mally sufficiently stable to allow isolation and determination of activation parameters for thermolysis (Table IV). Thermal decomposition of $Cp^*{}_2TiMe_2$,[2c] $Cp^*{}_2Ti(Me)CH{=}CH_2$ (**13**), and $Cp^*{}_2Ti(Me)Ph$ (**14**) proceed by σ-bond metathesis, while $Cp^*{}_2Ti(Me)CH_2Ph$ (**17**) decomposes by homolysis of the Ti–CH_2Ph bond. The different decomposition mechanisms of **13**, **14**, and $Cp^*{}_2TiMe_2$ versus **17** become evident in the activation entropies, with respectively negative and positive values. The activation enthalpies of these reactions fall within a narrow range (Table IV) of 88–116 $kJ{\cdot}mol^{-1}$, and it seems that there is always a low-energy pathway for decomposition of $Cp^*{}_2Ti(Me)R$.[42]

The differences in entropy of activation are more pronounced, although the Gibbs energy of activation involved with the process at ambient temperature is small (maximum ~11 $kJ{\cdot}mol^{-1}$). The largest ordering in the transition state for hydrogen transfer is the orthometalation reaction in $Cp^*{}_2Ti(Me)Ph$ (**14**). This is not without precedent, since approximately the same value for $\Delta S^{\ddagger}$ was found for the thermolysis of $Cp^*{}_2ZrPh_2$.[3f] The kinetic isotope effect $k_H/k_D = 5.1$ in the thermolysis of **14** indicates a linear and symmetrical transition state, as found for $Cp^*{}_2Zr(Ph\text{-}d_5)_2$.[3f] Interesting is the comparison of $\Delta S^{\ddagger}$ and the kinetic isotope effect for the α-hydrogen abstraction reactions in thermolysis of **13** and $Cp^*{}_2TiMe_2$. In the first case an sp^2 C–H bond is broken (vinylidene intermediate); in the second case an sp^3 C–H bond (carbene intermediate). The loss of rotational freedom to reach the transition state is approximately equal for both processes. However, the isotope effect in the former case is twice as large and indicates a more symmetric transition state.[47]

This study has demonstrated that $Cp^*{}_2Ti(Me)R$ compounds are easily prepared and that they are good model systems to study C–H activation in tetravalent titanium compounds $Cp^*{}_2Ti(R)R'$. They provide information about low-energy pathways for hydrogen transfer and homolytic Ti–C bond splitting in titanium chemistry which is relevant for catalytic processes like Ziegler-Natta polymerization of olefins and useful for synthetic strategies to generate reactive organometallic species.

Acknowledgment.

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Registry No. **1**, 107534-13-4; **2**, 131954-93-3; **2b**, 140361-93-9; **3**, 131954-94-4; **4**, 131954-95-5; **5**, 131954-96-6; **6**, 131954-90-0; **7**, 140361-76-8; **8**, 125937-73-7; **9**, 140361-77-9; **10**, 140361-78-0; **11**, 140361-79-1; **12**, 140361-80-4; **13**, 140361-81-5; **13b**, 140361-86-0; **13c**, 140361-87-1; **14**, 134026-50-9; **14b**, 140361-89-3; **14c**, 140361-90-6; **15**, 140361-82-6; **16**, 140361-83-7; **17**, 140361-84-8; **17b**, 140361-92-8; **18**, 140361-85-9; $Cp^*{}_2TiMe$, 99476-26-3; $Cp^*{}_2TiEt$, 99476-27-4; $Cp^*{}_2TiPr\text{-}n$, 99476-28-5; $Cp^*{}_2TiCH{=}CH_2$, 131954-86-4; $Cp^*{}_2TiPh$, 115564-94-8; $Cp^*{}_2TiOPr\text{-}n$, 131954-83-1; $Cp^*{}_2Ti(CD{=}CD_2)Cl$, 140361-88-2; $Cp^*{}_2TiCD{=}CD_2$, 135973-58-9; $Cp^*{}_2Ti(Ph\text{-}d_5)Cl$, 140361-91-7; $Cp^*{}_2Ti(Me\text{-}d_3)$, 135973-60-3; $Cp^*{}_2TiMe_2$, 11136-41-7; $Cp^*{}_2TiCH_2CMe_3$, 103351-92-4; $Cp^*{}_2TiCH_2Ph$, 135973-67-0; $Cp^*{}_2Ti(CH_2Ph)Cl$, 140361-94-0; $(Cp^*\text{-}d_{15})_2TiCl_2$, 83314-28-7; $(Cp^*{}_2Ti)_2N_2$, 11136-46-2; Cp*FvTi, 124018-05-9; Cp*FvClTi, 133983-60-5; $LiC{\equiv}CMe$, 4529-04-8; CH_3CD_2MgBr, 111582-47-9; $PbCl_2$, 7758-95-4; $CdMe_2$, 506-82-1; D_2, 7782-39-0; ethene, 74-85-1; 1,3-butadiene, 106-99-0; benzene-d_6, 1076-43-3; 1,2-diphenylethane, 103-29-7.

Supplementary Material Available: Textual details on the synthesis and characterization of Cp*FvTiR (R = Cl, $CH{=}CH_2$, Ph, CH_2Ph) and $(Cp^*\text{-}d_{15})_2TiCl_2$ and tables of ^1H and ^{13}C NMR data (5 pages). Ordering information is given on any current masthead page.

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Synthesis and C–H Activation Reactions of (η^5-Indenyl)(trimethylphosphine)iridium Alkyl and Hydride Complexes

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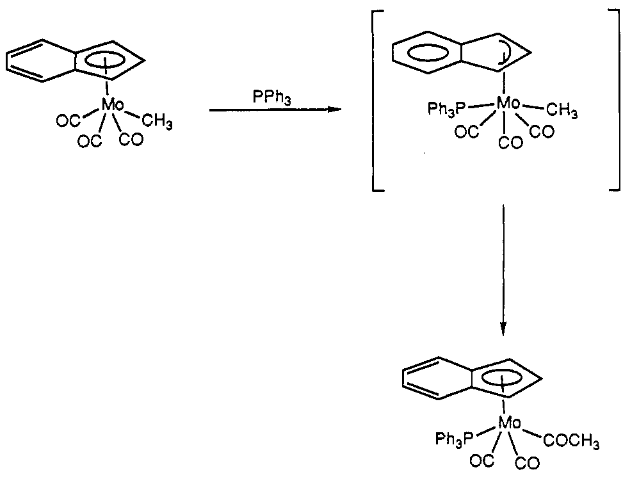
To obtain C–H oxidative addition products susceptible to further chemical transformation, the synthesis of a series of indenyliridium complexes that parallel the pentamethylcyclopentadienyl systems shown earlier to successfully activate alkane carbon–hydrogen bonds has been developed. Efficient routes to several members of the series $(\eta^5\text{-}C_9H_7)Ir(PMe_3)(X)(Y)$, where X and Y are alkyl, aryl, and hydride ligands, are described. The structure of the (methyl)(phenyl)iridium complex $(\eta^5\text{-}C_9H_7)Ir(PMe_3)(CH_3)(Ph)$ (**4b**) has been determined by X-ray diffraction: space group $P2_1/c$ with $a = 7.6688$ (6) Å, $b = 18.5650$ (16) Å, $c = 12.3855$ (9) Å, $\alpha = 90.0°$, $\beta = 98.674$ (7)°, $\gamma = 90.0°$, and $Z = 4$; $R = 0.0164$; $R_w = 0.0223$ on the basis of 1972 data having $F_o^2 > 3\sigma(F_o^2)$. In spite of the increased lability of these complexes caused by the presence of the indenyl ligand, they retain both the thermal and photochemical C–H activating properties associated with the corresponding pentamethylcyclopentadienyl complexes. Thus $(\eta^5\text{-}C_9H_7)Ir(PMe_3)H_2$ (**7**) undergoes loss of H_2 on irradiation and in benzene and cyclohexane solvent leads to $(\eta^5\text{-}C_9H_7)Ir(PMe_3)(C_6H_5)(H)$ (**6b**) and $(\eta^5\text{-}C_9H_7)Ir(PMe_3)(C_6H_{11})(H)$ (**6d**), respectively. Thermolysis of $(\eta^5\text{-}C_9H_7)Ir(PMe_3)(CH_3)(H)$ (**6a**) occurs to eliminate methane at a temperature lower than that for the Cp* analogue and in benzene and cyclohexane once again leads successfully to the phenyl and cyclohexyl hydrides **6b** and **6d**.

Introduction

Substitution of the η^5-indenyl ligand for the η^5-cyclopentadienyl ligand in transition-metal complexes has been shown to promote associative reactions between nucleophilic substrates and the metal center. Among the simplest examples is that of ligand substitution. Green and coworkers reported the greater reactivity of $(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2$ over $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2$ toward substitution of

Scheme I



the bound ethylenes by other alkenes, dienes, and alkynes.[1] Basolo and co-workers have similarly observed a 3 × 10^8-fold enhancement in the rate of CO substitution by triphenylphosphine (PPh_3) for (η^5-C_9H_7)Rh$(CO)_2$ over (η^5-C_5H_5)Rh$(CO)_2$.[2] Recently, several new routes to group 9 indenyl complexes have been developed and these have been used to explore a number of structure and reactivity aspects of this class of materials.[3]

The indenyl ligand also facilitates dative-ligand-induced migratory insertion reactions. The first observation of a rate acceleration in bimolecular reactions of η^5-indenyl complexes relative to η^5-cyclopentadienyl complexes was that of Hart-Davis and Mawby for the reaction of (η^5-C_9H_7)Mo$(CO)_3CH_3$ with PPh_3 to yield (η^5-C_9H_7)Mo$(CO)_2(PPh_3)COCH_3$, the result of CO insertion into the Mo–CH_3 bond.[4] To explain the rate acceleration and the observed first-order dependence on both the metal complex and PPh_3, an η^3-indenyl intermediate (cf. Scheme I) was proposed. The indenyl ligand behaves as a π-allyl ligand to accommodate the electrons of the incoming PPh_3, with this binding mode being more accessible for the indenyl ligand because of the resulting aromatization of the fused benzene ring.[5]

Basolo and co-workers have referred to this phenomenon as the "indenyl ligand effect".[2a] Forschner and Cutler have also since noted the greater facility of ligand-induced carbonylation in (η^5-C_9H_7)Fe$(CO)_2CH_3$ compared to that in (η^5-C_5H_5)Fe$(CO)_2CH_3$.[6] The possible intervention of η^3-indenyl intermediates has been given further credence by the crystallographic characterization of several η^3-C_9H_7 metal complexes,[7] including those formed from the addition of dative ligands to η^5-C_9H_7 metal complexes.[8]

Facilitation of dissociative reactions by the indenyl ligand has also been documented in the literature. Mawby and co-workers reported that the observed rate constants for the reaction of (η^5-Ind)Mo$(CO)_3$X (X = Cl, Br, I) with phosphines and phosphites had both an associative and a dissociative component.[9] The rates for both the associative and dissociative pathways were faster than those of the corresponding η^5-Cp complexes. Huggins and co-workers have recently reported similar rate behavior for ligand substitution in the tungsten analogue (η^5-Ind)W$(CO)_3$Cl.[10]

Several systems now exist in which alkane C–H bonds undergo oxidative addition to transition-metal centers, leading to hydrido(alkyl)metal complexes (eq 1).[11,12] Converting these C–H activation products to functionalized organic compounds, however (eq 2), has been a difficult task.

$$\text{M} + \text{R–H} \rightarrow \text{R–M–H} \qquad (1)$$

$$\text{R–M–H} \rightarrow \text{R–X} \qquad (2)$$

The apparent reluctance of many metal alkyl hydrides to open a new coordination site at the metal center renders them resistant to the coordination of a new dative ligand (such as CO, alkene, or alkyne) and, consequently, to migratory insertion of the R or H group to such dative ligands. Cyclopentadienyl- and (pentamethylcyclopentadienyl)iridium complexes provide a particulary dramatic example of this problem. Complexes of general structure Cp*(PMe_3)Ir(R)(H) are some of the most thermally stable alkyl hydrides discovered thus far,[13] and the corresponding dialkyl complexes Cp*$(PMe_3)IrR_2$ are stable to exceptionally high temperatures; neither system undergoes migratory insertion or β-elimination reactions.

The ease with which the indenyl ligand undergoes η^5 to η^3 to η^1 hapticity changes, facilitating the incorporation of additional ligands at transition-metal centers, suggested that it might be an attractive substitute for the Cp* ligand in C–H activating systems.[14] However, the synthesis of

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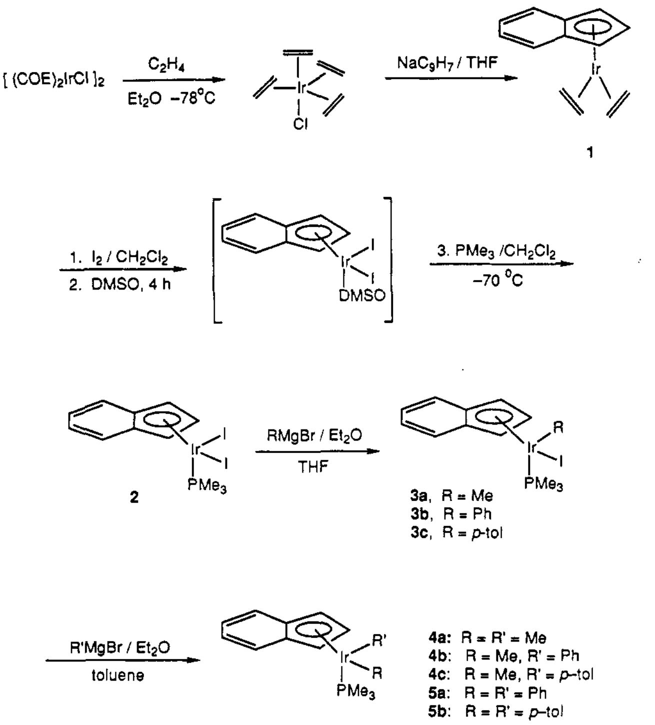
(14) (a) Marder, T. B.; Roe, D. C.; Milstein, D. *Organometallics* **1988**, *7*, 1451. Ghosh and Graham have substituted the tris(3,5-dimethylpyrazolyl)borato ligand, (HBPz*$_3$), for the Cp* ligand to effect the overall addition of ethylene and CO to benzene to give propiophenone in the (HBPz*$_3$)Rh(CO) system: (b) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 375.

Scheme II



such materials has posed a difficult challenge in the past. This paper reports the development of methods for the synthesis of indenyliridium complexes and a detailed study of their C–H activating behavior. In a companion paper we discuss the substitution and insertion chemistry of several of the starting complexes and C–H oxidative addition products.

Results

Synthesis of (η^5-Ind)(PMe_3)IrI_2 (2). In deciding upon a potential precursor to the family of (η^5-Ind)(PMe_3)Ir(III) complexes, we targeted the diiodide compound 2 via a synthetic route analogous to one used for the Cp analogue, Cp(PMe_3)IrI_2.[15] This route involved oxidation of the Ir(I) bis(ethylene) complex CpIr(C_2H_4)$_2$ with 1 equiv of molecular iodine to form the known polymer $[CpIrI_2]_x$.[16] Subsequent addition of a stoichiometric amount of PMe_3 to a CH_2Cl_2 suspension of the polymer at low temperature and warming to ambient temperature afforded Cp(PMe_3)IrI_2 in high yields.

Addition of 1 equiv of I_2 to the indenyl bis(ethylene) compound (η^5-Ind)Ir(C_2H_4)$_2$ (1)[17] similarly formed a dark purple precipitate, presumably an analogous polymeric material (Scheme II). However, simple addition of a stoichiometric amount of PMe_3 at low temperature did not afford the diiodide compound 2 in appreciable yields, but apparently led to multiple phosphine substitution. We sought to control this reaction by breaking up the polymer with a poorer ligand. Accordingly, addition of a 40–50% excess of DMSO to the polymeric material in CH_2Cl_2 led to a homogeneous solution in about 4 h. Dropwise addition of a cold CH_2Cl_2 solution of PMe_3 to the resulting mixture gave the diiodide complex 2 in 70–80% isolated yields (Scheme II). Spectroscopic data support the presence of an η^5-coordinated indenyl ligand. The ^1H NMR spectrum in $CDCl_3$ shows a complex AA′BB′ multiplet at δ 7.47 ppm for the four aromatic protons on the indenyl ring, and the Cp-type protons appear as a doublet at δ 5.83 ppm and a multiplet with phosphorus coupling at δ 5.22 ppm. The ^{13}C NMR shift of the indenyl quaternary carbons at δ 114.2 ppm indicates only a slight distortion toward the η^3 binding mode,[18] a property shared by the other η^5-indenyl compounds discussed later in this paper.

Synthesis of (Methyl)- and (Aryl)indenyliridium Complexes. Substitution of one of the iodide ligands in the diiodide complex 2 with hydrocarbyl ligands was accomplished by the reaction of 2 with the appropriate Grignard reagent, RMgBr (Scheme II). For example, treatment of compound 2 with 1.5 equiv of CH_3MgBr in THF for 45 min at ambient temperature afforded a 40% isolated yield of the expected product, (η^5-Ind)(PMe_3)Ir(CH_3)I (**3a**). Because the metal center in **3a** is a stereocenter, the complex is chiral, and the two halves of the indenyl ligand are diastereotopic. This is manifested in both the ^1H and the ^{13}C NMR spectra. In the ^1H NMR spectrum in acetone-d_6, the four aromatic indenyl protons appear as four separate multiplets while the three Cp-type protons appear as three separate multiplets. Similarly, separate resonances for all nine indenyl carbons can also be observed.

Reaction of the diiodide complex 2 with 1 equiv of the aryl Grignard reagents PhMgBr and p-tolMgBr proceeded at rates slower than that for CH_3MgBr. Complete conversion of the starting material 2 was observed at approximately 5 h, as monitored by TLC on alumina. The chirality of both products, (η^5-C_9H_7)Ir(PMe_3)(C_6H_5)I (**3b**) and (η^5-C_9H_7)Ir(PMe_3)(p-$CH_3C_6H_4$)I (**3c**), was again confirmed by their spectroscopic features.

Reaction of diiodide complex 2 with Grignard reagents having alkyl groups with β-hydrogens does not proceed straightforwardly. Decomposition pathways, possibly through β-elimination, appear to limit the synthetic utility of this route to alkyl-substituted derivatives of 3 containing β-hydrogens. The dimethyl complex **4a** was synthesized directly from the diiodide complex 2 by reaction with a 5-fold excess of CH_3MgBr and was isolated in 40% yield by sublimation. Reaction of a given iodoaryl complex (η^5-C_9H_7)Ir(PMe_3)(R)I (**3b** or **3c**) with the appropriate Grignard reagent R′MgBr resulted in the clean formation of the mixed (η^5-C_9H_7)Ir(PMe_3)(R)(R′) complexes (Scheme II). Although isolated yields were only fair, purification of the products by chromatography on alumina III was straightforward.

Complexes in which R = R′ were readily identified because the plane of symmetry in these achiral molecules makes the two halves of the indenyl ligand chemically equivalent, as in the case of the diiodide complex 2. Complexes in which R ≠ R′ have spectroscopic features similar to those of the (iodo)(alkyl) complexes (η^5-C_9H_7)Ir(PMe_3)(R)I (3), in which the two halves of the indenyl ligand are inequivalent. In addition, the ^{31}P NMR shift for the phosphine ligand at δ −40 ppm is characteristic of this family of η^5-indenyl, three-legged piano-stool structures (see Experimental Section).

Molecular Structure of (η^5-C_9H_7)Ir(PMe_3)(C_6H_5)CH_3 (4b).[19] Crystals of compound **4b** suitable for sin-

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[15] Buchanan, J. M. Ph.D. Thesis, University of California, Berkeley, 1985.

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[17] Merola, J. S.; Kacmarcik, R. T. *Organometallics* **1989**, *8*, 778. Although the bis(ethylene) complex 1 has been reported, no details of its synthesis or spectral data have appeared. Consequently, the full details of our synthetic approach to complex 1 and its complete spectroscopic and analytical characterization are provided in the Experimental Section.

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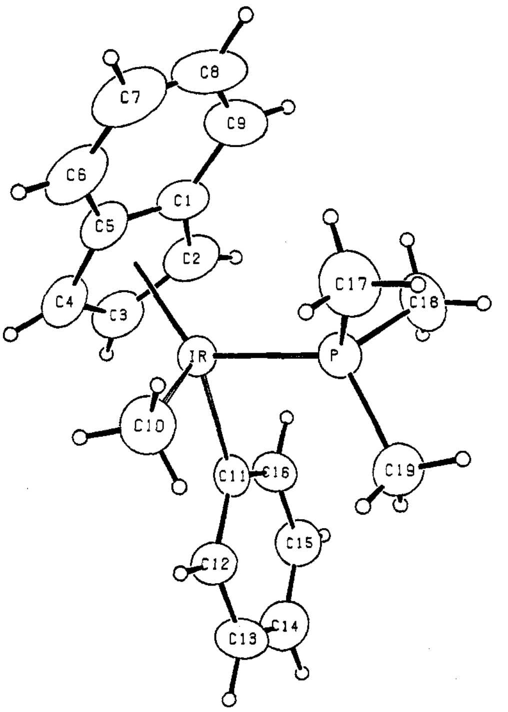


Figure 1. ORTEP diagram and labeling scheme for (η^5-C_9H_7)Ir(PMe_3)(Ph)Me (**4b**). The ellipsoids are scaled to represent the 50% probability surface. Hydrogen atoms are given as arbitrarily small spheres for clarity.

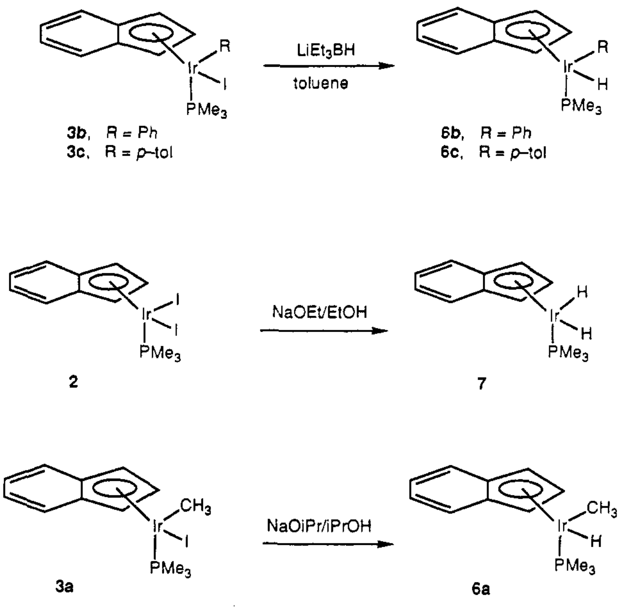
Table I. Selected Intramolecular Distances and Angles for 4b[a]

	Distances		
Ir-P	2.228 (1)	C1-C9	1.427 (5)
Ir-C1	2.381 (3)	C2-C3	1.432 (6)
Ir-C2	2.282 (4)	C3-C4	1.395 (5)
Ir-C3	2.232 (3)	C4-C5	1.443 (5)
Ir-C4	2.226 (3)	C5-C6	1.400 (5)
Ir-C5	2.339 (3)	C6-C7	1.350 (7)
Ir-C10	2.109 (4)	C7-C8	1.397 (7)
Ir-C11	2.043 (3)	C8-C9	1.364 (7)
Ir-Cp	1.943	C-CPh(av	1.38 (2)
C1-C2	1.416 (5)	P-C(av)	1.81 (1)
C1-C5	1.427 (5)		
	Angles		
Cp-Ir-P	130.41	C-P-C(av)	102 (2)
Cp-Ir-C10	122.45	Ir-P-C17	111.83 (14)
Cp-Ir-C11	125.76	Ir-P-C18	114.86 (15)
P-Ir-C10	87.18 (12)	Ir-P-C19	119.67 (13)
P-Ir-C11	86.78 (9)	C17-P-C18	103.45 (22)
C10-Ir-C11	92.14 (15)	C17-P-C19	103.64 (21)
IndCp(av)	108 (1)	C18-P-C19	101.50 (20)
aromC-C-C(av)	119 (3)		

[a] Complete tables are provided as supplementary information.

gle-crystal X-ray diffraction analysis were obtained by slow crystallization from acetone-d_6 at −40 °C. An ORTEP diagram with the accompanying labeling scheme for complex **4b** is presented in Figure 1. Selected interatomic bond distances and angles are presented in Table I. The molecule exhibits the usual localized allylene structure of the η^5-indenyl ligand in the pseudooctahedral, three-legged piano-stool geometry. The ligand–iridium–ligand bond angles for the methyl, phenyl, and phosphine moieties deviate less than 3.5° from 90°, as expected for a pseudooctahedron. The Ir–Ph bond distance (2.043 (3) Å) is significantly shorter than the Ir–CH_3 distance (2.109 (4) Å).

Scheme III



The projection of the Ir atom onto the plane of the five-membered ring of the indenyl ligand is 0.16 Å from the ring centroid. Otherwise, the distortions of the indenyl ligand toward an η^3 binding mode are minimal (ring-slippage parameter[3a,c,f,18] = 0.106 (3) Å). The five-carbon ring is planar to within 0.03 Å, while the entire ligand is planar to within 0.05 Å. The dihedral angle between the allyl and arene planes is only 5.7 ± 2.2°. As Faller et al. have noted, for most other structures containing η^5-indenyl ligands the ligand with the greatest trans influence is situated trans to the ene portion of the five-carbon ring.[20] This was rationalized by postulating that greater aromatization of the benzene ring is aided by decreased ene-to-metal interaction. However, in the molecular structure of **4a**, the ligand with the smallest trans influence, Ph,[21] is oriented trans to the ene portion of the Cp-type ring. We do not have a good explanation for this observation.

Synthesis and Arene Exchange of (η^5-C_9H_7)Ir(PMe_3)(Ar)H (6b, Ar = Ph; 6c, Ar = *p*-tol). The reaction of the aryl iodide compounds **3b** and **3c** with $LiEt_3BH$ in toluene for 14 h afforded the corresponding aryl hydride complexes **6b** and **6c** in 70–80% yield after crystallization from toluene/pentane (Scheme III). The presence of Ir–H moieties was confirmed by the IR spectra of **6b** and **6c**, which exhibit Ir–H stretching frequencies at 2232 cm^{-1} for **6b** and 2216 cm^{-1} for **6c**. Note that these stretching frequencies are about 100 cm^{-1} higher than the corresponding ones for the analogous compounds Cp*Ir(PMe_3)(Ph)H[11a] and CpIr(PMe_3)(Ph)H.[13] The ^1H NMR spectra of **6b** and **6c** provided additional evidence with upfield metal hydride resonances at δ −22.22 ppm for **6b** and δ −22.65 ppm for **6c**. These resonances appear about 5 ppm upfield from the corresponding Ir–H resonances for the Cp* and Cp phenyl hydrides. Substitution of a Cp ligand for Cp* makes only a slight difference in the properties of the iridium hydride complexes,[13,15] but these data demonstrate that, for some reason we do not yet

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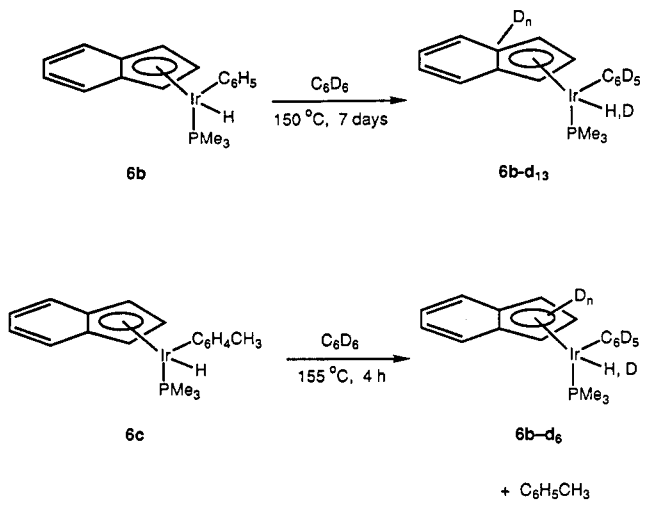
(19) The structure determination was performed by Dr. Frederick J. Hollander, crystallographer at the University of California, Berkeley X-ray crystallographic facility (CHEXRAY).

(20) For a discussion on the conformation and degree of slippage of η^5-indenyl and η^5-cyclopentadienyl ligands based upon X-ray crystal data, see: Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929.

(21) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons, Inc.: New York, 1988; p 1299.

Scheme IV



understand, the change induced by the Ind ligand is substantially greater.

The differences in the physical properties of indenyl aryl hydrides are also manifested in their reactivity. Thermolysis of the phenyl hydride **6b** in benzene-d_6 at 150 °C led to partial deuteration of the phenyl hydride **6b** after 20 h (Scheme IV). This observation stands in contrast to the results of the extended thermolysis of Cp*Ir(PMe_3)(Ph)H in benzene-d_6 at 190 °C, which showed no exchange of the bound benzene with the bulk solvent.[13]

The partial deuteration of the indenyl phenyl hydride **6b**, however, was not as simple as one would predict from the mechanisms postulated for alkane exchange in the Cp*Ir(PMe_3)(R)H system[11d] and of arene exchange in the Cp*Rh(PMe_3)(Ar)H system.[22] As expected, the benzene initially lost from the phenyl hydride **6b** appeared to be benzene-d_0, as judged by the sharp, intense resonance at δ 7.146 ppm. The aryl ligand was deuterated as expected, but the hydride position contained an extensive amount of protium. Correspondingly, the ^1H NMR spectrum indicated that deuterium appeared to have been specifically incorporated into one of the three Cp-type positions in the indenyl ligand, namely the one with the most downfield resonance at δ 5.64 ppm. Further thermolysis at 150 °C over a period of 7 days resulted in deuteration of all positions other than the bound PMe_3, as confirmed by mass spectroscopy of the product **6b**–d_{13} (Scheme IV). Significant decomposition of the phenyl hydride complex was observed upon extended thermolysis.

We attempted to gain additional insight into this unusual deuteration pattern by heating the tolyl hydride **6c** to 155 °C in benzene-d_6 (Scheme IV). Inspecting the reaction mixture by ^1H NMR spectroscopy after 4 h indicated a similar deuteration pattern. Partial conversion of the tolyl hydride to the phenyl hydride was indicated by the appearance of the resonance of toluene at δ 2.10 ppm and the decrease in the tolyl methyl resonance of **6c** at δ 2.28 ppm. Surprisingly, the decrease in the Ir–H resonance for **6c** was accompanied by the appearance of the Ir–H resonance of **6b**. Unfortunately, inspection of the Cp region was not straightforward due to the coincidental overlap of all the resonances of both **6c** and **6b**. However, it was evident that there was a corresponding decrease in the most downfield Cp-type resonance at δ 5.64 ppm.

These observations leave unresolved a number of questions as to the mechanism of arene exchange in this system. At short times, the reaction appears to proceed via loss and subsequent readdition of arene with the complication of H–D exchange between the Ir–H position and one of the Cp positions of the indenyl ring. One possible pathway for the indenyl exchange involves reversible, stereospecific hydrogen transfer to the indenyl ligand,[23] followed by overall 1,3-hydrogen shift across the five-carbon ring and reversible, stereospecific hydrogen transfer back to the metal. In summary, although we did not pursue a detailed mechanistic study of these transformations, it is clear that arene exchange at the metal center and reversible metal-to-indenyl ligand hydrogen-transfer reactions are accessible processes in this system.

Synthesis of the Dihydride Complex (η^5-C_9H_7)Ir(PMe_3)H_2 (7) and the Corresponding Hydridomethyl Complex 6a. In an attempt to prepare the hydrido iodide complex (η^5-C_9H_7)Ir(PMe_3)(H)I by the classic β-elimination route,[24] the diiodide complex **2** was treated with a concentrated basic (NaOEt) ethanolic solution for 16 h at ambient temperature (Scheme III). Inspection of the crude reaction product by ^1H NMR spectroscopy revealed that the major hydride-containing product possessed a hydride resonance with an intensity greater than one hydride per PMe_3 ligand. Isolation of the product showed that the major product was the dihydride **7**. The dihydride's tendency to occlude solvent has so far precluded satisfactory elemental analysis, but it has been fully characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR, IR, and high-resolution mass spectroscopy. Its unique spectral features include an Ir–H resonance in the ^1H NMR spectrum at δ −20.67 ppm and the appearance of two Ir–H stretches in the IR spectrum at 2184 and 2130 cm^{-1}. Only one Ir–H stretch has been observed for the Cp* and Cp dihydrides.

The indenyl dihydride **9** is very pale yellow in color. Unlike its Cp* and Cp analogues, whose UV–visible absorption spectra indicate negligible absorption above 350 nm, the dihydride **9** displays a significant amount of absorption in the tail of its spectrum in pentane up to 400 nm. The absorbance increases rapidly below 400 nm with shoulders at 345 nm ($\epsilon = 8.9 \times 10^2$) and 313 nm ($\epsilon = 1.4 \times 10^3$).

Having successfully applied the basic alcohol β-elimination route to the synthesis of the dihydride **7**, we treated the iodomethyl complex (η^5-C_9H_7)Ir(PMe_3)(CH_3)I (**3a**) with NaO(i-Pr) in 2-propanol. The hydridomethyl complex **6a** was isolated from the reaction mixture in 65% yield by sublimation. It exhibits a ^1H NMR resonance at δ −22.35 ppm and an Ir–H stretch in the IR region at 2204 cm^{-1}.

Photochemically- and Thermally-Induced Oxidative C–H Addition Reactions of Indenyliridium Dihydrides and Alkyl Hydrides. Photolysis of dihydride **7** in benzene for 15 h resulted in 43% yield of the hydridophenyl compound **6b** after complete conversion of **7** (Scheme V), as analyzed by $^{31}P\{^1H\}$ NMR spectroscopy (using the dichloride complex Cp*Ir(PMe_3)Cl_2 as an external standard). The solution of the dihydride **7** darkened upon photolysis, but not nearly to the extent observed for the Cp and Cp* dihydrides. The buildup of unidentified

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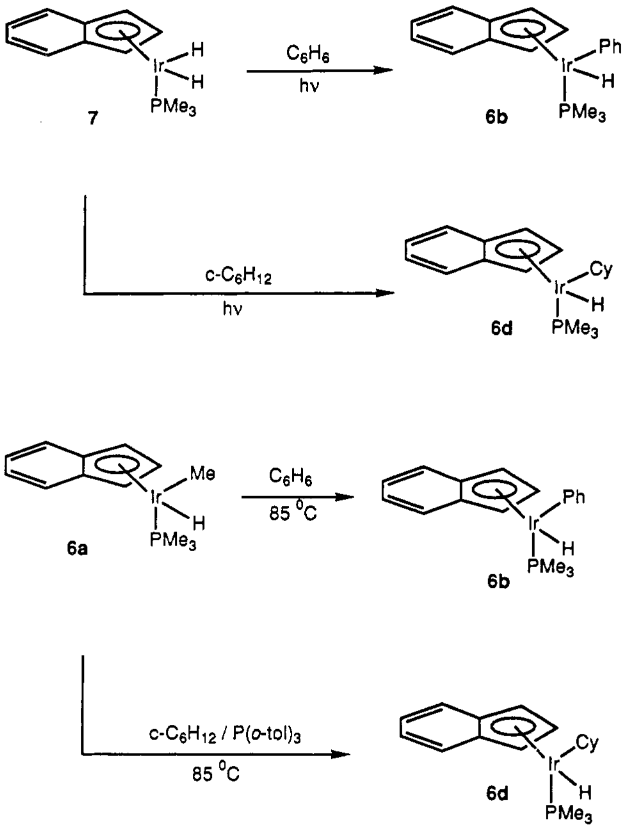
[22] Feher, F. J.; Jones, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 4814 and references therein.

[23] For some examples of hydrogen or alkyl transfers to or from η^5-Cp ligands, see: (a) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. (b) Werner, H.; Hofmann, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 794. (c) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1974**, 516. (d) McNally, J. P.; Copper, N. J. *J. Am. Chem. Soc.* **1989**, *111*, 4500. (e) McNally, J. P.; Glueck, D. S.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 4838. (f) Schubert, U.; Schenkel, A. *Chem. Ber.* **1988**, *121*, 939. (g) Schubert, U.; Schenkel, A.; Muller, J. *J. Organomet. Chem.* **1985**, *292*, C11.

[24] (a) Chatt, J.; Shaw, B. L. *Chem. Ind.* **1960**, 931. (b) Lewis, J.; Nyholm, R. S.; Reddy, G. K. N. *Chem. Ind.* **1960**, 1386. (c) Vaska, L. *J. Am. Chem. Soc.* **1961**, *83*, 756.

Scheme V



absorbing materials turned the solution orange and made the photochemical transformation slightly less efficient as the photolysis proceeded. However, continued photolysis led to complete conversion of the dihydride, albeit with formation of some decomposition products along with **6b**. Similarly, the photolysis of **7** in cyclohexane for 20 h resulted in a 19% yield of the cyclohexyl hydride **6d** based on 94% conversion, as analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. Because of the significant amount of decomposition of the cyclohexyl hydride **6d** under photolytic conditions, preparative-scale photochemical synthesis was not practical. However, the isolation of the cyclohexyl hydride **6d** as the product of a thermal C–H oxidative addition reaction has been accomplished, as described below.

Thermolysis of the methyl hydride **6a** in benzene at 85 °C resulted in the loss of methane and the formation of the phenyl hydride **6b** with a half-life of about 25 h (Scheme V). This reaction also proceeds very slowly at 65 °C with a half-life of approximately 12.5 days. Use of P(*o*-tol)$_3$ as an internal standard indicated no detectable decomposition of the organometallic species. The reaction temperatures at which methane is lost from complex **6a** are significantly lower than those required for the Cp*Ir(PMe$_3$)(R)H and CpIr(PMe$_3$)(R)H systems. For example, cyclohexane is lost from the Cp*Ir(PMe$_3$)(cyclohexyl)H compound in benzene at 100 °C with a half-life of about 4.5 days, with the thermolysis more conveniently run at 130 °C.

Thermolysis of compound **6a** in cyclohexane at 85 °C similarly resulted in the loss of methane and the formation of the cyclohexyl hydride **6d**. However, the product **6d** appeared to be thermally unstable, giving rise to unidentifiable decomposition products. The addition of P(*o*-tol)$_3$ to the reaction mixture slowed the decomposition of product but did not stop it. After 60 h at 85 °C, two-thirds of the methyl hydride **6a** had decomposed, with about three-fourths of that going to the cyclohexyl hydride **6d** (based on P(*o*-tol)$_3$ as an internal standard), for an overall yield of 50%. Separation of the reaction mixture by preparative-scale thin-layer chromatography afforded a 26% isolated yield of the cyclohexyl hydride **6d**.

Conclusions

In this work we have developed efficient syntheses of indenyliridium complexes that parallel the pentamethylcyclopentadienyl systems capable of successfully activating alkane carbon–hydrogen bonds. Indenyliridium dialkyl, (aryl)(alkyl), diaryl, hydrido(alkyl), and hydrido(aryl) complexes are now accessible, as is the parent dihydride (η^5-C_9H_7)Ir(PMe$_3$)H$_2$. In spite of the increased lability of these complexes caused by the presence of the indenyl ligand, they retain both the thermal and photochemical C–H activating properties associated with the corresponding pentamethylcyclopentadienyl complexes. Thus (η^5-C_9H_7)Ir(PMe$_3$)H$_2$ undergoes loss of H$_2$ on irradiation and in alkane and arene solvents leads to (η^5-C_9H_7)Ir(PMe$_3$)(R)(H). Similarly, thermolysis of (η^5-C_9H_7)Ir(PMe$_3$)(CH$_3$)(H) occurs to eliminate methane at a temperature lower than that of the Cp* analogue but in cyclohexane solvent still leads to the cyclohexyl hydride (η^5-C_9H_7)Ir(PMe$_3$)(C$_6$H$_{11}$)(H). The alkyl hydrides (as well as the other indenyl complexes described here) are stable enough to isolate and characterize, but (as hoped) they are more reactive than their Cp* analogues. This reactivity includes migratory insertion of ligands such as CO and alkynes, and the details of this chemistry are described in the following paper.

Experimental Section

General Information. All manipulations were conducted under a nitrogen or argon atmosphere using standard Schlenk, vacuum line, or unless otherwise noted, a Vacuum Atmospheres HE 553 Dri-Lab with attached Mo-40-1H Dri-Train. NMR spectra were obtained on Bruker AM-500 and AM-400 spectrometers, as well as on the 200-, 250-, and 300-MHz instruments constructed from Cryomagnets, Inc., magnets and Nicolet computers and software. $^{31}P\{^1H\}$ NMR spectra were recorded in ppm downfield from external 85% H$_3$PO$_4$. ^{13}C chemical shifts are reported in ppm downfield from TMS.

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 1550 Fourier transform (FT) spectrometer interfaced to a Model 7500 computer and a Nicolet 510 FT-IR spectrometer interfaced to a Nicolet 620 workstation. Mass spectra were obtained at the UCB Mass Spectrometry Facility on AEI MS-12 and Finnegan 4000 mass spectrometers. Elemental analyses were performed by the UCB Microanalytical Laboratory. NMR tubes were degassed and flame-sealed by attachment of the tubes to Cajon Ultra Torr SS-6-UT-6-4 $^3/_8$–$^1/_4$in. reducing unions fitted with Kontes K-826500 high-vacuum Teflon stopcocks (referred to as "Cajon adaptors"). "Glass bombs" refer to cylindrical, medium-walled Pyrex vessels joined to Kontes K-826500 high-vacuum Teflon stopcocks. Quantitative vacuum transfer of volatile reagents was done with known-volume bulbs connected to a high-vacuum line equipped with an MKS Baratron instrument. Reactions proceeding at elevated temperatures were carried out in either a Neslab Model RTE-8DD circulating water or a Neslab Model EX-250HT high-temperature oil bath. The temperature was calibrated externally with a platinum RTD immersion probe of a Fisher LCD thermometer. Alumina III for column chromatography was prepared by heating a 1:1 (w:w) mixture of 80–200-mesh basic alumina (Fisher Scientific) and 60-mesh neutral alumina (Alfa) under vacuum and subsequently adding 6 wt % H$_2$O. Preparative-scale thin-layer chromatography (TLC) plates (Analtech Alumina GF, 1000 micron, 20 × 20 cm) were pretreated by eluting the plates with CH$_3$OH and heating them for at least 1 h in a 150 °C glass-drying oven.

Unless otherwise indicated, all solvents and reagents were purchased from commerical suppliers and used without further purification. Benzene, toluene, diethyl ether (Et_2O), and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl, pentane and hexane from $LiAlH_4$, and cyclohexane, cyclooctane, CH_2Cl_2, CH_3CN from CaH_2 under nitrogen. Acetone was stirred over $MgSO_4$ for 1 day, vacuum-transferred onto activated 3-Å sieves for 1 day, and distilled from the sieves under vacuum. Ethanol was distilled from Mg and vacuum-transferred prior to use. 2-Propanol was stored over CaH_2 under vacuum and vacuum-transferred prior to use. Deuterated solvents were treated as their protiated analogues and vacuum-transferred prior to use. Grignard reagents (RMgX) were purchased from Aldrich. Trimethylphosphine (PMe_3) was purchased from Strem and dried over 1:5 Na:K alloy. Sodium indenide (NaC_9H_7) was prepared by the reaction of indene and sodium dispersion in THF under argon. Aniline hydriodide ($PhNH_3I$) was prepared from the reaction of aniline and hydriodic acid (47% solution in water), recrystallized from ethanol, and dried under high vacuum. The $[(COE)_2IrCl]_2$ dimer was synthesized according to published procedures.[25]

(η^5-C_9H_7)Ir(C_2H_4)$_2$ (1). In the drybox, 9.80 g (10.9 mmol) of $[(COE)_2IrCl]_2$ was slurried in 400 mL of Et_2O in a 1-L three-neck round-bottom flask equipped with a vacuum stopcock and two rubber septa. The reaction mixture was transferred into a hood, where C_2H_4 was bubbled through the slurry under Ar. After 10 min, the reaction mixture became a homogeneous, red solution, at which point the mixture was cooled to −78 °C with a dry ice–2-propanol bath. Upon cooling, the solution turned pale green and a white solid, presumably $(C_2H_4)_4IrCl$,[26] precipitated from the mixture. A THF solution of NaC_9H_7 (6.04 g, 43.7 mmol, 4.0 equiv in 150 mL), prepared in the drybox, was then added under Ar to the cold slurry by cannula, and the resulting mixture was allowed to warm to ambient temperature over a period of 2 h with slow C_2H_4 bubbling. After removal of the volatile materials under vacuum, the flask was transferred back into the drybox, where the product was extracted from the residue with eight 20-mL portions of Et_2O and filtered through a small pad of alumina III supported on a 60-mL fritted-glass filter. Et_2O was removed under vacuum, the orange residue was slurried with a 10-mL portion of Et_2O, and the supernatant was decanted by pipet. The residue was further washed with 5-mL portions (at least three) of Et_2O until the extracts became consistently bright yellow. The resulting residue was dried under vacuum to give a first crop of 6.28 g (17.3 mmol, 79% yield) of 1 as a bright yellow solid. An additional 1.19 g of 1 may be recovered from the Et_2O extracts by sublimation at 50 °C, 10^{-2} Torr, to give an overall yield of 7.47 g (20.6 mmol, 94%). ^1H NMR (C_6D_6, 20 °C): δ 7.01 (m, 4 H), 5.71 (t, J = 2.5 Hz, 1 H), 4.77 (d, J = 2.5 Hz, 2 H), 2.85 (v br, 4 H), 0.75 (v br, 4 H) ppm. ^1H NMR (toluene-d_8, −40 °C): δ 6.99 (m, 4 H), 5.70 (t, J = 2.5 Hz, 1 H), 4.64 (d, J = 2.5 Hz, 2 H), 2.94 (m, 4 H), 0.79 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 124.8 (s), 120.6 (s), 108.5 (s), 83.4 (s), 73.9 (s), 24.2 (s) ppm. IR (KBr pellet): 3065, 3037, 2969, 1328, 1172, 1162, 1002, 834, 816, 788, 741 cm^{-1}. MS (EI): m/e 364, 334 (M^+, base). Anal. Calcd for $C_{13}H_{15}Ir$: C, 42.96; H, 4.16. Found: C, 43.36; H, 4.23.

(η^5-C_9H_7)Ir(PMe_3)I_2 (2). A 1-L three-neck round-bottom flask equipped with a stirbar, two septa, and a vacuum stopcock was charged with 1.82 g (5.01 mmol) of the bis(ethylene) complex (η^5-C_9H_7)Ir(C_2H_4)$_2$ (1) in the drybox. The flask was taken out of the box and into a hood, where 500 mL of CH_2Cl_2 was added under N_2 by syringe to dissolve the solid. As an Et_2O solution of I_2 (1.27 g, 5.00 mmol in 40 mL) was added to the stirred solution by syringe, a dark purple precipitate formed. Subsequently, 0.5 mL (7.0 mmol, 1.4 equiv) of DMSO was also added by syringe. After 4 h of stirring at ambient temperature, the mixture became essentially homogeneous but contained traces of undissolved solid which had the appearance of bright red silt. One septum was replaced with a stopcock, and the middle neck was fitted with a 125-mL pressure-equalizing addition funnel. The apparatus was then purged with argon for 1 h. Meanwhile, 100 mL of CH_2Cl_2 was degassed in a 250-mL three-neck round-bottom flask, equipped with two septa and a vacuum stopcock, using three freeze–pump–thaw cycles. From a known-volume bulb, 1.1 equiv of PMe_3 (200 Torr, 508.51 mL, 293 K, 5.57 mmol) was condensed into CH_2Cl_2 at 77 K. As soon as the PMe_3 solution had thawed, the cold solution was transferred to the addition funnel by cannula, and the PMe_3 was added dropwise to the red mixture over a period of at least 45 min.

The resulting mixture was allowed to stir for 12 h, at which time the volatile materials were removed under vacuum. The dark red residue was slurried with a 10-mL portion of CH_2Cl_2, and the supernatant was decanted by pipet. The residue was further washed with 5-mL portions (at least three) of CH_2Cl_2 until the extracts became consistently bright red. The resulting residue was dried under vacuum to give a first crop of 2.14 g (3.36 mmol, 67% yield) of 2 as a bright red solid. An additional crop of 2 can be recovered from the CH_2Cl_2 extracts by column chromatography on alumina III, eluting with CH_2Cl_2 after washing off faster running impurities with hexane and Et_2O. Removal of the solvent gave an additional 0.47 g of 2 for an overall yield of 2.61 g (4.10 mmol, 82%). The product thus obtained was pure by NMR spectroscopy and was used without further purification. A small amount of compound 2 was recrystallized from CH_2Cl_2 at −20 °C by layering an equal volume of hexane over the solution and dried under high vacuum for elemental analysis. ^1H NMR ($CDCl_3$): δ 7.47 (m, 4 H), 5.83 (d, J = 2.3 Hz, 2 H), 5.22 (m, 1 H), 2.11 (d, J = 11.7 Hz, 9 H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −20.3 ppm. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −17.8 ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 130.9 (s), 126.7 (s), 114.2 (s), 83.3 (s), 67.7 (s), 20.8 (d, J = 46.8 Hz) ppm. IR (KBr pellet): 3110, 3064, 2982, 2904, 1414, 1303, 1285, 954, 868, 749, 741, 685, 450 cm^{-1}. MS (EI): m/e 638, 511 (M^+, base). Anal. Calcd for $C_{12}H_{16}PI_2Ir$: C, 22.62; H, 2.53. Found: C, 22.89; H, 2.57.

(η^5-C_9H_7)Ir(PMe_3)(CH_3)I (3a). Method A. To a well-stirred THF solution of the diiodide complex (η^5-C_9H_7)Ir(PMe_3)I_2 (2) (320 mg, 0.50 mmol in 20 mL) in the drybox was added by syringe 1.5 equiv of CH_3MgBr (0.25 mL of a 3.0 M solution in Et_2O, 0.75 mmol). The reaction mixture was allowed to stir at ambient temperature for 45 min, at which time the reaction was quenched by passing the mixture through a small pad of alumina III supported on a 30-mL fritted-glass filter and flushing with additional THF. After the volatile materials were removed under vacuum, the residue was dissolved in a minimum amount of toluene and loaded on an alumina III column. Elution began with pentane. As a yellow band moved toward the bottom of the column, clearly separated from an immobile orange band, a 1:1 pentane/Et_2O mixture was used to elute the dimethyl complex (η^5-C_9H_7)Ir(PMe_3)(CH_3)$_2$ (4a) (see below), as a bright yellow fraction in 16% yield (33 mg, 0.08 mmol). Product 3a was initially eluted as a bright orange band with a 1:1 pentane/Et_2O mixture, which was replaced with pure Et_2O after the elution of the yellow band was completed. This gave compound 3a in 42% yield (112 mg, 0.21 mmol), which was pure by NMR spectroscopy and used without further purification. Complex 3a was recrystallized from Et_2O at −40 °C to give analytically pure material.

Method B. In the drybox, 82 mg (0.20 mmol) of the dimethyl complex 4a and 53 mg (0.24 mmol, 1.2 equiv) of $PhNH_3I$ were dissolved in 5 mL of acetone. After the evolution of methane appeared to stop after 30 min, the volatile materials were removed under vacuum. Column chromatography, as described above, afforded 83 mg (0.16 mmol, 80% yield) of iodomethyl product 3a. ^1H NMR (acetone-d_6): δ 7.47 (m, 1 H), 7.32 (m, 1 H), 7.23 (m, 1 H), 7.14 (m, 1 H), 5.86 (m, 1 H), 5.55 (br, 1 H), 5.50 (m, 1 H), 1.52 (d, J = 10.9 Hz, 9 H), 1.45 (d, J = 6.2 Hz, 3 H) ppm. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −37.8 ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 127.2 (s), 127.1 (s), 124.5 (s), 122.1 (s), 113.7 (s), 112.4 (s), 95.1 (s), 71.5 (d, J = 13.4 Hz), 63.2 (s), 15.6 (d, J = 40.9 Hz), −31.5 (d, J = 9.1 Hz) ppm. IR (KBr pellet): 2932, 2888, 1320, 1284, 1224, 960, 944 (sh), 856, 744, 680 cm^{-1}. MS (EI): m/e 526 (M^+). Anal. Calcd for $C_{13}H_{19}PIIr$: C, 29.72; H, 3.65. Found: C, 29.37; H, 3.61.

(η^5-C_9H_7)Ir(PMe_3)(C_6H_5)I (3b). In the drybox, 640 mg (1.00 mmol) of the diiodide complex 2 was dissolved in 20 mL of THF. To the well-stirred solution was added by syringe 2.0 equiv of PhMgBr (0.67 mL of a 3.0 M solution in Et_2O, 2.01 mmol). The reaction mixture was allowed to stir at ambient temperature for 5 h, at which time the reaction was quenched by passing the mixture through a small pad of alumina III supported on a 30-mL fritted-glass filter and flushing with additional THF. After the

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volatile materials were removed under vacuum, the residue was dissolved in a minimum amount of toluene, and an equal volume of hexane was layered over the resulting solution. Product **3b** crystallized from the mixture with $^1/_3$ equiv of toluene (by ^{1}H NMR spectroscopy) at -40 °C to give a 76% yield (472 mg, 0.76 mmol). Product **3b** can be obtained free of toluene by dissolving the crystals in benzene and lyophilizing the solid under high vacuum. An additional crop of product **3b** can be recovered and isolated from the mother liquor along with the diphenyl complex $(\eta^5\text{-}C_9H_7)Ir(PMe_3)(C_6H_5)_2$ (**5a**) (see below), by column chromatography on alumina III. ^{1}H NMR (acetone-d_6): δ 7.76 (m, 2 H), 7.63 (m, 1 H), 7.39 (m, 2 H), 7.20 (m, 1 H), 6.75 (m, 3 H), 6.24 (m, 1 H), 5.82 (br, 1 H), 5.33 (m, 1 H), 1.38 (d, J = 11.0 Hz, 9 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ -39.4 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 144.2 (s), 128.9 (s), 128.1 (s), 127.5 (s), 126.9 (s), 122.8 (s), 122.4 (d, J = 14.2 Hz), 121.0 (s), 116.7 (s), 112.2 (s), 98.6 (d, J = 2.5 Hz), 75.7 (d, J = 14.4 Hz), 62.0 (s), 14.9 (d, J = 41.7 Hz) ppm. IR (KBr pellet): 3056, 3039, 2974, 2910, 1569, 1473, 1460, 1282, 1059, 1022, 953, 944, 871, 751, 736, 699 cm^{-1}. MS (EI): m/e (M$^+$, base). Elemental analysis was obtained on the solvate. Anal. Calcd for $C_{18}H_{21}PIIr\cdot{}^1/_3C_6H_5CH_3$: C, 39.51; H, 3.86. Found: C, 39.51; H, 3.96.

$(\eta^5\text{-}C_9H_7)Ir(PMe_3)(p\text{-}CH_3C_6H_4)I$ (3c). The iodo(p-tolyl) complex **3c** was prepared by a procedure similar to the one described for the iodo(phenyl) compound **3b**, starting with the diiodide complex **2** and 2 equiv of p-tolMgBr. Product **3c** was isolated by column chromatography on alumina III. The faster running yellow band of the ditolyl complex $(\eta^5\text{-}C_9H_7)Ir(PMe_3)(p\text{-}CH_3C_6H_4)_2$ (**5b**) was eluted with a 1:1 mixture of pentane/Et$_2$O. Product **3c** was then eluted with Et$_2$O to afford a 71% yield (429 mg, 0.71 mmol). ^{1}H NMR (acetone-d_6): δ 7.61 (m, 3 H), 7.38 (m, 2 H), 7.19 (m, 1 H), 6.58 (d, J = 7.7 Hz, 2 H), 6.22 (m, 1 H), 5.80 (br, 1 H), 5.31 (m, 1 H), 2.17 (s, 3 H), 1.37 (d, J = 11.0 Hz, 9 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ -39.5 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 143.9 (d, J = 3.3 Hz), 131.5 (s), 129.1 (s), 128.8 (d, J = 1.3 Hz), 127.4 (s), 126.9 (s), 121.0 (s), 117.4 (d, J = 13.7 Hz), 116.6 (s), 112.3 (s), 98.7 (d, J = 3.1 Hz), 75.7 (d, J = 14.6 Hz), 61.9 (s), 20.5 (s), 14.9 (d, J = 42.1 Hz) ppm. IR (KBr pellet): 3052, 2997, 2908, 1480, 1416, 1319, 1302, 1283, 1051, 954, 881, 802, 749 cm^{-1}. MS (EI): m/e 602, 511 (M$^+$, base). Anal. Calcd for $C_{19}H_{24}PIIr$: C, 37.94; H, 3.85. Found: C, 38.32; H, 3.98.

$(\eta^5\text{-}C_9H_7)Ir(PMe_3)(CH_3)_2$ (4a). To a well-stirred toluene slurry of the diiodide complex $(\eta^5\text{-}C_9H_7)Ir(PMe_3)I_2$ (**2**) (320 mg, 0.50 mmol in 20 mL) in the drybox was added by syringe 10 equiv of CH_3MgBr (1.7 mL of a 3.0 M solution in Et$_2$O, 5.1 mmol). The reaction mixture was allowed to stir at ambient temperature for 45 min, at which time the mixture appeared to be a suspension of a white solid in a bright yellow solution. The excess Grignard reagent was quenched by passing the mixture through a 15-mL pad of alumina III supported on a 30-mL fritted-glass filter, which resulted in a vigorous evolution of methane. The product was recovered from the alumina by flushing with Et$_2$O. Removal of the solvent and subsequent sublimation at 50 °C and 10^{-2} Torr afforded a 42% yield (86 mg, 0.21 mmol) of the dimethyl complex **4a** as a golden yellow solid. ^{1}H NMR (acetone-d_6): δ 7.31 (m, 2 H), 6.97 (m, 2 H), 5.38 (m, 2 H), 5.35 (m, 1 H), 1.23 (d, J = 10.3 Hz, 9 H), 0.34 (d, J = 5.2 Hz, 6 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ -38.8 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 123.7 (s), 121.9 (s), 110.3 (s), 95.8 (s), 69.3 (d, J = 7.8 Hz), 15.1 (d, J = 37.4 Hz), -33.2 (d, J = 7.7 Hz) ppm. IR (KBr pellet): 2916, 2876, 2808, 1320, 1284, 1236, 952, 744 cm^{-1}. MS (EI): m/e 383 (M$^+$, base). Anal. Calcd for $C_{14}H_{22}PIr$: C, 40.67; H, 5.36. Found: C, 40.78; H, 5.36.

$(\eta^5\text{-}C_9H_7)Ir(PMe_3)(C_6H_5)CH_3$ (4b). In the drybox, 124 mg (0.20 mmol) of the iodo(phenyl) complex, $(\eta^5\text{-}C_9H_7)Ir(PMe_3)(C_6H_5)I\cdot{}^1/_3C_7H_8$, was dissolved in 5 mL of toluene. To this stirred solution was added by syringe 2.25 equiv of CH_3MgBr (0.15 mL of a 3.0 M solution in Et$_2$O, 0.45 mmol). The reaction mixture was allowed to stir for 1 day, after which time the solution had turned from orange to light yellow. The excess CH_3MgBr was quenched by passing the reaction mixture through a 15-mL plug of alumina III supported on a 30-mL fritted-glass filter. The reaction product was completely eluted from the alumina with three additional 10-mL portions of Et$_2$O. The solvent was removed under vacuum, and the resulting residue was dissolved in a minimum amount of toluene and loaded onto an alumina III column. Elution of a bright yellow band with a 3:1 (v:v) mixture of pentane/Et$_2$O and subsequent removal of solvent yielded 25 mg (0.053 mmol, 26%) of the (phenyl)methyl complex **4b** as a yellow solid. ^{1}H NMR (acetone-d_6): δ 7.37 (m, 1 H), 7.21 (m, 1 H), 7.09 (m, 2 H), 7.00 (m, 2 H), 6.68 (m, 2 H), 6.67 (m, 1 H), 5.61 (m, 1 H), 5.53 (m, 1 H), 5.30 (m, 1 H), 1.13 (d, J = 10.4 Hz, 9 H), 0.65 (d, J = 6.0 Hz, 3 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ -38.0 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 140.5 (d, J = 2.6 Hz), 126.83 (s), 126.81 (d, J = 12 Hz), 124.6 (s), 124.4 (s), 122.4 (s), 122.3 (s), 121.5 (s), 111.8 (s), 111.5 (s), 99.1 (d, J = 2.0 Hz), 69.8 (d, J = 6.5 Hz), 68.5 (d, J = 9.2 Hz), 14.6 (d, J = 38.4 Hz), -30.8 (d, J = 8.9 Hz) ppm. IR (KBr pellet): 2920, 1568, 1472, 1320, 1284, 1060, 1024, 956, 940, 748, 736, 700 cm^{-1}. MS (EI): m/e 476, 384 (M$^+$, base). Anal. Calcd for $C_{19}H_{24}PIr$: C, 47.99; H, 5.09. Found: C, 47.85; H, 5.19.

Table II. Crystal and Data Collection Parameters for Complex 4b

empirical formula: $IrPC_{19}H_{24}$

(A) Crystal Parameters at T = 25 °C[a,b]

space group: $P2_1/c$
fw = 475.6
a = 7.6688 (6) Å
b = 18.5650 (16) Å
c = 12.3855 (9) Å
α = 90.0°
β = 98.674 (7)°
γ = 90.0°
V = 1743.2 (5) Å^3
Z = 4
d_{calc} = 1.81 g cm^{-3}
μ_{calc} = 77.1 cm^{-1}
size: 0.12 × 0.13 × 0.43 mm

(B) Data Measurement Parameters

radiation: Mo Kα (λ = 0.71073 Å)
monochromator: highly-oriented graphite (2θ = 12.2°)
detector: crystal scintillation counter, with PHA
reflns measd: $+h,+k,\pm l$
2θ range: 3–45°
scan type: θ–2θ
scan width: $\Delta\theta = 0.60 \pm 0.35 \tan\theta$
θ scan speed: 0.72–6.70 deg/min
background: measured over 0.25* ($\Delta\theta$) added to each end of the scan
vertical aperture = 3.0 mm
horizontal aperture = $2.0 \pm 1.0 \tan\theta$ mm
no. of reflns collcd: 2552
no. of unique reflns: 2266
intensity standards: (542), (248), (2,11,4); measured every 1 h of X-ray exposure time. Over the data collection period no decrease in intensity was observed.
orientation: Three reflections were checked after every 200 measurements. Crystal orientation was redetermined if any of the reflections were offset by more than 0.10° from their predicted positions. Reorientation was performed one time during data collection.

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 28 and 32°. [b] The esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) of the reported value.

Single-Crystal X-ray Diffraction Study of Complex 4b. Pale yellow/orange columnar and blocky crystals of compound **4b** were obtained by slow crystallization from acetone-d_6 in an NMR tube at -40 °C in the drybox freezer. Fragments cleaved from some of these crystals were mounted on glass fibers using polycyanoacrylate cement. Preliminary precession photographs indicated monoclinic Laue symmetry and yielded approximate cell dimensions.[27] The crystal used for data collection was then transferred to our Enraf-Nonius CAD-4 diffractometer and centered in the beam. Automatic peak search and indexing procedures yielded the same monoclinic reduced primitive cell. The final cell parameters and specific data collection parameters for this data set are given in Table II. The 2552 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. No correction for crystal decomposition was necessary. Inspection of the azimuthal scan data showed a

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(27) For a description of the apparatus and protocols, see: Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5831.

variation I_{min}/I_{max} = 0.92 for the average curve. An empirical absorption correction based on the observed variation was applied to the data. Inspection of the systematic absences indicated uniquely space group $P2_1/c$. Removal of systematically absent and redundant data left 2266 unique data in the final data set.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. In a difference Fourier map calculated following the refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks were found corresponding to the positions of most of the hydrogen atoms. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.25 times the B_{eqv} of the atoms to which they were attached. They were included in the structure factor calculations, but not refined. The final residuals for 191 variables refined against the 1972 data for which $F_o^2 > 3\sigma(F_o^2)$ were R = 1.64%, R_w = 2.23%, and GOF = 1.547. The R value for all 2266 data was 2.79%. In the final cycles of refinement a secondary extinction coefficient was included (maximum correction: 15% on F).

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p-factor, used to reduce the weight of intense reflections, was set to 0.02 in the last cycles of refinement. The analytical forms of the scattering factor tables for the neutral atoms were used and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion. Inspection of the residuals ordered in ranges of sin $(\theta)/\lambda$, $|F_o|$, and parity and the value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.74 e/Å^3, and the lowest excursion −0.44 e/Å^3. Both were located near the Ir atom. The positional and thermal parameters of all atoms and anisotropic thermal parameters (B's) are provided as supplementary material.

(η^5-C_9H_7)Ir(PMe_3)(p-$CH_3C_6H_4$)CH_3 (4c). The methyl(p-tolyl) complex **4c** was prepared by a procedure similar to the one described for the methyl(phenyl) compound **4b**, starting with 120 mg (0.20 mmol) of the iodo(p-tolyl) complex, (η^5-C_9H_7)Ir(PMe_3)(p-$CH_3C_6H_4$)I, and 2.25 equiv of CH_3MgBr (0.15 mL of a 3.0 M solution in Et_2O, 0.45 mmol). Chromatography on alumina III yielded 23 mg (0.047 mmol, 23%) of the methyl(p-tolyl) complex **4c** as a yellow solid. ^1H NMR (acetone-d_6): δ 7.36 (m, 1 H), 7.21 (m, 1 H), 7.08 (m, 2 H), 6.88 (d, J = 7.8 Hz, 2 H), 6.53 (d, J = 7.8 Hz, 2 H), 5.59 (br, 1 H), 5.50 (br, 1 H), 5.28 (br, 1 H), 2.12 (s, 3 H), 1.12 (d, J = 10.5 Hz, 9 H), 0.64 (d, J = 6.1 Hz, 3 H) ppm. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −38.1 ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 140.2 (d, J = 2.7 Hz), 129.9 (s), 127.9 (s), 124.5 (s), 124.3 (s), 122.3 (d, J = 5.1 Hz), 121.6 (d, J = 11.7 Hz), 111.7 (s), 111.5 (s), 99.1 (d, J = 1.7 Hz), 69.8 (d, J = 7.1 Hz), 68.4 (d, J = 9.2 Hz), 20.7 (s), 14.7 (d, J = 38.6 Hz), −30.8 (d, J = 8.9 Hz) ppm. IR (KBr pellet): 2919, 1479, 1321, 1281, 1050, 958, 941, 801, 743 cm^{-1}. MS (EI): m/e 490, 384 (M$^+$, base). Anal. Calcd for $C_{20}H_{26}PIr$: C, 49.06; H, 5.35. Found: C, 48.90; H, 5.30.

(η^5-C_9H_7)Ir(PMe_3)(C_6H_5)$_2$ (5a). In the drybox, 124 mg (0.20 mmol) of the iodo(phenyl) complex, (η^5-C_9H_7)Ir(PMe_3)(C_6H_5)I·$^1/_3C_7H_8$, was dissolved in 5 mL of toluene. To this stirred solution was added by syringe 2.25 equiv of PhMgBr (0.15 mL of a 3.0 M solution in Et_2O, 0.45 mmol). The reaction mixture was allowed to stir for 5 days. The excess PhMgBr was quenched by passing the reaction mixture through a small plug of alumina III supported on a fritted-glass filter. The reaction product was completely eluted from the alumina with three additional 10-mL portions of Et_2O. The solvent was removed under vacuum, and the resulting residue was dissolved in a minimum amount of toluene and loaded onto an alumina III column. Elution of a bright yellow band with a 1:1 (v:v) mixture of pentane/Et_2O and subsequent removal of solvent yielded 39 mg (0.073 mmol, 36%) of the diphenyl complex **5a** as a yellow solid. ^1H NMR (acetone-d_6): δ 7.40 (m, 2 H), 7.28 (m, 2 H), 7.00 (m, 4 H), 6.7 (m, 6 H), 5.76 (m, 2 H), 5.23 (m, 1 H), 1.20 (d, J = 10.5 Hz, 9 H) ppm. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −39.1 ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 142.65 (s), 127.0 (s), 126.6 (d, J = 11.8 Hz), 125.7 (s), 122.7 (s), 121.7 (s), 115.4 (s), 102.6 (s), 70.0 (d, J = 7.7 Hz), 15.1 (d, J = 39.8 Hz) ppm. IR (KBr pellet): 3050, 1568, 1472, 1320, 1285, 1056, 1020, 955, 941 (sh), 734 cm^{-1}. MS (EI): m/e 538 (M$^+$). Anal. Calcd for $C_{24}H_{26}PIr$: C, 53.62; H, 4.87. Found: C, 53.90; H, 4.90.

(η^5-C_9H_7)Ir(PMe_3)(p-$CH_3C_6H_4$)$_2$ (5b). The bis(p-tolyl) complex **5b** was prepared by a procedure similar to the one described for the diphenyl compound **5a**, starting with 120 mg (0.20 mmol) of the iodo(p-tolyl) complex and 2.0 equiv of p-tolMgBr (0.4 mL of a 1.0 M solution in Et_2O, 0.4 mmol). Column chromatography on alumina III yielded 34 mg (0.06 mmol, 30%) of the bis(p-tolyl) complex **5b** as a yellow solid. ^1H NMR (acetone-d_6): δ 7.38 (m, 2 H), 7.26 (m, 2 H), 6.87 (d, J = 7.7 Hz, 4 H), 6.53 (d, J = 7.7 Hz, 4 H), 5.71 (br, 2 H), 5.20 (br, 1 H), 2.15 (s, 6 H), 1.19 (d, J = 10.6 Hz 9 H) ppm. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −39.1 ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 142.4 (d, J = 2.4), 130.2 (s), 128.0 (s), 125.5 (s), 122.6 (s), 121.6 (d, J = 12.1), 115.2 (s), 102.5 (d, J = 2.3), 69.9 (d, J = 7.9), 20.7 (s), 15.1 (d, J = 39.8) ppm. IR (KBr pellet): 2919, 1479, 1321, 1281, 1050, 958, 941, 801, 743, cm^{-1}. MS (EI): m/e 566, 384 (M$^+$, base). Because of the tendency of complex **5b** to occlude variable amounts of solvent, satisfactory elemental analysis has not been obtained for this compound.

(η^5-C_9H_7)Ir(PMe_3)H_2 (7). In the drybox, 320 mg (0.50 mmol) of the diiodide complex (η^5-C_9H_7)Ir(PMe_3)I_2 (**2**) and 680 mg (10.0 mmol, 20 equiv) of NaOEt were weighed into a 50-mL round-bottom flask equipped with a stirbar and vacuum stopcock. The reaction flask was evacuated on a vacuum line, and approximately 10 mL of EtOH was transferred to the reaction mixture under vacuum. The reaction mixture, initially a slurry of the diiodide complex **2** in a 1 M NaOEt solution, was allowed to stir at ambient temperature for 16 h, at which time the mixture was a homogeneous, dark red solution. The volatile materials were removed under vacuum, and the residue was brought back into the drybox. The residue was extracted with four 5-mL portions of toluene, and the extracts were concentrated to about 5 mL. The concentrated toluene solution was loaded onto an alumina III column, and a fast running, yellow impurity was washed down with hexane. Elution of the second yellow band with a 1:1 hexane/Et_2O mixture afforded 49 mg (0.13 mmol, 25% yield) of the dihydride **7**. An orange tinge to the compound can be removed by slow sublimation at 50 °C, 10^{-2} Torr, to give **7** as a pale yellow solid. ^1H NMR (C_6D_{12}): δ 7.25 (m, 2 H), 6.76 (m, 2 H), 5.41 (m, 2 H), 5.38 (m, 1 H), 1.30 (d, J = 10.4 Hz, 9 H), −20.67 (d, J = 29.8 Hz, 2 H) ppm. $^{31}P\{^1H\}$ NMR (C_6D_{12}): δ −45.5 ppm. $^{13}C\{^1H\}$ NMR (C_6D_{12}): δ 122.8 (s), 122.6 (s), 108.8 (s), 87.1 (d, J = 2.7 Hz), 65.3 (d, J = 6.1 Hz), 24.1 (d, J = 38.9 Hz) ppm. IR (KBr pellet): ν_{Ir-H} 2184, 2130 cm^{-1}. UV-Vis (n-pentane): λ_{max} = 313 nm, $\epsilon = 1.4 \times 10^3$; λ_{max} = 345 nm, $\epsilon = 8.9 \times 10^2$. High-resolution MS (EI): m/e calcd for $C_{12}H_{18}PIr$, 386.0776 (M$^+$, ^{193}Ir); m/e found, 386.0770 (M$^+$, ^{193}Ir).

Photolysis of Dihydride 7. The photolysis apparatus consisted of a 450-W Canrad-Hanovia mercury immersion lamp with an Ace 7830-60 power supply and an Ace 7874B-38 immersion well. The immersion well was secured in a vacuum-jacketed Quartz dewar filled with a water/methanol mixture cooled to 5–10 °C by a Lauda K-4/RD refrigerated bath circulator. An external ^{31}P NMR standard was prepared by flame-sealing the narrow end of a 9-in. pipet, dissolving 5 mg (0.01 mmol) of the dichloride complex, Cp*Ir(PMe_3)Cl_2, in two drops of CH_2Cl_2, and placing the solution into the pipet. Solvent was added to give a solution level of about 5 cm. A compressed pipet bulb was placed over the open end of the pipet, and the capillary end was flame-sealed under slight vacuum. In an analytical photolysis experiment, 9 mg (0.02 mmol) of dihydride **7** was dissolved, in the drybox, in about 0.6 mL of either benzene or cyclohexane and loaded into an 8-in. 5-mm Wilmad 505-PS thin-walled NMR tube. The external standard was placed in the tube and held in the middle with a Teflon insert. The tube was fitted with a Cajon adaptor, degassed with two freeze–pump–thaw cycles on a vacuum line, and flame-sealed. The photochemical reaction was monitored periodically by $^{31}P\{^1H\}$ NMR spectroscopy. After photolysis had been ceased, the reaction mixture was brought back into the drybox, where the tube was cracked and the volatile materials removed under vacuum. The residue was dissolved in either C_6D_6 or acetone-d_6 and analyzed by ^1H NMR spectroscopy. The identities of the products were confirmed by comparison with spectral data of materials obtained by independent synthesis, as described below.

(η^5-C_9H_7)Ir(PMe_3)(CH_3)H (6a). In the drybox, 162 mg (0.31 mmol) of the iodomethyl complex **3a** and 63 mg (0.77 mmol, 2.5 equiv) of Na(O-i-Pr) were added to a 50-mL round-bottom flask equipped with a stirbar and vacuum stopcock. 2-Propanol (15 mL) was transferred into the flask under vacuum. Upon warming to ambient temperature, the solid began to dissolve. After the mixture became homogeneous, the solution was allowed to stir for 1 h at ambient temperature. The volatile materials were then removed under vacuum, and the flask was returned to the drybox. The tan residue was extracted with Et_2O until the residue was white, and the extracts were filtered through a small plug of alumina III supported on a 15-mL fritted-glass filter. The reaction product was washed from the alumina with additional portions of Et_2O. The volatile materials were removed under vacuum, leaving a dark orange oil. Sublimation at 50 °C, 10^{-2} Torr, afforded 80 mg (0.20 mmol, 65% yield) of **6a** as a golden yellow solid. The hydridomethyl complex **6a** can be stored for extensive periods at −40 °C in the drybox freezer. ^1H NMR (acetone-d_6): δ 7.46 (d, J = 8.1 Hz, 1 H), 7.23 (d, J = 8.3 Hz, 1 H), 7.04 (m, 1 H), 6.94 (m, 1 H), 5.64 (br, 1 H), 5.40 (br, 1 H), 5.30 (br, 1 H), 1.34 (d, J = 10.4 Hz, 9 H), 0.28 (d, J = 5.5 Hz, 3 H), −22.35 (d, J = 30.8 Hz, 1 H) ppm. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −40.95 ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 124.3 (s), 123.1 (s), 122.4 (s), 121.4 (s), 112.6 (s), 109.4 (s), 88.6 (d, J = 2.0 Hz), 69.0 (s), 65.1 (d, J = 15.3 Hz), 19.4 (d, J = 38.2 Hz), −47.7 (d, J = 7.1 Hz) ppm. IR (KBr pellet): ν_{Ir-H} 2204 cm^{-1}. MS (EI): m/e 400, 115 (M^+, base). Anal. Calcd for $C_{13}H_{20}PIr$: C, 39.09; H, 5.05. Found: C, 38.83; H, 4.99.

(η^5-C_9H_7)Ir(PMe_3)(C_6H_5)H (6b). In the drybox, 216 mg (0.35 mmol) of the iodophenyl complex, (η^5-C_9H_7)Ir(PMe_3)(C_6H_5)I·$^1/_3C_7H_8$, was dissolved in 20 mL of toluene. To this stirred solution was added by syringe 2.0 equiv of $LiEt_3BH$ (0.70 mL of a 1.0 M THF solution, 0.70 mmol). The reaction mixture was allowed to stir for 9 h, after which time the solution had turned from orange to light yellow. The excess $LiEt_3BH$ was quenched by passing the reaction mixture through a 15-mL plug of alumina III supported on a 30-mL fritted-glass filter. The reaction product was completely eluted from the alumina with three additional 10-mL portions of Et_2O. The volatile materials were removed under vacuum, leaving a bright yellow solid. The residue was dissolved in a minimum amount of toluene, and the resulting solution was layered with an equal volume of pentane to be cooled to −40 °C in the drybox freezer. Crystallization afforded 129 mg (0.28 mmol, 80% yield) of **6b** as a golden yellow solid. ^1H NMR (C_6D_6): δ 7.3–6.8 (complex aromatic, 9 H), 5.64 (m, 1 H), 5.36 (m, 1 H), 5.07 (m, 1 H), 0.86 (d, J = 10.5 Hz, 9 H), −22.22 (d, J = 30.7 Hz, 1 H) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −41.6 ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 144.6 (s), 128.3 (s), 127.1 (s), 125.1 (d, J = 12.1 Hz), 124.0 (s), 122.9 (s), 121.6 (s), 120.7 (s), 112.9 (s), 111.6 (s), 89.9 (d, J = 1.4 Hz), 67.0 (d, J = 14.1 Hz), 66.2 (s), 18.8 (d, J = 39.6 Hz) ppm. IR (KBr pellet): ν_{Ir-H} 2232 cm^{-1}. MS (EI): m/e 462, 78 (M^+, base). Anal. Calcd for $C_{18}H_{22}PIr$: C, 46.84; H, 4.80. Found: C, 47.09; H, 4.88.

(η^5-C_9H_7)Ir(PMe_3)(p-$CH_3C_6H_4$)H (6c). The tolyl hydride complex **6c** was prepared in fashion similar to the phenyl hydride compound **6b**, starting with 180 mg (0.30 mmol) of the iodotolyl complex, (η^5-C_9H_7)Ir(PMe_3)(p-$CH_3C_6H_4$)I. Crystallization afforded 105 mg (0.22 mmol, 74% yield) of **6c** as a golden yellow solid. ^1H NMR (acetone-d_6): δ 7.56 (d, J = 8.5 Hz, 1 H), 7.27 (m, 1 H), 7.10 (m, 2 H), 6.67 (d, J = 7.6 Hz, 2 H), 6.41 (d, J = 7.6 Hz, 2 H), 5.78 (m, 1 H), 5.49 (br, 1 H), 5.33 (m, 1 H), 2.08 (s, 3 H), 1.21 (d, J = 10.7 Hz, 9 H), −22.65 (d, J = 30.4 Hz, 1 H) ppm. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −40.0 ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 144.5 (s), 129.6 (s), 128.1 (s), 124.6 (s), 124.3 (s), 122.6 (s), 122.1 (s), 120.9 (d, J = 12.4 Hz), 113.7 (s), 111.8 (s), 89.8 (d, J = 1.5 Hz), 67.4 (s), 66.4 (d, J = 14.4 Hz), 20.8 (s), 19.1 (d, J = 40.4 Hz) ppm. IR (KBr pellet): ν_{Ir-H} 2216 cm^{-1}. MS (EI): m/e 476, 91 (M^+, base). Anal. Calcd for $C_{19}H_{24}PIr$: C, 47.99; H, 5.09. Found: C, 47.77; H, 5.46.

(η^5-C_9H_7)Ir(PMe_3)(c-C_6H_{11})H (6d). In the drybox, a glass bomb was charged with 63 mg (0.16 mmol) of the hydridomethyl complex **6a** and 30 mg (0.10 mmol) of P(o-tol)$_3$ dissolved in about 10 mL of cyclohexane. The solution was degassed using three freeze–pump–thaw cycles and sealed under vacuum with the vacuum stopcock. Concurrently, 4 mg (0.01 mmol) of **6a** and 2.0 mg (0.007 mmol) of P(o-tol)$_3$ were dissolved in 0.6 mL of cyclohexane and loaded into an 8-in. NMR tube fitted with a Cajon adaptor. This solution was similarly degassed, and the tube was flame-sealed under vacuum. Both the bomb and the tube were placed in an 85 °C oil bath, and $^{31}P\{^1H\}$ NMR spectra of the mixture in the tube were obtained periodically as a means of monitoring the reaction. After 61 h, $^{31}P\{^1H\}$ NMR analysis showed that the approximate ratio of **6d** to **6a** was 3 to 2, and the approximate yield of **6d** was 50%. The volatile materials in the bomb were then removed under vacuum, and the two reaction vessels were brought back into the drybox. The NMR tube was cracked, and its contents were combined with that of the bomb. The crude reaction mixture was loaded onto a preparative alumina TLC plate pretreated with a minimum amount of Et_2O. The plate was eluted with a 2:1 (v:v) mixture of pentane/Et_2O. The first yellow band was scraped from the plate, and the product **6d** was extracted from the alumina with Et_2O and filtered through a fritted-glass filter. Removal of the solvent under vacuum afforded 21 mg (0.045 mmol, 27% yield) of **6d** as a golden yellow solid. ^1H NMR (acetone-d_6): δ 7.38 (m, 2 H), 7.03 (m, 1 H), 6.84 (m, 1 H), 5.62 (m, 1 H), 5.45 (m, 1 H), 5.42 (m, 1 H), 2.0 (m, 1 H), 1.8–1.0 (m, 10 H), 1.36 (d, J = 10.2 Hz, 9 H), −22.36 (d, J = 31.8 Hz, 1 H) ppm. $^{31}P\{^1H\}$NMR (acetone-d_6): δ −41.7 ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 124.0 (s), 123.2 (s), 122.7 (s), 121.4 (s), 113.1 (s), 110.8 (s), 93.9 (d, J = 2.0 Hz), 68.1 (d, J = 8.4 Hz), 66.7 (d, J = 5.7 Hz), 48.4 (d, J = 3.0 Hz), 44.1 (d, J = 2.7 Hz), 32.5 (s), 32.3 (s), 28.2 (s), 19.6 (d, J = 37.5 Hz), 3.1 (d, J = 5.5 Hz) ppm. IR (KBr pellet): ν_{Ir-H} 2118, 2145 (sh) cm^{-1}. High-resolution MS (EI): m/e calcd for $C_{18}H_{28}PIr$, 468.1558 (M^+, ^{193}Ir); m/e found, 468.1534 (M^+, ^{193}Ir).

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Supplementary Material Available: Textual description of experimental details, tables of data for the X-ray diffraction study of (η^5-C_9H_7)Ir(PMe_3)(CH_3)(Ph) (**4b**) including intramolecular distances, intramolecular angles, positional parameters, anisotropic thermal parameters (B's), and root-mean-square amplitudes, and ORTEP stereo diagrams (13 pages); a listing of structure factors (14 pages). This information is provided with the archival edition of the journal, available in many libraries. Alternatively, ordering information is given on any current masthead page.

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