3772 *Organometallics* **1993**, *12*, 3772–3775

Observation of Intermediates in the Protonation of $(\eta^5\text{-}C_9H_7)Ir(\eta^4\text{-}C_8H_{12})$ with CF_3CO_2H

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Summary: Protonation of $(\eta^5\text{-}C_9H_7)Ir(\eta^4\text{-}C_8H_{12})$ *(1) in* $CDCl_3$ *at −50 °C with 1 equiv of trifluoroacetic acid resulted initially in the formation of free indene and a species assigned as the dinuclear iridium cyclooctadiene complex* $(Ir(\eta^4\text{-}C_8H_{12})(\mu\text{-}O_2CCF_3))_2$ *(2); the mixture slowly reacted to give* $[(\eta^6\text{-}C_9H_8)Ir(\eta^4\text{-}C_8H_{12})]^+$ *(3). The metal protonated form of 1,* $[(\eta^5\text{-}C_9H_7)Ir(\eta^4\text{-}C_8H_{12})H]^+$ *(**1H**⁺), was observed only at low temperature in the presence of excess acid. Proton abstraction from* **3**$\cdot[BF_4]$ *with "Proton Sponge" in dichloromethane gave 1.*

Introduction

The protonation of η^5-indenyl olefin complexes of rhodium and iridium frequently yields η^6-indene complexes (eq 1).[1-3] McGlinchey and co-workers[1] showed that the reaction of $(\eta^5\text{-}C_9H_7)Rh(\eta^2\text{-}C_2H_4)_2$ with trifluoroacetic acid

$$(\eta^5\text{-}C_9H_7)M(ol)_2 \underset{M\,=\,Rh,\,Ir}{\overset{H^+}{\rightarrow}} [(\eta^6\text{-}C_9H_8)M(ol)_2]^+ \quad (1)$$

at ambient temperature gave $[(\eta^6\text{-}C_9H_8)Rh(\eta^2\text{-}C_2H_4)_2][O_2CCF_3]$ and proposed that the reaction proceeds by the initial formation of $[(\eta^5\text{-}C_9H_7)Rh(\eta^2\text{-}C_2H_4)_2H]^+$, followed by proton transfer to the indenyl ligand. Although no rhodium hydride resonance was observed in solution, even at low temperature, their proposed mechanism was supported by deuterium labeling studies in the presence of deuterated acid.[1] This metal to ligand proton transfer mechanism has also been proposed by Salzer and Taschler[2] for the reaction of $(\eta^5\text{-}C_9H_7)Rh(\eta^4\text{-}C_8H_{12})$ with CF_3CO_2H and by Sowa and Angelici[3] for the reaction of $(\eta^5\text{-}C_9H_7)Ir(\eta^4\text{-}C_8H_{12})$ with CF_3SO_3H. In the latter case, a signal due to a short-lived hydride species was observed.[3] We report our results for the reaction of $(\eta^5\text{-}C_9H_7)Ir(\eta^4\text{-}C_8H_{12})$ (1) with trifluoroacetic acid, specifically the NMR spectroscopic observation and characterization of a new intermediate complex $(Ir(\eta^4\text{-}C_8H_{12})(\mu\text{-}O_2CCF_3))_2$ (2).

Results

The protonation of 1 with 1 equiv of CF_3CO_2H in $CDCl_3$ at −50 °C, observed by ^1H NMR, gave initially free indene, as indicated by the characteristic CH_2 resonance at δ 3.44 as well as other CH signals from δ 7.5 to 6.6, and a new iridium complex that exhibited pairs of multiplets for the vinyl and α-methylene protons of the cyclooctadiene ring. These results are shown in Figure 1a and listed in Table I. The resonances of the new complex were assigned with the aid of two-dimensional NMR methods (vide infra) to the dinuclear complex $(Ir(\eta^4\text{-}C_8H_{12})(\mu\text{-}O_2CCF_3))_2$ (2).

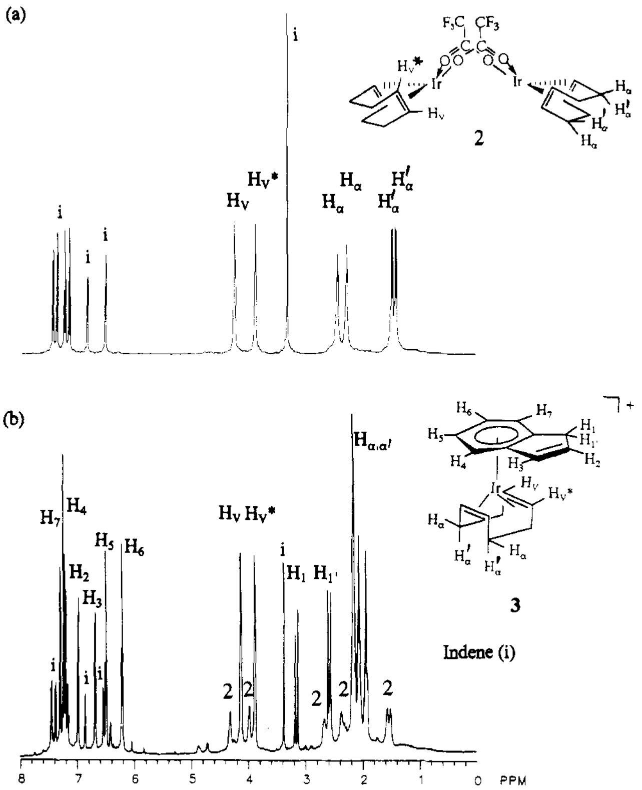

Figure 1. ^1H NMR spectrum after addition of 1 equiv of CF_3CO_2H to 1 in $CDCl_3$ at −50 °C: (a) immediately after mixing, showing 2 and free indene; (b) after 5 days at −20 °C, showing a mixture of indene and 3.

Monitoring the sample at −20 °C showed a slow conversion of 2 to $[(\eta^6\text{-}C_9H_8)Ir(\eta^4\text{-}C_8H_{12})][O_2CCF_3]$ (3). This assignment is based on comparison of its ^1H NMR spectrum to data for $[(\eta^6\text{-}C_9H_8)Ir(\eta^4\text{-}C_8H_{12})][BF_4]$, originally prepared by Sievert and Muetterties,[4] and for the species identified as $[(\eta^6\text{-}C_9H_8)Ir(\eta^4\text{-}C_8H_{12})][O_3SCF_3]$ by Sowa and Angelici.[3] In Figure 1b is shown the ^1H NMR spectrum of the solution after 5 days at −20 °C; intense resonances for 3, free indene, and a small amount of 2 are visible. Approximately 85% of 1 was converted into 3 by this time, as determined by the ratio of the methylene proton of indene (δ 3.44) to that of H_1 of 3. After 1 week, the conversion of 1 to 3 was complete.

Two-dimensional correlation spectroscopy was used to assign the ^1H and $^{13}C\{^1H\}$ NMR resonances of 2. An attached proton test (APT) spectrum distinguished the vinyl resonances C_V and C_V* from the methylene resonances C_α and C_α* of coordinated cyclooctadiene. These resonances were correlated to the proton resonances by tracing the cross-peaks in a ^1H–^{13}C heteronuclear correlation (HETCOR) spectrum, given as supplementary

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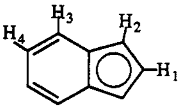
Table I. ^{1}H NMR Data[a] for Compounds **1**, **1H$^+$**, **2**, and **3**

	C_9H_7[b]				C_8H_{12}[c]			
cmpd	H_1	H_2	H_3	H_4	H_V	H_V*	H_α	H_α'
1	5.96 (t)	5.33 (d)	7.27 (m)	7.11 (m)	3.83 (s)		1.69 (m)	1.51 (m)
1H$^+$ [d]	6.04 (t)	5.81 (d)	7.79 (m)	7.62 (m)	4.84 (br)	4.56 (br)	2.39 (m), 2.30 (m)	1.77 (m), 1.23 (m)
2					4.26 (m)	3.90 (m)	2.47 (m), 2.31 (m)	1.55 (m), 1.45 (m)
3[e]					4.22 (m)	4.03 (m)	2.24 (m)	2.12 (m), 2.04 (m)

[a] Recorded at 500 MHz in $CDCl_3$ at −50 °C (**1**, **1H$^+$**, **2**) and at −20 °C (**3**). [b] The numbering scheme for the indenyl ligand in complexes **1** and **1H$^+$** is shown below. [c] The signals for the 1,5-C_8H_{12} ligand are assigned broadly as vinyl (H_V) or methylene (H_α) protons. The further specific assignment of the downfield methylene multiplets (H_α) to the exo methylene protons and of the upfield multiplets (H_α') to the endo methylene protons is well established by studies of closely related compounds reported in refs 3 and 8a. A specific stereochemical assignment of the separate vinylic signals (H_V, H_V*) can be made only in the case of **2** (see diagram in Figure 1a), based on assignments given in ref 8a. [d] The hydride signal for **1H$^+$** occurs at δ −14.71. [e] Signals for the C_9H_8 ring in **3** are as follows (see numbering scheme in Figure 1b): δ 7.35 (d, H_4), 7.22 (d, H_7), 7.07 (m, H_2), 6.75 (d, H_3), 6.56 (t, H_6), 6.34 (t, H_5), 3.24 (d, H_1), 2.72 (d, $H_{1'}$, $J(H_1–H_{1'})$ = 22 Hz).



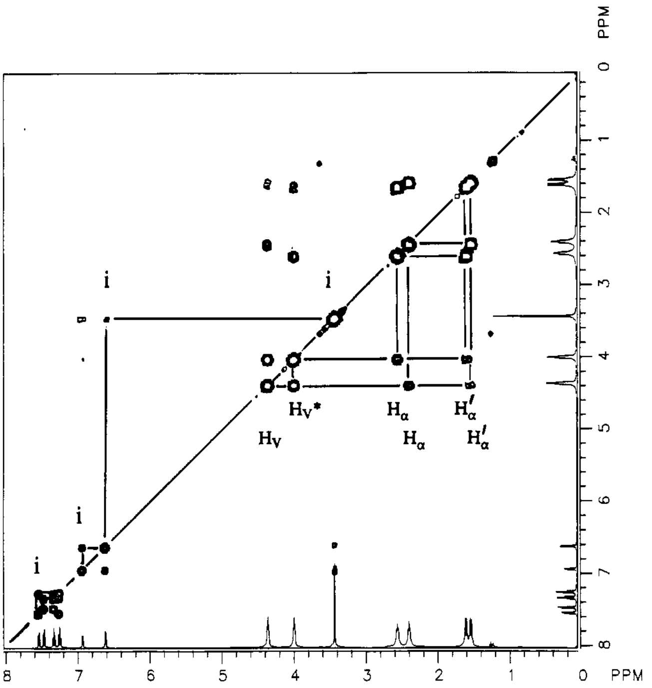


Figure 2. ^{1}H–^{1}H COSY spectrum of **2** and free indene in $CDCl_3$ at −50 °C. Resonances of indene are labeled with (i).

material. The HETCOR spectrum showed that the two ^{1}H signals at δ 4.26 and 3.90 correspond to different sets of vinyl protons of the coordinated cyclooctadiene ring. Other sets of proton resonances correspond to separate sets of exo and endo methylene protons (H_α and H_α') of the cyclooctadiene ring. The correlation of these resonances to the vinyl protons was determined from the connectivities of the cross peaks in the ^{1}H–^{1}H correlation (COSY) spectrum of **2**, as shown in Figure 2. The only structure corresponding to such a unique set of resonances would have two $Ir(\eta^4\text{-}C_8H_{12})^+$ centers bridged by two trifluoroacetate groups, i.e. $(Ir(\eta^4\text{-}C_8H_{12})(\mu\text{-}O_2CCF_3))_2$ (**2**). Many structurally analogous dinuclear cyclooctadiene complexes of rhodium with bridging carboxylate ligands[5] have been isolated, and related rhodium and iridium complexes with bridging pyridyl,[6] pyrazolyl,[7] and hydroxypyridinate[8] ligands are known.

In a variable temperature ^{1}H NMR experiment the distinct "up/down" vinyl signals and the corresponding α-methylene signals of **2** were observed to coalesce above 40 °C. The variable temperature spectra are given as supplementary material. The value of ΔG_c^* was determined to be 15 kcal/mol by using the equations $k_c = (k_bT_c/h)\exp[-\Delta G_c^*/RT_c]$ and $k_c = \pi\Delta v_0/2$, with T_c = 328 K and Δv_0 = 180 Hz for the vinyl resonances.

When excess acid was added to **1** at −50 °C, a new set of resonances was observed, which are listed in Table I. A strong metal hydride signal at δ −14.71 suggested this product to be $[(\eta^5\text{-}C_9H_7)Ir(\eta^4\text{-}C_8H_{12})H]^+$ (**1H$^+$**), and this formulation was confirmed by analysis of the ^{1}H–^{1}H COSY spectrum. Furthermore, the data obtained for the 1,5-C_8H_{12} ligand correspond well with the results obtained in the detailed study by Sowa and Angelici of $[(\eta^5\text{-}C_5H_5)Ir(\eta^4\text{-}C_8H_{12})H][CF_3SO_3]$ and related compounds.[3] The T_1 relaxation time for the hydride resonance (δ −14.71) of **1H$^+$** at −50 °C was determined to be 360 ms.

As stated above, 1 equiv of acid gave initial resonances for **2** and free indene, but as excess acid was added, the resonances for **^{1}H$^+$** increased in intensity at the expense of free indene, until at 6 equiv of trifluoroacetic acid there was approximately a 50:50 mixture of **1H$^+$** and indene present. The incremental quenching of this solution of **1H$^+$** with 2, 4, and then 6 equiv of D_2O resulted in loss of the resonance at δ −14.7, incorporation of deuterium in free indene (as shown by the decrease in the relative intensity of the indene methylene resonance at δ 3.44 from two protons to one), and the growth of resonances for **2**.

In a separate experiment, 6 equiv of CF_3CO_2H were added to **1** in $CDCl_3$ at −50 °C, and the resulting solution of **1H$^+$** was stored at −20 °C. After 1 week, a ^{1}H NMR spectrum of this solution at 20 °C did not show any signals of **1H$^+$**. Resonances due to **3**, free indene, and residual **2**, along with a set of broad multiplets of equal intensity at δ 1.25 and 0.86 were recorded. The yield of **3** was approximately 30%, as determined by the ratio of the methylene proton signal of indene (δ 3.44) to that of H_1 of **3**.

As shown in eq 2, when $[(\eta^6\text{-}C_9H_8)Ir(\eta^4\text{-}C_8H_{12})][BF_4]$ was treated with Proton Sponge in dichloromethane at 35

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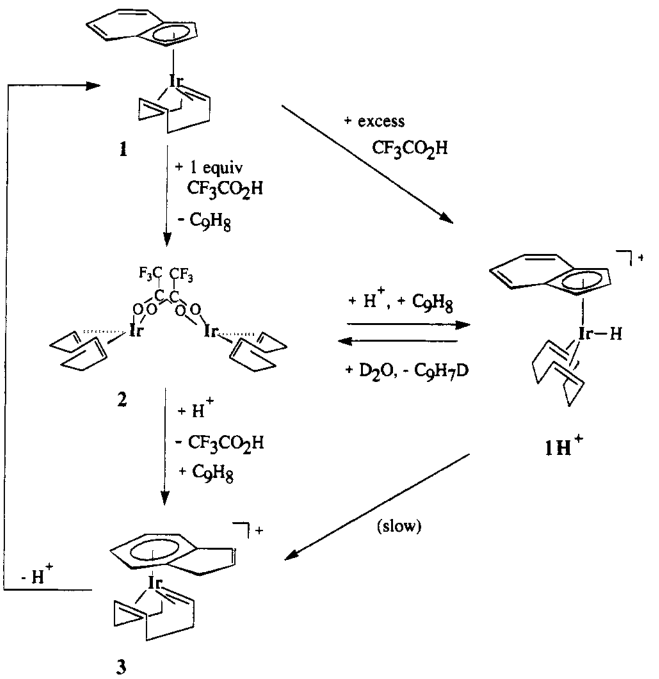
Scheme I



°C for 3 h, sublimation from the reaction residue gave 1 in 50% yield.

$$\underset{3[BF_4]}{[(\eta^5\text{-}C_9H_8)Ir(\eta^4\text{-}C_8H_{12})][BF_4]} \xrightarrow[CH_2Cl_2, 35 °C]{C_{10}H_6[N(CH_3)_2]_2} \underset{1}{(\eta^5\text{-}C_9H_7)Ir(\eta^4\text{-}C_8H_{12})} \quad (2)$$

Discussion

Our observations connected with the protonation of 1 by CF_3CO_2H are summarized in Scheme I. The unexpected result is the formation of trifluoroacetate-bridged dinuclear complex 2, which has been characterized by using combined ^1H and ^{13}C 2D-NMR data. Mann and co-workers[8] reported similar data for a set of rhodium and iridium hydroxypyridinate complexes, for example $[Ir(\eta^4\text{-}C_8H_{12})(\mu\text{-mhp})]_2$, where mhp is 6-methyl-2-hydroxypyridinate. The Rh and Ir complexes adopt an "open-book" geometry both in the solid state and in solution. A fluxional process was observed for 2 that interconverts the inequivalent (up/down) vinylic cyclooctadiene protons. This equilibration could be due to rotation of the cyclooctadiene ligand about the diene coordination axis or to inversion of the folded structure at the position of the bridging ligands. However, for 2 an inversion process involving the trifluoroacetate bridges seems more likely, since no fluxional processes were recorded for the related complexes $[M(\eta^4\text{-}C_8H_{12})(\mu\text{-pyz}]_2$, where M = Rh or Ir and pyz = pyrazolyl.[8c]

Our results indicate that in the presence of only 1 equiv of acid, 1 gives 3 over a period of days by a stepwise, intermolecular process. The mechanism involves the initial generation of free indene and the formation of complex 2. The formation of indene may be due either to direct attack of acid at the indenyl ligand or to transfer of a proton from the metal in a transient $1H^+$ complex. However, no observable amount of $1H^+$ was formed under these conditions. The intermolecular addition of free indene to 2 to give 3 parallels the work of Sievert and Muetterties,[4] who showed that solvated cationic iridium complexes such as $[Ir(\eta^4\text{-}C_8H_{12})(acetone)_x][BF_4]$ easily gave η^6-arene complexes, e.g., $[(\eta^6\text{-}C_9H_8)Ir(\eta^4\text{-}C_8H_{12})][BF_4]$. It seems likely that the conversion of 2 to 3 is acid catalyzed, with the leaving group being neutral trifluoroacetic acid rather than anionic trifluoroacetate.

McGlinchey and co-workers[1a] have also reported observing free indene in solution when excess CF_3CO_2H was added to $(\eta^5\text{-}C_9H_7)Rh(\eta^2\text{-}C_2H_4)_2$ at low temperature. It is thus possible that an intermediate such as $(Rh(\eta^2\text{-}C_2H_4)_2(\mu\text{-}O_2CCF_3))_2$ may be involved in the overall transformation they described.

In the presence of excess acid (6 equiv), only $1H^+$ was observed, but it was stable only at low temperature. The relatively long T_1 for the high-field signal (δ −14.71) of $1H^+$ indicated that it is not due to an agostic C···H···Ir species.[10] Sowa and Angelici[3] reported the transient appearance of a similar signal at δ −13.3 upon addition of CF_3SO_3H (ca. 2 equiv) to 1 in $CDCl_3$ at room temperature.

The incremental addition of D_2O to the solution of $1H^+$ showed that 2 was generated. This suggests that $1H^+$ could be an intermediate in the formation of 2 under weaker acid conditions, where trifluoroacetate can act as a nucleophile and become coordinated to the iridium center. It is not clear whether the slow conversion of $1H^+$ to 3 proceeds via 2. However, the formation of 3 is definitely slower and less selective under conditions of excess acid, where $1H^+$ is initially observed, than it is with 1 equiv of acid, where 2 is the dominant initial species.

After 1 week with $1H^+$ at −20 °C in excess acid, broad multiplets of equal intensity at δ 0.86 and 1.25, further multiplets from δ 1.9 to 2.8, and smaller multiplets from δ 4.7 to 5.5 were observed. A set of resonances at δ 6.23 and 6.42, overlapping with the resonances of H_6 and H_5 of 3, were also recorded. Taken together, these resonances suggest the formation of an iridium(III) η^3-cyclooctadienyl complex, i.e., $((\eta^5\text{-}C_9H_7)Ir(\eta^3\text{-}C_8H_{13}))(O_2CCF_3)$. The trifluoroacetate moiety might well be coordinated in order to achieve an 18-electron configuration. Hawthorne and co-workers[11] showed that the reaction of [PPN][*closo*-$(\eta^4\text{-}C_8H_{12})Rh(C_2B_9H_9(CH_3)_2)$] with CF_3CO_2H in CD_2Cl_2 formed a rhodium(III) metallacarborane with a η^3-cyclooctadienyl ligand. In this case, however, the isolated complex had a 16-electron configuration at rhodium. The ^1H NMR spectrum of the metallacarborane complex exhibited equally intense broad multiplets at δ 1.08 and 1.43 for four methylene protons of the $\eta^3\text{-}C_8H_{13}$, along with other multiplets for additional methylene protons at δ 1.80 and 2.54 and for the allylic protons at δ 4.68 (triplet) and 5.85 (doublet). Similar data have been reported by Werner and co-workers[12] for the η^3 portion of the cyclooctadienyl ligand in $HIr(\eta^1,\eta^3\text{-}C_8H_{12})(Ph_2PCH_2PPh_2)$.

Treatment of $[(\eta^6\text{-}C_9H_8)Ir(\eta^4\text{-}C_8H_{12})]BF_4$ with Proton Sponge in dichloromethane gave 1 in 50% isolated yield. This reaction is presumably initiated by abstraction of an exo proton from the methylene group of the η^6-coordinated indene, generating a zwitterionic intermediate, which then undergoes η^6 to η^5 migration of the metal center to produce 1. Several examples of such rearrangements upon deprotonation of indene complexes have been reported, and a

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molecular orbital analysis of this and related "haptotropic" rearrangements has been presented.[13]

In summary, although an intramolecular conversion of **1H$^+$** to **3**, involving metal-to-ligand proton transfer and metal migration from the five-membered ring to the six-membered ring, cannot be eliminated unambiguously, it is more likely that the formation of **3** upon protonation of **1**, at least with trifluoroacetic acid, proceeds intermolecularly via **2**. On the other hand, the reverse transformation effected upon deprotonation of **3** appears to proceed via an intramolecular pathway.

Experimental Section

General Information. All manipulations were conducted under an atmosphere of nitrogen using standard Schlenk techniques. $(Ir(\eta^4\text{-}C_8H_{12})Cl)_2$[14] and $[(\eta^6\text{-}C_9H_8)Ir(\eta^4\text{-}C_8H_{12})][BF_4]$[4] were prepared by literature methods. $IrCl_3{\cdot}xH_2O$ was purchased from Johnson Matthey Co. Cyclooctadiene, indene, potassium hydride in mineral oil (35% w/w), trifluoroacetic acid, and Proton Sponge (1,8-bis(dimethylamino)naphthalene) were purchased from Aldrich Chemical Co. and used as received. All solvents were dried and distilled before use. Deuterated chloroform was distilled from phosphorus pentoxide and then passed through a short column of activated basic alumina immediately before use. ^1H (500-MHz), ^{13}C (125-MHz), and correlation NMR spectra were recorded on a General Electric GN-500 FT NMR spectrometer. Microanalyses were performed by the staff of the Microanalytical Laboratory of the School of Chemical Sciences.

$(\eta^5\text{-}C_9H_7)Ir(\eta^4\text{-}C_8H_{12})$ (1). To $(Ir(\eta^4\text{-}C_8H_{12})Cl)_2$ (200 mg, 0.30 mmol) in diethyl ether (200 mL) at 0 °C was added potassium indenide in THF (3.7 mL, 0.61 mmol, 0.17 mmol/mL), prepared separately by the addition of 1 equiv of KH to a solution of indene (1.0 g, 0.86 mmol) in THF (50 mL). The solution immediately turned purple and was stirred for an additional 4 h. Decolorizing carbon was added, and the solution was filtered via a filter cannula. The dark green filtrate was reduced in volume to ca. 5 mL and eluted down a column (20 × 2 cm) of activated neutral alumina with diethyl ether (100 mL). The yellow band was collected, and the solution was reduced in volume to ca. 2 mL under reduced pressure. This dark yellow solution was held at −20 °C overnight, and the pale yellow crystals that formed were isolated by filtration, washed with diethyl ether (ca. 2 mL), and dried in vacuo. Yield: 195 mg, 0.47 mmol, 85%. Anal. Calcd for $IrC_{17}H_{19}$: C, 49.02; H, 4.60. Found: C, 49.10; H, 4.64. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 123.5 (C_3), 120.5 (C_4), 109.7 (C_{2a}), 83.9 (C_1), 71.4 (C_2), 50.1 (C_V, C_8H_{12}), 32.8 (C_α, C_8H_{12}). Complex **1** was prepared previously by using lithium indenide and isolated in 86% yield.[15]

Protonation of 1 with 1 equiv of CF_3CO_2H. An NMR tube was charged with **1** (30 mg, 0.072 mmol) and $CDCl_3$ (0.5 mL). The tube was cooled to −50 °C in an NMR probe and then quickly withdrawn, and CF_3CO_2H (5.7 μL, 8.4 mg, 0.074 mmol) was added. The contents of the tube were inverted, causing the initially pale yellow solution to turn deep red. Both ^1H and $^{13}C\{^1H\}$ NMR spectra of the solution were recorded at −50 °C. The proton spectrum consisted of the resonances for free indene and **2**. The carbon spectrum consisted of resonances for free indene at δ 144.5 (C_{3a}), 143.5 (C_{1a}), 134.5 (C_3), 131.7 (C_2), 126.0 (C_5), 124.3 (C_6), 123.6 (C_4), 120.8 (C_7), and 38.9 (C_1) and for **2** at δ 66.1 (C_V, C_8H_{12}), 57.5 ($C_V{*}$, C_8H_{12}), 31.6 (C_α, C_8H_{12}), and 30.8 (C_α, C_8H_{12}). After the sample had been stored for 1 week at −20 °C, the ^1H NMR spectrum showed complete conversion to **3**.

Protonation of 1 with Excess CF_3CO_2H. The reaction was conducted as above with **1** (30 mg, 0.072 mmol), $CDCl_3$ (0.5 mL), and the stepwise addition of CF_3CO_2H (total 34 μL, 50.4 mg, 0.44 mmol). A ^1H NMR spectrum of the solution, recorded at −50 °C and after all of the acid was added, showed resonances for free indene and **1H$^+$** (ca. 1:2). After the stepwise addition of D_2O (total 8 μL, 9 mg, 0.45 mmol), a ^1H NMR spectrum showed resonances for **2** and free indene (the indene resonances at δ 6.83 and 3.44 integrated as 1:1). No resonances were observed for **1H$^+$**.

Reaction of $[(\eta^6\text{-}C_9H_8)Ir(\eta^4\text{-}C_8H_{12})]BF_4$ with Proton Sponge. To $[(\eta^6\text{-}C_9H_8)Ir(\eta^4\text{-}C_8H_{12})]BF_4$ (30 mg, 0.60 mmol) in dichloromethane (10 mL) was added freshly sublimed 1,8-bis(dimethylamino)naphthalene (12.0 mg, 0.60 mmol), and the mixture was heated at 35 °C for 3 h with stirring. The solvent was removed from the reaction mixture under reduced pressure, and the residue was sublimed at 110 °C (10^{-1} Torr). The pale yellow microcrystalline sublimate was identified as **1** on the basis of its ^1H NMR spectrum. Yield: 12 mg, 0.03 mmol, 50%.

Acknowledgment. This research was supported by the National Science Foundation Grant CHE 89-15349.

Supplementary Material Available: Figures of ^1H–^{13}C HETCOR and APT spectra of **2** at −50 °C, variable temperature ^1H NMR spectra of **2**, ^1H NMR spectra of **1H$^+$** at −50 °C (a) immediately after formation and (b) after 1 week, showing conversion to **3**, and ^1H NMR spectra of **1H$^+$** at −50 °C after addition of (a) 2 equiv of D_2O and (b) 6 equiv of D_2O (4 pages). Ordering information is given on any current masthead page.

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