be derived from such data. To solve this problem, we sought a nonphotochemical method for generating the putative $Cp^*Ir(PMe_3)$ fragment at ambient or subambient temperatures.

In previous attempts, we investigated several methods for reducing the Ir(III) halide complexes $Cp^*(L)IrX_2$ and $Cp^*(L)Ir(H)(X)$ without success. We now report that base-induced geminal dehydrohalogenation of $Cp^*(PMe_3)Ir(H)(Cl)$ (**1**) by *tert*-butyllithium results in overall elimination of HCl and generation of an intermediate species capable of undergoing oxidative addition with arene and alkane C−H bonds.[28] However, the C−H activating species is not the initially formed intermediate. By monitoring the reaction at low temperature, we have been able to detect the very reactive iridate salt $Cp^*(PMe_3)Ir(Li)(Cl)$ and characterize it both spectroscopically and chemically. We describe the results of these studies and provide evidence that hydrocarbon oxidative addition selectivity can be influenced by the departing salt.

Results and Discussion

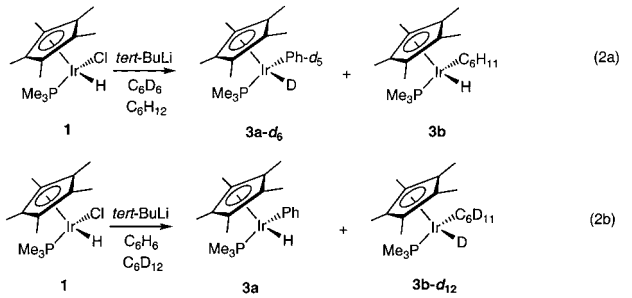
Spectroscopic and Chemical Identification of $Cp^*(PMe_3)Ir(Li)(Cl)$. Treatment of a benzene solution of hydrido chloride **1** with 1 equiv of *tert*-butyllithium at room temperature produced a rapid color change from yellow to gold and caused precipitation of LiCl. Analysis of the reaction mixture by ^1H NMR spectroscopy revealed the formation of the previously characterized $Cp^*(PMe_3)Ir(C_6H_5)(H)$ (**3a**) and $Cp^*(PMe_3)IrH_2$ (**4**) in a 3.8:1 ratio (64% overall yield). Similarly, reactions of **1** with *tert*-butyllithium in cyclohexane, cyclopentane, and cyclooctane generated the corresponding known cyclohexyl, cyclooctyl, and cyclopentyl hydrides **3b**−**d** (eq 1).[2]



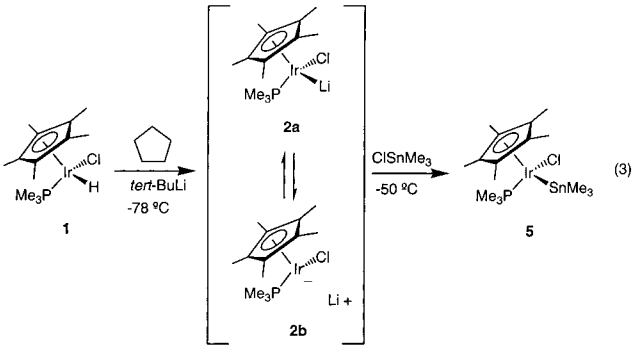
The most straightforward mechanism for this reaction involves deprotonation of the hydrido chloride, **1,** to give the chloroiridate, **2a**, followed by spontaneous elimination of LiCl to generate $Cp^*(PMe_3)Ir$. Double-label crossover experiments are consistent with this mechanism. Thus, treatment of **1** with *tert*-butyllithium in $C_6D_6-C_6H_{12}$ mixtures provided only **3a**-d_6 and **3b** with no detectable concentrations of $Cp^*(PMe_3)Ir(C_6D_5)(H)$ as determined by ^1H NMR spectroscopy (eq 2a). Similarly, reaction of **1** with *tert*-butyllithium in $C_6H_6-C_6D_{12}$ mixtures provided only **3a** and **3b**-d_{12} (eq 2b). The intramolecularity of the reaction eliminates the possibility that it occurs by initial deprotonation of the alkane or arene to form cyclohexyl- or phenyllithium followed by subsequent displacement of chloride to form the hydride complex.

Additional evidence for the intervention of chloroiridate **2a** was obtained by its generation at low temperature and trapping with chlorotrimethyltin. Treatment of a cyclopentane solution of **1** with *tert*-butyllithium at −78 °C and warming to −50 °C produced a red-pink solution. Addition of a cyclopentane

(22) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246.
(23) Bell, T. W.; Brough, S.-A.; Partridge, M. G.; Perutz, R. N.; Rooney, A. D. *Organometallics* **1993**, *12*, 2933.
(24) Kiel, W. A.; Ball, R. G.; Graham, W. A. G. *J. Organomet. Chem.* **1990**, *383*, 481.
(25) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1993**, *115*, 554.
(26) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449.
(27) Mobley, T. A.; Schade, C.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 7822.
(28) Mainz, V.; Andersen, R. A. *Organometallics* **1984**, *3*, 675.



solution of chlorotrimethyltin induced a rapid color change to yellow-gold and afforded the chloro trimethylstannyl derivative **5** upon workup in 70% yield based on recovered **1** (eq 3).

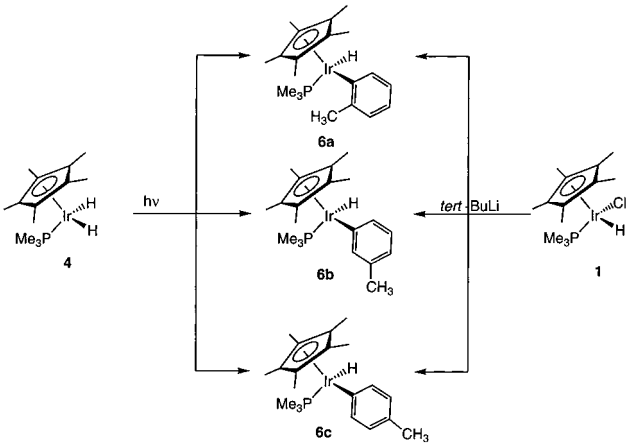


The postulated chloroiridate **2a** could be observed directly by ^{1}H, ^{31}P{^{1}H}, and ^{7}Li NMR spectroscopy. Deprotonation of **1** with *tert*-butyllithium in THF-d_8 at −78 °C afforded a red-pink solution. The ^{1}H NMR spectrum recorded at −31 °C revealed a Cp* singlet (1.81 ppm) and broadened PMe_3 doublet (1.38 ppm) indicative of a fluxional process. Cooling to −101 °C caused the PMe_3 signal to separate into two broad resonances centered at 1.44 and 1.32 ppm. Similar behavior was observed by ^{31}P{^{1}H} NMR spectroscopy. At −31 °C, a single sharp signal appeared at −43.33 ppm. The line broadened at −65 °C and, upon further cooling to −101 °C, existed as two broad but baseline-resolved singlets in a 2:1 ratio at −42.4 and −43.3 ppm, respectively. The process responsible for exchange became apparent when **2a** was examined with ^{7}Li NMR spectroscopy. At −101 °C, two resonances located at 1.92 and 3.91 ppm were observed. The upfield resonance was attributable to free lithium ion (or lithium ion in a solvent-separated ion pair) by comparison with the ^{7}Li shift of a THF solution of LiCl. Warming to −80 °C caused the two resonances to coalesce, indicating rapid equilibrium between **2a** and **2b** (eq 3). Determination of the coalescence temperatures in the ^{1}H, ^{31}P, and ^{7}Li NMR spectra provides an estimate of 9.1 kcal mol^{-1} for the free energy barrier for the **2a** ⇌ **2b** interconversion.

Inter- and Intramolecular Selectivity Studies of Hydrocarbon Oxidative Addition. In accord with the data presented above, we hypothesized that the elimination of LiCl from the iridate complex **2a** generated the 16-electron Cp*(PMe_3)Ir fragment which subsequently underwent oxidative addition of alkane and arene C−H bonds to provide the activation products **3a**−**d**. To provide support for this hypothesis, we examined the intramolecular C−H bond selectivity for oxidative addition of toluene and the intermolecular selectivity for C−H activation of cyclohexane, cyclooctane, and benzene and compared these selectivities to those observed in the photolysis of Cp*(PMe_3)-IrH_2 in neat toluene and in the hydrocarbon mixtures.

The intramolecular selectivities for the oxidative addition of the *o*-, *m*-, and *p*-C−H bonds of toluene for photolytically

Scheme 1



generated "Cp*(PMe_3)Ir" were obtained by dissolving Cp*-(PMe_3)IrH_2 in toluene and irradiating the resulting solution with a medium-pressure mercury lamp for a period of 4 h at 29 °C to effect 15% conversion[29] to the oxidative addition products (Scheme 1). Upon completion of the photolyses, the solutions were concentrated in vacuo. The product mixture was dissolved in C_6D_6 and subjected to analysis by ^{31}P{^{1}H} NMR spectroscopy and the ratios of *o*-, *m*-, and *p*-tolyl hydride complexes (**6a**−**c**) were determined to be 1.41:1.94:1, respectively. After statistical correction for the number of hydrogen atoms at each position, the relative selectivity for activation of the ortho, meta, and para positions was 0.71:0.97:1, respectively. The benzyl hydride complex arising from activation of the toluene methyl group was also observed. However, in the base-induced elimination reactions, this product (formed in approximately 15% yield) can also arise from nucleophilic substitution of chloride by benzyl anion, and we therefore chose not to include it in selectivity comparisons. Positive assignments were made by comparison of the spectra to authentic samples prepared by an independent route (see Experimental Section). All three independently synthesized tolyl hydride complexes **6a**−**c** were found to be thermally and photolytically stable, undergoing no detectable interconversion upon extended photolysis or thermolysis at 75 °C. Similarly, for studies of the intermolecular selectivities with respect to oxidative addition of benzene, cyclohexane, and cyclooctane, a solution of dihydride complex **4** was dissolved in binary or ternary mixtures of benzene, cyclohexane, and cyclooctane and irradiated similarly to 15% conversion at 29 °C to the corresponding phenyl, cyclohexyl, and cyclooctyl hydride complexes **3a**−**c**. Isolation of the reaction products and determination of the product ratios were carried out as described for the photolytic experiments using NMR spectroscopy. The relative ratios of phenyl, cyclooctyl, and cyclohexyl hydride products derived via photolysis of dihydride complex **4** in the present study were determined to be 1.74:0.34:1, respectively, calculated on a per mole basis and adjusted for relative concentration in the reaction solution. After statistical correction for the number of hydrogens at each position, the selectivities were determined to be 3.48:0.25:1, respectively. These C−H bond selectivities are somewhat different from those obtained a number of years ago by the first workers investigating this system (4.00:0.09:1).[2] We do not know the reason for the differences, but they may be a result of improved analytical

(29) While photolability of the product alkyl and aryl hydride complexes would lead to erroneous C−H bond selectivities, the photoreversions of the products are known to be slow and insignificant at low overall conversion of the starting dihydride complex (see ref 2).

Table 1. Intramolecular Selectivities for Oxidative Addition of Toluene by Iridium Precursors **1** and **4** Calculated on a Per-Hydrogen Basis

precursor/activation method	temp (°C)	**6a**	**6b**	**6c**
$Cp^*(PMe_3)IrH_2/h\nu$	29	0.71	0.97	1
$Cp^*(PMe_3)Ir(H)(Cl)$/*tert*-butyllithium[a]	27	0.21	0.79	1

[a] Absolute yields established in separate runs with pure hydrocarbons (see text).

methods and the modest photoinstability of some of the C−H activation products.

To determine the intramolecular selectivity for toluene activation and the intermolecular selectivities for benzene, cyclohexane, and cyclooctane activation in the $Cp^*(PMe_3)Ir(H)(Cl)$/*tert*-butyllithium reaction, a solution of $Cp^*(PMe_3)Ir(H)(Cl)$ in toluene or a mixture of the hydrocarbons and a solution of *tert*-butyllithium in toluene (or hydrocarbon mixture) were mixed at 27 °C. After vigorous stirring for a period of 90 min, the solution was filtered through Celite and concentrated in vacuo to give the product mixture. Dissolution in C_6D_6 and NMR analysis as described above provided the intra- and intermolecular selectivities. The intramolecular selectivities for toluene activation were calculated from the relative integrations of the $^{31}P\{^1H\}$ signals for each of the *o*-, *m*-, and *p*-tolyl hydride complexes and are presented in Table 1. The intermolecular selectivities for activation of benzene, cyclohexane, and cyclooctane were determined analogously and are presented in Table 2. In control experiments, the C−H bond selectivities (concentration normalized) were found to be independent of the order of addition of reagents as well as the absolute ratios of benzene to cycloalkane. For example, a 10-fold decrease in benzene concentration did not affect the relative selectivities of the C−H activating fragment (after correction for the relative concentrations). Further, the product ratios were independent of whether the reactions were quenched with a weak acid (e.g., acetone), suggesting that removal of one product from the reaction mixture by selective deprotonation was not occurring.

Surprisingly, we observed that the intramolecular selectivities for toluene activation and the intermolecular selectivities for benzene, cyclohexane, and cyclooctane activation by base-induced LiCl elimination were markedly different from those observed in the photolysis of $Cp^*(PMe_3)IrH_2$. Since the product ratios are determined by the relative rate constants for activation of the various substrates (which are, in turn, determined by the free energies of activation), we conclude that C−H bond activation by dihydride photolysis and base-induced LiCl elimination *must occur through different reactive intermediates.* The simplest interpretation is that the Li and/or Cl atoms or ions must interact in some way with the 16-electron $Cp^*(PMe_3)Ir$ fragment and influence the subsequent steps of C−H bond cleavage.

If this interpretation were correct, one would expect that the selectivities might be further altered by the elimination and subsequent interaction of a different cation−anion pair. To this end, we prepared the bromide analogue $Cp^*(PMe_3)Ir(H)(Br)$ (**7**) and subjected both **1** and **7** to treatment with bases derived from different alkali metal sources. Because of the difficulty in preparing and isolating the sodium and potassium congeners of *tert*-butyllithium, we prepared benzylsodium and benzylpotassium for use in the selectivity studies. In addition, we prepared benzyllithium-$(thf)_2$ to determine if a change in the structure of the Brønsted base also affected the selectivity. The results of these studies are presented in Table 2.

As illustrated in Table 2, within experimental uncertainty, we observed no effect of substitution of bromide for chloride on the intermolecular selectivities for hydrocarbon activation. For comparisons of reactions effected using the same alkali metal cation, the selectivity data for hydrocarbon activation by base-induced elimination of MX (M = Li, Na, K; X = Cl, Br) are the same within the experimental uncertainties so as to rule out any effect of the halide component in determining the selection of the hydrocarbon substrate. Further, while we found that the benzyllithium and *tert*-butyllithium elimination reactions provided C−H bond selectivities that differed within the experimental uncertainties, the difference was small, indicating that the structure of the deprotonating base did not dramatically influence the hydrocarbon selectivity. In contrast, we observed a pronounced effect of the metal cation component on the selectivity toward intermolecular benzene activation. While the ratios of cyclohexyl hydride to cyclooctyl hydride products appeared unaffected by the change in the metal cation, the selectivity for benzene activation increased with descent in the alkali metal series, increasing from 5.90 for reaction of **2** with benzyllithium to 9.68 for reaction of **2** with benzylpotassium.

We attempted to determine if a more pronounced change in the halide component of the salt would affect hydrocarbon selectivities by preparing the iodide analogue (**8**) of **1**. When a solution of the iodide complex **8** in benzene was treated with a solution of *tert*-butyllithium in benzene, we observed unreacted **8,** dihydride complex **4**, and a second unidentified product in a 2.1:1:1.2 ratio. The unidentified product exhibited two doublets located at −5.68 (J_{P-P} = 23 Hz) and −42.18 (J_{P-P} = 26 Hz) in its $^{31}P\{^1H\}$ NMR spectrum, possibly suggesting the formation of a dinuclear bridged complex. However, we observed none of the phenyl hydride complex **3a** as was observed for the chloride and bromide congeners. At present, we do not know the mechanism of formation of the unidentified material or of **4**.

Isotope Effects for Oxidative Addition of Benzene and Cyclohexane. In an effort to further define the interaction of the eliminated salt with the $Cp^*(PMe_3)Ir$ fragment, we determined the isotope effects for the C−D activation of C_6D_6 and C_6D_{12} in intermolecular competition experiments using the photolytic and base-induced dehydrohalogenation methods. We found that the isotopic shift in the phosphine resonance in the $^{31}P\{^1H\}$ NMR spectra of products **3a-*d*$_6$** and **3b-*d*$_{12}$** was large enough to provide baseline resolution of the deuterated and the undeuterated product phosphine resonances. This allowed direct calculation of the isotope effects for activation of benzene and cyclohexane in competition experiments involving mixtures of $C_6H_6-C_6D_6$ and $C_6H_{12}-C_6D_{12}$. These results are presented in Table 3.

In general, the small magnitudes of the isotope effects observed in these experiments suggested very little breakage of the C−H (C−D) bond in the "selectivity-determining" step for both the photolytic and dehydrohalogenation methods. While both methods provided isotope effects for benzene activation which were indistinguishable within experimental uncertainty (cf. 1.26 vs 1.22), a significantly higher isotope effect for cyclohexane activation was observed with the photolytic method in comparison to the dehydrohalogenation method (cf. 1.48 vs 1.15), further distinguishing the mechanisms of these two C−H bond cleavage reactions. The isotope effect determined in the present photolytic study (k_H/k_D = 1.48) compares well with that determined previously in our group (k_H/k_D = 1.38).[2]

Previously, Jones and Feher[21] reported a clever use of intra- vs intermolecular isotope effects[30,31] for the determination of

(30) Dolbier, W. R.; Dai, S.-H. *J. Am. Chem. Soc.* **1968**, *90*, 5028.
(31) Dolbier, W. R.; Dai, S.-H. *J. Am. Chem. Soc.* **1972**, *94*, 3946.

Table 2. Effect of Cation−Anion Pair on Intermolecular Oxidative Addition Selectivity for C−H Activation of Benzene, Cyclohexane, and Cyclooctane[a]

iridium precursor	base/method	elimination product	intermolecular selectivity		
			C_6H_6	C_8H_{16}	C_6H_{12}
4	*hν*	H_2	3.48 ± 0.12	0.26 ± 0.02	1
2	*tert*-butyllithium	LiCl	4.98 ± 0.12	0.74 ± 0.02	1
2	benzyllithium-2THF	LiCl	5.90 ± 0.72	0.81 ± 0.06	1
7	*tert*-butyllithium	LiBr	4.62 ± 0.70	0.74 ± 0.08	1
2	benzylsodium	NaCl	5.68 ± 0.64	0.71 ± 0.08	1
7	benzylsodium	NaBr	6.92 ± 0.96	0.68 ± 0.12	1
2	benzylpotassium	KCl	9.68 ± 0.96	0.73 ± 0.06	1
7	benzylpotassium	KBr	8.00 ± 1.04	0.71 ± 0.08	1

[a] Selectivity data are reported on a per-hydrogen basis relative to cyclohexane.

Table 3. Determination of Isotope Effects for Oxidative Addition of Benzene and Cyclohexane in C_6H_6/C_6D_6 and C_6H_{12}/C_6D_{12} Mixtures and for Oxidative Addition of Benzene-*1,3,5-d*$_3$

precursor complex	activation method	isotope effect		
		C_6H_6/C_6D_6	C_6H_{12}/C_6D_{12}	$C_6H_3D_3$
4	*hν*	1.26 ± 0.06	1.48 ± 0.12	1.29 ± 0.12
2	*tert*-butyllithium	1.22 ± 0.04	1.15 ± 0.10	1.15 ± 0.10

precomplexation of benzene prior to C−H activation by the closely related "Cp*(PMe_3)Rh" system. By comparing the isotope effect for oxidative addition of C_6D_6 (k_H/k_D = 1.05) with the intramolecular isotope effect for C−H bond activation in benzene-*1,3,5-d*$_3$ (k_H/k_D = 1.4), Jones concluded that η^2-coordination of the arene occurred prior to the oxidative addition. Subsequently, a similar strategy aimed at identifying arene precoordination in oxidative addition of benzene by Cp*(η^3-allyl)IrH showed that the difference between the intermolecular isotope effect (k_H/k_D = 1.20 ± 0.02) and the intramolecular isotope effect (k_H/k_D = 1.28 ± 0.04) was not significant enough to postulate η^2-coordination of benzene prior to oxidative addition.[22] When an analogous experiment was performed in the present study, we found the inter- and intramolecular isotope effects to be identical within experimental error (for both activation methods, Table 3), suggesting that *arene coordination via π-electron donation does not lie along the reaction coordinate toward oxidative addition by the iridium congener*. The observation of arene precoordination via π-electron donation in the Cp*(PMe_3)Rh and not in the Cp*(PMe_3)Ir may be a result of the tendency of iridium to form stronger M−C bonds which leads to erosion of the barrier that separates a π-arene complex from a phenyl hydride product. Alternatively, the iridium system may involve arene precomplexation, but this coordination may occur through a C−H σ-complex wherein one would not necessarily expect a β-secondary isotope effect.

Origin of Hydrocarbon Selectivity for Base-Induced Oxidative Addition. Previously in our group, studies have shown that thermal rearrangement of alkyl hydride complexes of the Cp*(PMe_3)Ir fragment can occur at rates competitive with external alkane exchange, indicating that the barrier to hydrocarbon exchange through σ-complex formation[32−35] (or alternatively, loss of hydrocarbon to form the naked 16-electron Cp*(PMe_3)Ir fragment) must be comparable to the barrier to reductive elimination leading to that σ-complex.[27] These experiments suggest a potential energy surface for hydrocarbon activation of the general shape described in Figure 2a. Thus, in this system, the selectivity toward C−H bond activation is

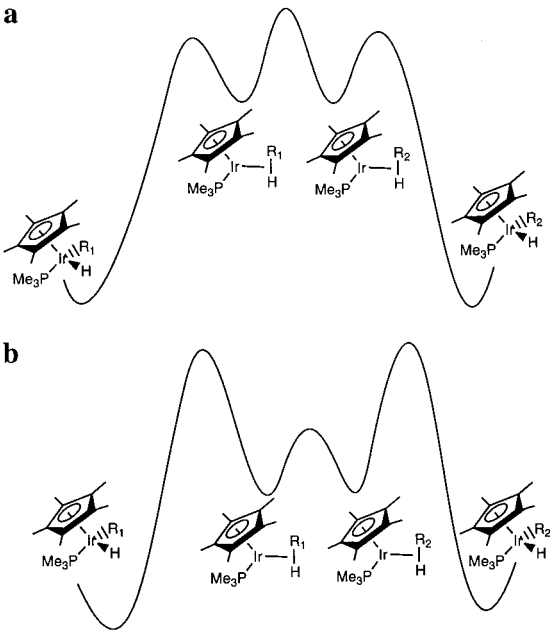


Figure 2. Possible reaction coordinates for C−H activation from equilibrating alkane complexes: (a) non-Curtin−Hammett situation and (b) Curtin−Hammett controlled process.

determined by the relative barrier heights leading to formation of the alkane complexes of the Cp*(PMe_3)Ir fragment.

Alternatively, flash kinetic studies of hydrocarbon activation by photolysis of Cp*Rh(CO)$_2$ in liquid Kr or Xe have shown that the solvates Cp*Rh(CO)(L) (L = Kr, Xe) are formed within the flash with subsequent displacement of the solvent by alkane to establish an equilibrium between the noble gas and alkane complexes.[8−11,36−38] The direct observation of the alkane complex indicates that oxidative addition of alkane must be rate-determining, leading to a potential energy surface of the shape described in Figure 2b. In contrast to the iridium system, this result indicates that the C−H bond selectivity exhibited by the rhodium system is under Curtin−Hammett control, being determined only by the relative transition state energies resulting from insertion into the different C−H bonds.

The direct observation of chloroiridate complex **2a** in the dehydrohalogenation reaction, as well as differences in the intra- and intermolecular selectivities and kinetic isotope effects on branching in comparison to those observed in the photolysis of complex **4**, provide compelling evidence that hydrocarbon activation proceeds via different intermediate species. To be

(32) Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1998**, *120*, 9953.
(33) Gross, C. L.; Girolami, G. S. *J. Am. Chem. Soc.* **1998**, *120*, 6605.
(34) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125.
(35) Wick, D. D.; Reynolds, K. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 3974.
(36) Piacenti, F.; Calderazzo, F.; Bianchi, M.; Rosi, L.; Frediani, P. *Organometallics* **1997**, *16*, 4235.
(37) Rosi, L.; Piancenti, F.; Bianchi, M.; Frediani, P.; Salvini, A. *Eur. J. Inorg. Chem.* **1999**, 67.
(38) Sun, X.-Z.; Grills, D. C.; Nikiforov, S. M.; Poliakoff, M.; George, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 7521.

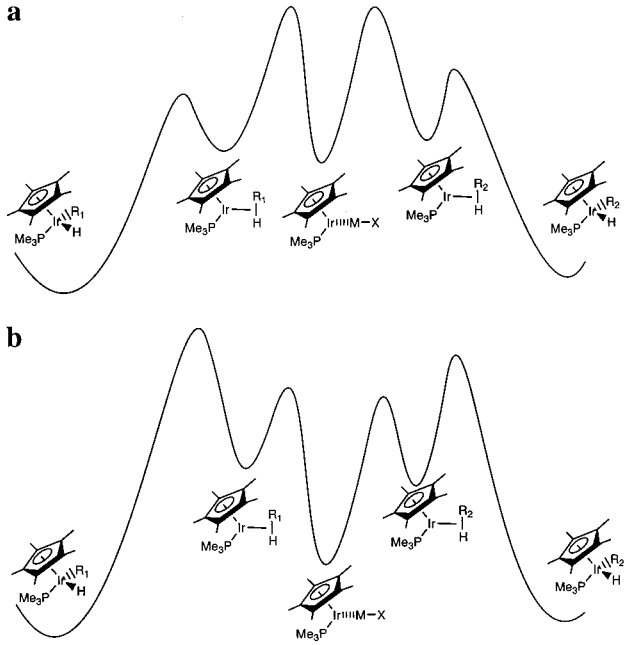
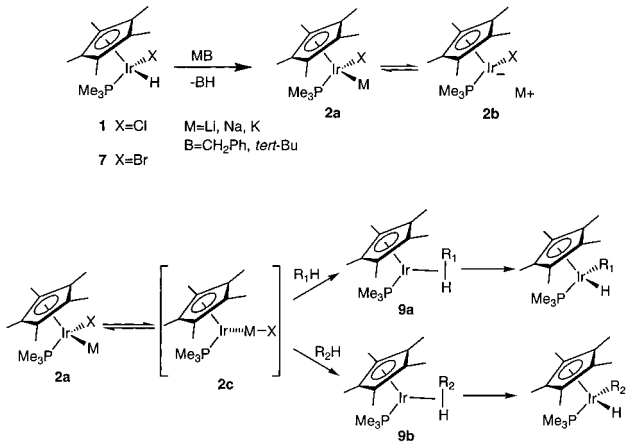


Figure 3. Possible reaction coordinates for C−H activating intermediates generated by base-induced HCl elimination.

Scheme 2



consistent with our observations, the departing salt must in some way be retained in the selectivity-determining step to influence the subsequent steps that lead to the final C−H bond activation product. A mechanism consistent with the observed data is illustrated in Scheme 2. In this mechanism, reaction of base with Cp*(PMe_3)Ir(H)(X) leads to complex **2a** which we postulate to be in equilibrium with the ion pair **2b** on the basis of our observation of lithium exchange in VT NMR studies. Elimination then occurs, but we postulate that the extruded metal halide molecule remains coordinated to the Ir center, probably through the alkali metal M, to account for its observed effect on the C−H bond activation selectivity. Subsequent coordination of hydrocarbon to the salt complex **2c** leads to formation of hydrocarbon complexes **9a** and **9b** which can react further to give the ultimate oxidative addition products.

As with the two cases described above, one can envision two extreme reaction coordinate diagrams for hydrocarbon activation by complex **2c** which differ only in the rate-determining steps (Figures 3). In Figure 3a, we illustrate a sequence wherein complex **2c** undergoes reaction with hydrocarbon in a rate-determining and irreversible step to form the hydrocarbon complexes **9a** and **9b**, which subsequently undergo rapid reaction to form the oxidative addition products. Alternatively, Figure 3b pictures a reaction that proceeds by reversible displacement of the salt MX in formation of the hydrocarbon complexes **9a** and **9b** followed by rate-determining insertion into the C−H bonds to form the hydrocarbon activation products. However, this latter possibility can be eliminated from consideration because, as in the case of oxidative addition by Cp*Rh(CO), the product ratios are under Curtin−Hammett control and are determined only by the relative energies of different C−H insertion transition states. If this diagram pertained to the dehydrohalogenation reaction, then *the product ratios and isotope effects would be required to be identical with those observed in the photolytic dihydrogen elimination reaction.* That the benzene−cycloalkane selectivity actually *increases* as we descend the alkali metal series (wherein one would expect the solubilities of the salts to decrease) suggests that the alkali metal ion must be retained in the selectivity-determining step, and, hence, alkane complex formation must be irreversible. Although we are reluctant to try to assign physical causes to the changes in selectivity, we agree with a referee's suggestion that the increase in selectivity for the meta and para isomers of toluene vs the ortho isomer seems consistent with the larger steric bulk of the metal center which contains an additional MX "ligand" in the hydrogen halide elimination reaction.

Conclusion

In summary, we have identified a novel mode of hydrocarbon activation by base-induced dehydrohalogenation of Cp*(PMe_3)Ir(H)(X). The reaction has been demonstrated to proceed via the intermediacy of the highly reactive haloiridate complexes Cp*(PMe_3)Ir(M)(X) (M = Li, Na, K; X = Cl, Br) which we have characterized spectroscopically and with chemical trapping. Comparisons of the intra- and intermolecular selectivities for hydrocarbon oxidative addition with those for the photochemically generated Cp*(PMe_3)Ir fragment have shown that the selectivity-determining intermediate must be different in the two reactions. We postulate that the eliminated salt remains in the coordination sphere of the Cp*(PMe_3)Ir fragment and interacts with the fragment primarily through the alkali metal atom, thereby affecting the C−H activation selectivity. The salt is subsequently displaced irreversibly in the formation of σ-complexes of arenes and cycloalkanes.

Experimental Section

General. Unless indicated otherwise, all manipulations were conducted in a Vacuum Atmospheres 553-2 drybox containing nitrogen purified by a MO-40-2 Dritrain or on vacuum lines using standard Schlenk techniques. ^{1}H, ^{13}C, ^{31}P, and ^{7}Li NMR spectra were obtained at the University of California, Berkeley (UCB) NMR facility on Bruker AMX series 300 and 400 MHz spectrometers. Infrared spectra were obtained in KBr matrices on a Mattson Galaxy series FT-IR 3000 spectrometer and are referenced to a polystyrene standard. Elemental analyses were performed at the UCB Microanalytical Laboratory. Mass spectrometric analyses were conducted at the UCB Mass Spectrometry Facility on Kratos MS-50 and AEI MS-12 mass spectrometers.

NMR spectra were obtained in Wilmad series 505-PP tubes. Flame-sealing of NMR tubes was effected under vacuum by connection of the tube to a Kontes stopcock equipped with a ground glass joint and connected via a Cajon Ultratorr adapter. Pentane, hexanes, benzene, toluene, diethyl ether, and tetrahydrofuran and their deuterated analogues were distilled under nitrogen from sodium benzophenone ketyl prior to use. Cyclohexane and cyclooctane were stirred for a minimum of 24 h over sodium and were filtered through activated alumina prior to use. Methylene chloride, chloroform, carbon tetrachloride, and acetonitrile were distilled from calcium hydride. *tert*-Butyllithium (Aldrich) was obtained as a solution and was filtered, concentrated in

vacuo, and recrystallized from pentane prior to use. Benzylmetalates (M = Li, Na, K) were prepared according to the procedure of Gilman (M = Li)[39] or Schlosser (M = Na, K).[40] Cp*(PMe_3)$IrCl_2$ was prepared according to the procedure of Maitlis.[41] *o*-, *m*-, and *p*-Tolylmagnesium reagents were purchased as solutions from Aldrich. Celite filtering aid was dried overnight in vacuo at 225 °C prior to use. All other reagents and solvents were obtained from commercial suppliers and were degassed (liquids) and used as received unless otherwise noted.

Determination of Kinetic C−H Bond Selectivities, Kinetic Isotope Effects, and Isotopic Label Crossover. In a typical thermal-activation experiment, a solid mixture of Cp*(PMe_3)Ir(H)(X) (X = Cl, Br, I) (15−17 mg, 0.034 mmol) and MR′ (M = Li, Na, K; R′ = *t*-Bu, benzyl) (2−4 mg, 0.031 mmol) was dissolved in a known mixture of one, two, or three hydrocarbons, and the resulting solution (in the case of *t*-BuLi) or suspension (other strong bases) was stirred at ambient temperature for a period of 3−12 h.[42] After filtration through Celite, the mixtures were concentrated in vacuo and the residues were dissolved in C_6D_6 and analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. In a typical photochemical activation experiment, 15 mg (0.037 mmol) of Cp*(PMe_3)IrH_2 was dissolved in a known mixture of one, two, or three hydrocarbons, and the solution was transferred to an NMR tube and sealed in vacuo. The tube was then irradiated with a medium pressure mercury lamp for a period of 4 h to effect approximately 15% conversion of the dihydride to C−H bond-activated products. Experiments were done in replicates of two or three (except for the activation of benzene-*1,3,5-d*$_6$ for which a single sample was prepared), and data were treated as described below. For NMR analysis, the $^{31}P\{^1H\}$ FID (24 transients incorporating a 1 min pulse delay) was transformed, and the spectrum was phased and integrated to determine the relative ratios of C−H activation products. For each of the replicate samples, the phasing and integration were performed a total of six times, and the results for each sample were averaged. The average for each replicate sample was then weighted according to its relative uncertainty, and the weighted averages of all replicates were averaged to determine a selectivity and uncertainty for each hydrocarbon pair. The uncertainties in the hydrocarbon selectivities are reported as standard errors in the mean which have been adjusted for sample size by multiplication of the appropriate Student t factor[43] for a two-sided 95% confidence level.

Cp*(PMe_3)Ir(H)(Cl) (1). In a glass reaction vessel was placed a solid mixture of Cp*(PMe_3)$IrCl_2$ (500 mg, 1.05 mmol) and $NaBH_4$ (190 mg, 5.02 mmol). The vessel was evacuated and *i*-PrOH (10 mL) was condensed in via vacuum transfer. The orange suspension was warmed to ambient temperature and was sonicated intermittently over a 1 h period to effect dissolution (CAUTION: substantial gas evolution). After 1 h, the bright yellow solution was evaporated to dryness in vacuo, the residue was extracted with three 2 mL portions of toluene, and the extract was filtered through a 1 cm Celite pad. After removal of the solvent under vacuum, the yellow solid was recrystallized from 12 mL of 16% toluene in hexanes at −40 °C to afford 375 mg of yellow crystalline (two crops) **1** in 81% yield. Spectral data for this compound matched those reported by Maitlis and co-workers.[41]

Cp*(PMe_3)Ir(H)(Br) (7). To a stirred solution of Cp*(PMe_3)$IrCl_2$ (300 mg, 0.63 mmol) in CH_2Cl_2 (8 mL) was added AgOTf (900 mg, 3.50 mmol). The solution was stirred for 40 min at ambient temperature and was filtered through Celite. The solvent was removed under vacuum and the residue was dissolved in THF (10 mL). To the stirred solution was added NaBr (1.63 g, 15.8 mmol), and the resulting suspension was stirred for 36 h at ambient temperature. After filtration and concentration, the crude product was recrystallized from CH_2Cl_2/petroleum ether to provide 273 mg (0.485 mmol) of Cp*(PMe_3)$IrBr_2$ in 77% yield. The complex was then placed in a glass reaction vessel containing $NaBH_4$ (74 mg, 1.94 mmol) and 2-propanol (approximately 5 mL) was condensed into the vessel via vacuum transfer. After warming to room temperature, the slurry was maintained at ambient temperature for a period of 1 h. After the volatile materials were removed under vacuum, the orange-yellow residue was extracted with two 5 mL portions of benzene, and the extracts were concentrated in vacuo. The crude complex was recrystallized from toluene−pentane with cooling to −40 °C to afford 194 mg (0.40 mmol) of Cp*(PMe_3)Ir(H)(Br) in 82% yield. ^1H NMR (C_6D_6): δ 1.72 (15 H, s), 1.38 (9 H, d, J_{P-H} = 10.5 Hz), −14.33 (1 H, d, J_{P-H} = 39.8 Hz) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 91.8 (CCH_3, d, J_{P-C} = 3.1 Hz), 19.1 (CH_3, d, J_{P-H} = 39.0 Hz), 10.15 (CH_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −39.95 ppm. MS (EI): *m*/*z* 484 (M^+).

Cp*(PMe_3)Ir(H)(I) (8). In a thick-walled glass reaction vessel was placed a solid mixture of Cp*(PMe_3)Ir(H)(Cl) (0.103 g, 0.234 mmol) and NaI (0.220 g, 1.47 mmol, 6.3 equiv). The mixture was dissolved in acetone (10 mL), and the vessel was sealed and evacuated to 60 mTorr. After heating the solution at 85 °C for 7 d, the volatile materials were removed in vacuo, and the solid residue was extracted with toluene and filtered through Celite. Concentration of the filtrate afforded an orange crystalline solid. The complex was purified by recrystallization (2×) by slow diffusion of pentane into a toluene solution at −40 °C. Cp*(PMe_3)Ir(H)(I) (85 mg, 0.160 mmol) was obtained as orange rhomboidal crystals in 68% overall yield after two recrystallizations. ^1H NMR (C_6D_6): δ 1.79 (15 H, s), 1.44 (9 H, d, J_{P-H} = 10.4 Hz), −15.43 (1 H, d, J_{P-H} = 37.6 Hz) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 92.1 (CCH_3), 21.0 (PCH_3, d, J_{P-C} = 40.0 Hz), 10.6 (CH_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −44.23 ppm. MS (EI): *m*/*z* 532 (M^+). Anal. Calcd for $C_{13}H_{25}IPIr$: C, 29.38; H, 4.74. Found: C, 29.10; H, 4.62.

Generation of Cp*(PMe_3)Ir(Li)(Cl) (2). Using an apparatus previously described,[44] solid *tert*-butyllithium (8.2 mg, 0.128 mmol) was placed in an NMR tube flame-sealed to a glass reaction vessel. A solution of Cp*(PMe_3)Ir(H)(Cl) (37 mg, 0.70 mmol) in 0.70 mL of THF-d_8 was placed in the reaction vessel, and the NMR tube was cooled to −196 °C. By tilting the apparatus without removing the attached NMR tube from the cooling bath, the solution of the iridium complex was carefully transferred to the NMR tube, freezing just above the solid *tert*-butyllithium. After evacuation to 40 mTorr, the NMR tube was flame-sealed and allowed to warm briefly by immersion for 20 s in a −78 °C bath to dissolve the reactants. The red solution was then maintained at −196 °C until the time of the NMR analysis. The tube was then thawed in the NMR probe pre-cooled to −80 °C and the ^1H, ^{31}P, and ^7Li spectra were recorded. ^1H NMR (THF-d_8): δ (−31 °C) 1.81 (15 H, br s), 1.38 (9 H, d), (−101 °C), 1.79 (15 H, br s), 1.44, 1.32 (total 9 H, br d). ^{31}P NMR (THF-d_8): δ (−31 °C) −43.33 ppm and (−101 °C) −42.4, −43.3 ppm. ^7Li NMR (THF-d_8): δ (−50 °C) 1.76 ppm and (−101 °C) 3.91, 1.92 ppm.

Low-Temperature Trapping of Cp*(PMe_3)Ir(Li)(Cl) with Cl-$SnMe_3$. In an oven-dried Schlenk flask was placed a solid mixture of Cp*(PMe_3)Ir(H)(Cl) (11.1 mg, 0.025 mmol) and *tert*-butyllithium (1.6 mg, 0.025 mmol, 1 equiv). The flask was connected to a vacuum manifold, and cyclopentane (5 mL) was added to the flask via vacuum transfer at −196 °C. The reaction flask was then warmed to −50 °C in an ethylene glycol−dry ice bath. After 60 min, complete dissolution of the hydrido chloride complex was realized, resulting in a rose-colored solution of Cp*(PMe_3)Ir(Li)(Cl). The solution was maintained at −50 °C for an additional 30 min, and a solution of $ClSnMe_3$ (6.4 mg, 0.032 mmol) in pentane (0.5 mL) was added via syringe. The solution developed a deep yellow color instantaneously, and stirring was continued at −50 °C for an additional 90 min. The reaction flask was then warmed to ambient temperature, and the volatile materials were removed under vacuum to provide a bright yellow oil. The oil was extracted with three 4 mL portions of pentane, and the extracts were filtered through Celite and concentrated in vacuo. Analysis of the yellow oil by ^1H NMR identified the tin complex Cp*(PMe_3)Ir($SnMe_3$)(Cl) (**5**) by comparison with an authentic sample (vide infra) and unreacted **1** in a 1:1 ratio.

Cp*(PMe_3)Ir($SnMe_3$)(Cl) (5). To a solution of Cp*(PMe_3)Ir($SnMe_3$)(H)[45] (75 mg, 0.132 mmol) in pentane (10 mL) was added

(39) Gilman, H.; McNinch, H. A. *J. Org. Chem.* **1961**, *26*, 3723.

(40) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508.

(41) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003.

(42) While we believe the reaction to be rapid, the low solubilities of the benzylsodium and benzylpotassium reagents in hydrocarbon solvents resulted in slow mass transfer and required longer stirring times to effect conversion of the starting materials to products.

(43) Skoog, D. A.; West, D. M. *Analytical Chemistry*, 3rd ed.; Saunders College Publishing: Philadelphia, PA, 1980.

(44) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332.

CCl_4 (159 mg, 100 μL, 1.04 mmol, 7.9 equiv). The solution was stirred at ambient temperature for a period of 18 h, and the volatile materials were removed under vacuum. The orange residue was recrystallized from a toluene−pentane mixture at −40 °C to yield 55 mg (91 μmol) of **4** as an orange crystalline solid in 69% yield from a first crop. Mp 188−190 °C. IR (KBr): 2966, 2908, 1376, 1282, 953, 752, 495 cm^{-1}. ^1H NMR (C_6D_6): δ 1.51 (15 H, d, J_{P-H} = 1.6 Hz), 1.27 (9 H, d, J_{P-H} = 10 Hz), 0.53 (9 H, s) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 92.7 (CCH_3), 18.4 (CH_3, d, J_{P-H} = 38 Hz), 9.71 (CH_3), −6.44 (CH_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −43.17 ppm. MS (EI): *m*/*z* 602 (M^+). Anal. Calcd for $C_{16}H_{33}ClPSnIr$: C, 31.88; H, 5.52. Found: C, 31.70; H, 5.45.

Cp*(PMe$_3$)Ir(*o*-C$_6$H$_4$CH$_3$)(Br). A solution of $[Cp^*IrCl_2]_2$ (350 mg, 0.440 mmol) in THF (10 mL) was placed in a 50 mL reaction vessel. A solution of *o*-tolylmagnesium bromide (0.5 mL of a 2 M solution in THF) was added via syringe, and the resulting mixture was stirred for 24 h at ambient temperature. To the deep red-brown slurry was added PMe_3 (72 mg, 0.94 mmol, 1.07 equiv) via vacuum transfer from a known-volume bulb. The resulting homogeneous solution was stirred for 48 h with no change in appearance from that which occurred immediately upon the phosphine addition. The volatile materials were removed in vacuo, and the residue was chromatographed down a 2 × 30 cm silica gel column employing 10−20% ether in pentane as the eluent. The leading yellow band was discarded, and a second orange band was collected to provide 160 mg (0.279 mmol) of Cp*(PMe_3)Ir(*o*-$C_6H_4CH_3$)(Br) as yellow-orange crystals upon evaporation in 32% yield. Recrystallization from ether−pentane afforded analytically pure material as a mixture of rotamers resulting from restricted rotation around the Ir−aryl bond. ^1H NMR ($CDCl_3$) (25 °C): δ 7.99 (0.41 H, d, *J* = 8.0 Hz), 7.21 (0.54 H, d, *J* = 7.2 Hz), 7.02 (0.48 H, d, *J* = 7.6 Hz), 6.96 (0.48 H, d, *J* = 7.6 Hz) ppm. $^{31}P\{^1H\}$ NMR (25 °C) ($CDCl_3$): δ −43.99 ppm. $^{13}C\{^1H\}$ NMR (59 °C) ($CDCl_3$): δ 148.1 (C), 145.1 (C−H), 143.0 (C), 142.1 (C, d, J_{P-C} = 11.2 Hz), 141.2 (C), 139.7 (C, d, J_{P-C} = 12.0 Hz), 130.4 (C−H), 127.7 (C−H), 124.8 (C−H), 123.3 (C−H), 122.4 (C−H), 122.3 (C−H), 92.8 (CCH_3), 92.7 (CCH_3), 28.9 (CH_3), 28.3 (CH_3), 17.1 (PCH_3, d, J_{P-C} = 38.5 Hz), 15.7 (PCH_3, d, J_{P-C} = 39.4 Hz), 9.1 (CH_3), 8.6 (CH_3) ppm. MS (EI): *m*/*z* 574 (M^+). Anal. Calcd for $C_{20}H_{31}BrPIr$: C, 41.81; H, 5.44. Found: C, 41.64; H, 5.36.

Cp*(PMe$_3$)Ir(*o*-C$_6$H$_4$CH$_3$)(H) (6a). In a reaction vessel was placed a solid mixture of Cp*(PMe_3)Ir(*o*-$C_6H_4CH_3$)(Br) (69 mg, 0.120 mmol) and $NaBH_4$ (17 mg, 0.480 mmol, 4 equiv). The vessel was evacuated on a vacuum line, *i*-PrOH (10 mL) was added via vacuum transfer, and the vessel was heated at 75 °C for a period of 8 h. Removal of the volatile materials under vacuum afforded a white solid. Extraction of the crude product with two 5 mL portions of pentane and filtration of the extracts through Celite afforded a pale yellow solid. Recrystallization from CH_3CN at −40 °C provided analytically pure Cp*(PMe_3)Ir(*o*-$C_6H_4CH_3$)(H) **(6a)** (54.1 mg) in 91% yield as a white crystalline solid. IR (KBr): 2972, 2904, 2142, 953, 739 cm^{-1}. ^1H NMR (C_6D_6): δ 7.58 (1 H, d, *J* = 7.6 Hz), 7.39 (1 H, d, *J* = 7.2 Hz), 7.11 (1 H, t, *J* = 7.0 Hz), 6.94 (1 H, t, *J* = 7.2 Hz), 2.63 (3 H, s), 1.78 (15 H, s), 1.03 (9 H, d, J_{P-H} = 10.0 Hz), −16.65 (1 H, d, J_{P-H} = 39 Hz) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.5 (C), 143.4 (C, d, J_{P-C} = 10.1 Hz), 138.6 (C−H), 127.9 (C−H), 124.4 (C−H), 121.8 (C−H), 92.4 (CCH_3), 32.2 (CH_3), 18.8 (PCH_3, d, J_{P-C} = 40 Hz), 10.3 (CH_3) ppm. Anal. Calcd for $C_{20}H_{32}PIr$: C, 48.37; H, 6.51. Found: C, 48.70; H, 6.68.

Cp*(PMe$_3$)Ir(*m*-C$_6$H$_4$CH$_3$)(Cl). To a stirred solution of Cp*(PMe_3)$IrCl_2$ (300 mg, 0.632 mmol) in THF (10 mL) was added *m*-tolylmagnesium chloride (0.65 mL of 1 M solution in THF, 0.65 mmol, 1.03 equiv). After the mixture was stirred for 5 h at ambient temperature, any unreacted Grignard reagent was destroyed by the addition of EtOH (0.50 mL), and the volatile materials were removed in vacuo. The crude product was purified by chromatography on a 2 × 30 cm silica gel column employing Et_2O as the eluent. A yellow band was collected and concentrated in vacuo to provide a yellow oil that solidified upon standing at ambient temperature. Recrystallization from Et_2O−pentane at −20 °C yielded 202 mg (0.381 mmol; 60%) of pure chloride. ^1H NMR (25 °C) ($CDCl_3$): δ 7.4−7.0 (2 H, br m), 6.78 (1 H, t, *J* = 14.8 Hz), 6.64 (1 H, d, *J* = 7.2 Hz), 2.18 (3 H, s), 1.58 (15 H, s), 1.37 (9 H, d, J_{P-H} = 10.4 Hz) ppm. $^{31}P\{^1H\}$ NMR (48 °C) ($CDCl_3$): δ −32.78 ppm. $^{13}C\{^1H\}$ NMR (48 °C) ($CDCl_3$): δ 140. 4 (C, d, J_{P-C} = 14.5 Hz), 140.1 (C−H, d, J_{P-C} = 3.2 Hz), 136.3 (C−H, d, J_{P-C} = 4.02 Hz), 135.9 (C), 126.8 (C−H), 122.4 (C−H), 92.4 (CCH_3), 21.2 (CH_3), 14.8 (PCH_3, d, J_{P-C} = 39.4 Hz), 8.1 (CH_3) ppm. MS (EI): *m*/*z* 530 (M^+). Anal. Calcd for $C_{20}H_{31}ClPIr$: C, 45.31; H, 5.89. Found: C, 45.32; H, 6.07.

Cp*(PMe$_3$)Ir(*m*-C$_6$H$_4$CH$_3$)(H) (6b). Into a glass reaction vessel was placed Cp*(PMe_3)Ir(*m*-$C_6H_4CH_3$)(Cl) (61 mg, 0.115 mmol) and $NaBH_4$ (17 mg, 0.460 mmol, 4 equiv). The vessel was evacuated, and *i*-PrOH (10 mL) was added via vacuum transfer. The vessel was sealed and heated at 75 °C for a period of 5 h. After removal of the volatile materials under vacuum, the residue was extracted with two 5 mL portions of pentane, and the extracts were filtered through a 1 cm Celite pad. Evaporation of the solvent gave an oily white solid that was recrystallized twice from acetonitrile to give 41 mg (0.083 mmol) of Cp*(PMe_3)Ir(*m*-$C_6H_4CH_3$)(H) (**6b**) as a white crystalline solid in 72% yield. IR (KBr): 2971, 2904, 2086, 1571, 949 cm^{-1}. ^1H NMR (C_6D_6): δ 7.64 (1 H, s), 7.51 (1 H, d, *J* = 7.2 Hz), 7.01 (1 H, t, *J* = 7.4 Hz), 6.90 (1 H, d, *J* = 7.6 Hz), 2.33 (3 H, s), 1.82 (15 H, s), 1.11 (9 H, d, J_{P-H} = 10.4 Hz), −17.07 (1 H, d, J_{P-H} = 37 Hz) ppm.$^{31}P\{^1H\}$ NMR (C_6D_6): δ −41.54 ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.7 (C, broad), 142.2 (C, broad), 136.4 (C, d, J_{P-C} = 12.8 Hz), 135.6 (C−H), 127.3 (C−H), 122.1 (C−H), 92.6 (CCH_3), 21.7 (CH_3), 19.1 (PCH_3, d, J_{P-C} = 40.2 Hz), 10.5 (CH_3) ppm. Anal. Calcd for $C_{20}H_{32}PIr$: C, 48.37; H, 6.51. Found: C, 48.69; H, 6.76.

Cp*(PMe$_3$)Ir(*p*-C$_6$H$_4$CH$_3$)(Br). This material was prepared by a procedure analogous to that described for preparation of the *o*-tolyl derivative (vide supra). ^1H NMR (25 °C) ($CDCl_3$): δ 7.5−7.2 (2 H, br s), 6.73 (2 H, d, *J* = 7.6 Hz), 2.22 (3 H, s), 1.63 (15 H, s), 1.46 (9 H, d, J_{P-H} = 10.0 Hz) ppm. $^{31}P\{^1H\}$ NMR (25 °C) ($CDCl_3$): δ −38.18 ppm. $^{13}C\{^1H\}$ NMR (25 °C) ($CDCl_3$): δ 140. 3 (C, br), 134.5 (C, d, J_{P-C} = 14.5 Hz), 130.5 (C−H), 128.5 (C−H), 92.7 (CCH_3), 20.6 (CH_3), 15.2 (PCH_3, d, J_{P-C} = 39.4 Hz), 9.0 (CH_3) ppm. Anal. Calcd for $C_{20}H_{31}BrPIr$: C, 41.81; H, 5.44. Found: C, 41.81; H, 5.32.

Cp*(PMe$_3$)Ir(*p*-C$_6$H$_4$CH$_3$)(H) (6c). In a glass reaction vessel was placed Cp*(PMe_3)Ir(*p*-$C_6H_4CH_3$)(Br) (50 mg, 0.094 mmol) and $NaBH_4$ (14.3 mg, 0.377 mmol, 4 equiv). The vessel was evacuated, and *i*-PrOH (5 mL) was added via vacuum transfer. The reaction vessel was then warmed to room temperature and maintained under reduced pressure until gas evolution ceased. The vessel was then sealed and heated at 75 °C for a period of 5 h. The colorless solution was then concentrated under vacuum, and the residue was extracted with two 5 mL portions of pentane, and the extracts were filtered through Celite. Removal of the solvent under vacuum provided 33.8 mg (0.075 mmol) of **6c** as a white crystalline solid in 80% yield. The complex was purified for elemental analysis by recrystallization from acetonitrile. IR (KBr): 2970, 2904, 2123, 1572, 951 cm^{-1}. ^1H NMR (C_6D_6): δ 7.63 (2 H, d, *J* = 7.6 Hz), 6.92 (2 H, d, *J* = 7.6 Hz), 2.31 (3 H, s), 1.82 (15 H, s), 1.10 (9 H, d, J_{P-H} = 10.0 Hz), −17.06 (1 H, d, J_{P-H} = 35 Hz) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −41.63 ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.7 (C, broad), 142.2 (C, broad), 136.4 (C, d, J_{P-C} = 12.8 Hz), 135.6 (C−H), 127.3 (C−H), 122.1 (C−H), 21.7 (CH_3), 19.1 (PCH_3, d, J_{P-C} = 40.2 Hz), 10.5 (CH_3) ppm. Anal. Calcd for $C_{20}H_{32}PIr$: C, 48.37; H, 6.51. Found: C, 48.36; H, 6.52.

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