

Solvent-Induced Reductive Elimination of Pentamethylcyclopentadiene from a (Pentamethylcyclopentadienyl)metal Hydride

Astrid Pedersen and Mats Tilset*

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

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In acetonitrile solution, Cp*Ir(PPh₃)(H)₂⁺BF₄⁻ smoothly undergoes elimination of pentamethylcyclopentadiene (Cp*H) to yield Ir(H)₂(PPh₃)(NCMe)₃⁺BF₄⁻ as the only Ir-containing product ($\Delta H^\ddagger = 69.0 \pm 2.1$ kJ/mol, $\Delta S^\ddagger = -82.0 \pm 7.6$ J/(K·mol), $k(20^\circ\text{C}) = 1.6 \times 10^{-4}$ s⁻¹). The elimination of Cp*H did not take place in neat dichloromethane. The rate law exhibited a mixed first- and second-order dependence on the acetonitrile concentration, in accord with a mechanism involving successive acetonitrile-mediated η^5 to η^3 to η^1 ring slippage reactions, the first of which is reversible.

Introduction

The Cp ligand¹ has been an integral part of the development of organotransition-metal chemistry since the discovery of ferrocene about 40 years ago.² Substituted Cp's have been introduced due to the opportunity that the substituents offer for fine-tuning the steric and electronic influence of the ligand.³ The Cp* ligand¹ has become increasingly popular as a sterically demanding and electron-rich substitute.⁴

The Cp-derived ligands are commonly viewed as relatively innocent spectator groups that do not usually directly participate in chemical reactions. A major reason for this is that the Cp ligand is quite strongly bonded to metals. For example, Mo-Cp bond energies have been estimated to be ca. 390 and 380 kJ/mol for CpMo(CO)₃H and Cp*Mo(CO)₃H, respectively,^{5a,b} and bond energies for a number of metallocenes are of comparable strengths.^{5c} Obviously, under normal thermal conditions the η^5 -Cp ligands cannot be brought to dissociate from a metal complex in a *single* reaction step. However, a reaction in which the ligand hapticity is reduced stepwise in an $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ ("ring slippage") fashion, with intervening ligand association steps to maintain the electron count at the metal center, provides a pathway by which a Cp ligand can dissociate without the need for excessive energy supply.⁶ The viability of the slippage processes has been supported by the isolation and characterization of η^3 - and η^1 -bonded Cp

and related ligands.⁶ CpRe(CO)(NO)H in the presence of PMe₃ reversibly yields (η^1 -Cp)Re(CO)(NO)(PMe₃)₂H, which in the presence of excess PMe₃ at elevated temperatures undergoes CpH loss.^{6c} It has been established that the $\eta^5 \rightarrow \eta^3$ ring slippage and its reverse are important in facilitating associative ligand substitution reactions⁷ and other processes⁸ at coordinatively saturated metal centers. The ability of the indenyl ligand to facilitate slippage processes is well-known.^{7,8a,b}

The elimination of the Cp ligand as cyclopentadiene (CpH) from (cyclopentadienyl)metal hydrides has been previously reported. In addition to the reaction of CpRe(CO)(NO)H discussed above, it has been observed that LMo(CO)₃H (L = Cp, Cp*) produces *fac*-Mo(CO)₃-(solvent)₃ along with CpH or Cp*H in some donor solvents by mechanisms which have not been investigated;^{9a,b} propionitrile solutions of IndW(CO)₃H¹ behave similarly.^{9b} The reaction of Cp*Rh(PMe₃)(H)₂ with excess PMe₃ generated Cp*H and Rh(PMe₃)₄H.^{9c} For this reaction, saturation kinetics indicated initial $\eta^5 \rightarrow \eta^3$ ring slippage followed by capture of the unsaturated intermediate by PMe₃.

We recently reported that, in acetonitrile solution, the dihydrogen complexes CpRu(CO)(PR₃)(H)₂⁺ (R = Ph, Me) undergo loss of CpH with concomitant formation of RuH(CO)(PR₃)(NCMe)₃⁺ at -40 °C.¹⁰ These reactions were catalyzed by the presence of bases, including the neutral hydrides CpRu(CO)(PR₃)H. It was envisioned that a base-catalyzed isomerization of the dihydrogen complex to the cationic *trans*-dihydride isomer, which could reductively eliminate CpH, might be responsible for this reaction. An alternative mechanism could be that the neutral hydride (generated in small quantities from the cationic dihydrogen complex in the presence of trace quantities of a base) underwent nucleophilic attack at the dihydrogen complex, thereby initiating the CpH elimination.

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Herein we describe the details of an investigation of the elimination of Cp*H from Cp*Ir(PPh₃)(H)₃⁺ in acetonitrile. The reaction, which also yields Ir(H)₂(PPh₃)(NCMe)₃⁺, is *not* base catalyzed and appears to involve active participation by the donor solvent.

Results and Discussion

Preparation and Characterization of Cp*Ir(PPh₃)(H)₃⁺BF₄⁻. Treatment of Cp*Ir(PPh₃)(H)₂ (1)¹¹ with HBF₄·Et₂O in ether yielded Cp*Ir(PPh₃)(H)₃⁺BF₄⁻ (2(BF₄⁻)) as a white powder. The addition of triethylamine to a freshly prepared acetonitrile-*d*₃ solution of 2(BF₄⁻) cleanly regenerated 1. The most interesting feature of the ambient-temperature ¹H NMR spectrum (300 MHz) of 2 in dichloromethane-*d*₂ was a broad signal at δ -12.8. When the sample was gradually cooled, this signal underwent further broadening and merged with the baseline and, at even lower temperatures, reappeared as a complex, incompletely resolved pattern in the region δ -11.8 to -13.4. At -91 °C, the signals were still rather broad, and a limiting low-temperature spectrum was not obtained. The fluxionality implied by these observations is reminiscent of the fluxional behavior of a series of complexes CpIr(PR₃)(H)₃⁺ 12a-c and of Cp*Ir(PMe₃)(H)₃⁺.^{12d} Abnormally large coupling constants were observed between the hydrides in the former, and this led initially to the proposal that the three hydrogens were bonded as a "trihydrogen" ligand.^{12a} The phenomenon was later shown to result from quantum mechanical exchange coupling between the three hydride ligands in a classical trihydride complex.^{12b,c,e} The classical structure was shown to prevail in the solid state by a neutron diffraction study of CpIr(PMe₃)(H)₃⁺BF₄⁻.^{12b} We suspect that 2 assumes a corresponding classical structure in solution.

Elimination of Cp*H from Cp*Ir(PPh₃)(H)₃⁺. When acetonitrile-*d*₃ solutions of 2(BF₄⁻) were left for extended time periods at ambient temperature, it was noted that a reaction took place which generated a novel hydride doublet at δ -21.89 (*J* = 22 Hz), along with several signals in the region δ 0.8–1.9. No intermediates were detected during the course of this reaction. When the sealed NMR tube was opened, a distinct smell of Cp*H was noticed. By comparison of the spectroscopic data with those of an authentic sample of Cp*H, it was established that the signals at δ 0.8–1.9 were indeed due to Cp*H. The formation of Cp*H was also verified by comparison of the ¹³C{¹H} NMR spectra. When the reaction was repeated with hexamethylbenzene as an internal standard for quantification purposes, it was found (¹H NMR) that the yield of Cp*H was quantitative within the experimental accuracy. The intensity of the new hydride signal corresponded to the presence of two hydrides per Cp*H. The product was isolated after a reaction that was performed in acetonitrile and was identified as Ir(H)₂(PPh₃)(NCMe)₃⁺ (3). It was isolated analytically pure as the tetrafluoroborate salt 3(BF₄⁻) in 50% yield. Spectroscopic

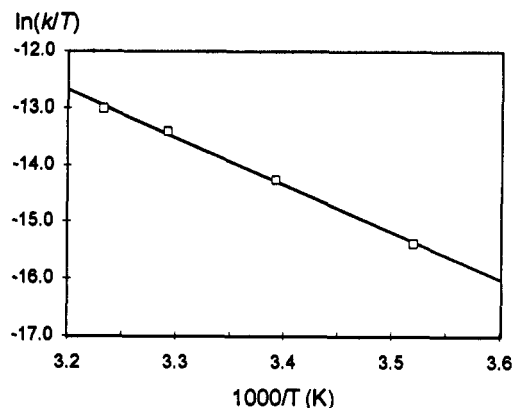
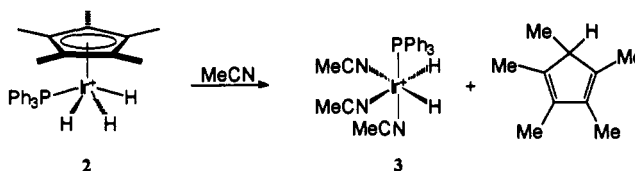


Figure 1. Eyring plot of the kinetic data for the elimination of Cp*H from 2 in acetonitrile-*d*₃.

Scheme I



and elemental analysis data for 3 are given in the Experimental Section. Only one type of hydride ligand and two kinds of coordinated acetonitrile ligands were seen in the ¹H NMR spectrum of 3. Assuming pseudo-octahedral coordination geometry, this is consistent with either a *cis*,*fac* or a *trans*,*mer* arrangement of the ligands. We assume that the *cis*,*fac* isomer depicted in Scheme I is preferred. The *cis* disposition of the hydrides is analogous to that found in structurally characterized IrH₂L₂L'₂⁺ complexes (L, L' = 2-electron-donor ligands).¹³

The strongly coordinating solvents acetone and DMSO were also checked for activity in this type of reaction, but with limited success. Solutions of 2(BF₄⁻) in acetone-*d*₆ underwent a slow reaction to produce a transient species that showed a hydride doublet at δ -10.62 (*J* = 30 Hz) in the ¹H NMR spectrum. Signals in the "Cp*" region of the spectrum were not sufficiently resolved to establish whether this species could be an η⁴-Cp*H complex. Even at prolonged reaction times, no evidence for the formation of free Cp*H was seen. A solution of 2(BF₄⁻) in DMSO-*d*₆ gave rise to a broad signal at δ -17.5 in the ¹H NMR spectrum, signaling extensive deprotonation of the cationic trihydride by the basic solvent. The solution gradually turned blue during the course of a few hours. Attempts at isolating the Ir-containing products from the reactions in acetone and DMSO have not been made.

Kinetics of the Elimination of Cp*H from 2. The progress of the elimination of Cp*H from 2(BF₄⁻) in acetonitrile-*d*₃ was monitored by ¹H NMR spectroscopy as described in the Experimental Section. The quantitative reaction exhibited clean first-order kinetics over 3–4 half-lives in the temperature range 10.9–36.1 °C. Repeated runs at one given temperature were reproducible to ±10%. Figure 1 shows an Eyring plot of ln(*k*/*T*) vs 1/*T*. The kinetic data, summarized in Table I, yielded Δ*H*[‡] = 69.0 ± 2.1 kJ/mol, Δ*S*[‡] = -82.0 ± 7.6 J/(K·mol), and *k*(20

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Table I. Kinetic Data for the Elimination of Cp*H from 2 in Acetonitrile-*d*₃^a

<i>T</i> (°C)	10 ⁵ <i>k</i> (s ⁻¹) ^b	<i>T</i> (°C)	10 ⁵ <i>k</i> (s ⁻¹) ^b
10.9	5.94 (0.15)	30.6	45.7 (1.3)
21.6	19.0 (0.63)	36.1	68.5 (2.8)

^a By ¹H NMR spectroscopy. ^b One standard error from the regression analyses in parentheses.

Table II. Kinetics of the Elimination of Cp*H from 2 in Acetonitrile-*d*₃/Dichloromethane-*d*₂ Mixtures^a

[acetonitrile- <i>d</i> ₃] (% v/v)	[acetonitrile- <i>d</i> ₃] (M)	10 ⁵ <i>k</i> _{obs} (s ⁻¹) ^b
10.0	1.9	0.80 (0.04)
20.0	3.8	1.25 (0.05)
50.0	9.6	7.47 (0.2)
70.0	13.4	11.6 (0.4)
83.3	15.9	13.2 (0.2)
91.7	17.6	16.3 (0.4)
100.0	19.1	19.0 (0.6)

^a Monitored by ¹H NMR spectroscopy. ^b One standard error from the regression analyses in parentheses.

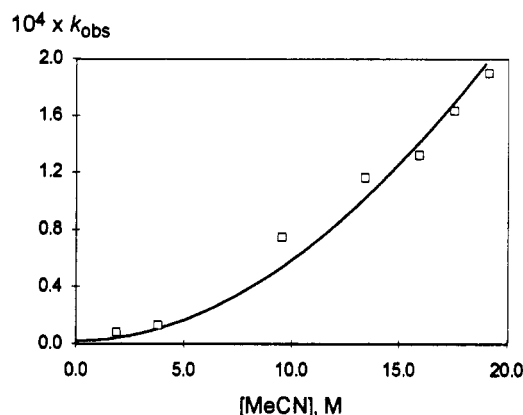


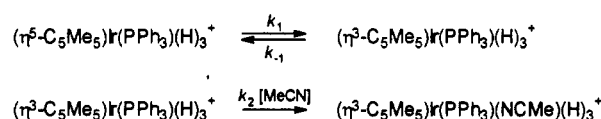
Figure 2. Observed rate constant vs the acetonitrile-*d*₃ concentration for the elimination of Cp*H from 2 in acetonitrile-*d*₃/dichloromethane-*d*₂ mixtures.

°C) = 1.6 × 10⁻⁴ s⁻¹ by interpolation. The negative entropy of activation is clearly indicative of an associative mechanism.

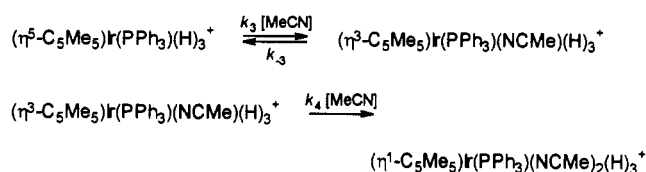
In a separate experiment, 0.2 equiv of the neutral hydride 1 was added to a solution of 2(BF₄⁻) in acetonitrile-*d*₃ and the progress of the ensuing reaction was monitored. The pseudo-first-order rate constant at 21.6 °C was (2.0 ± 0.02) × 10⁻⁴ s⁻¹, and we conclude that the reaction rate was not significantly affected by the presence of 1. This result contrasts with our previous report on the CpH elimination from the dihydrogen complexes CpRu(CO)(PR₃)(H₂)⁺ 10 and effectively eliminates the possibility that the loss of Cp*H in the present case is initiated by neutral hydride attack at the metal center of 1.

In dichloromethane-*d*₂, solutions of 2(BF₄⁻) were stable for several hours. After 18 h at ambient temperature, no more than 5–10% substrate decomposition to yield unidentified products was seen. Under these conditions, no evidence for the generation of Cp*H was seen in the ¹H NMR spectrum. In order to probe for the active involvement of acetonitrile, the kinetics were investigated in acetonitrile-*d*₃/dichloromethane-*d*₂ solvent mixtures at 21.6 °C. The observed pseudo-first-order rate constants are summarized in Table II, and a plot of *k*_{obs} vs [MeCN] is shown in Figure 2.

At the two lowest values for [MeCN], the reaction did not cleanly produce 2. Part of the substrate (ca. 30% at 1.9 M MeCN, less than 10% at 3.8 M MeCN) transformed

Scheme II

$$\text{Rate} = \frac{k_1 k_2 [\text{MeCN}]}{k_{-1} + k_2 [\text{MeCN}]} [\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+] \quad (1)$$

Scheme III

$$\text{Rate} = \frac{k_3 k_4 [\text{MeCN}]^2}{k_3 + k_4 [\text{MeCN}]} [\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+] = k_{\text{obs}} [\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+] \quad (2)$$

into Cp*Ir(PPh₃)(NCMe)H⁺.^{14a} A plausible pathway for the production of this species is an acetonitrile-independent reductive elimination of H₂ from 1, maybe via a dihydrogen complex intermediate.¹⁵ At low [MeCN], ion pairing is encouraged, and displacement of H₂ could be assisted by η¹ coordination of the BF₄⁻ counterion.¹⁶ Displacement of BF₄⁻ by acetonitrile would in this case give the observed product. In any case, whether H₂ loss is unassisted or not, it is reasonable that, at low [MeCN], this reaction dominates over reactions that proceed at acetonitrile-dependent rates. As a result of this side reaction, the intercept of the plot of *k*_{obs} vs [MeCN] should attain a nonzero, but positive, value.

Inspection of Figure 2 reveals a nonlinear dependence of the observed pseudo-first-order rate constant *k*_{obs} on [MeCN]. The solvent composition changes dramatically in this series of experiments. The observed effect therefore reflects the combination of bulk solvent effects and the effect that acetonitrile might exert on the microscopic (molecular) level, and these effects cannot be straightforwardly separated. This fact notwithstanding, it is still tempting to rationalize the observed concentration dependence on the basis of plausible reaction mechanisms.

For reactions that are initiated by η⁵ → η³ ring slippage and a following capture of the intermediate by the incoming ligand (Scheme II), rate law 1 is obtained. The equation predicts the possible observation of saturation kinetics at high [MeCN], resulting in *k*_{obs} being independent of [MeCN]. This is clearly not seen in Figure 2 and also should result in a curvature in the opposite direction of that seen in Figure 2. Such behavior was found for the reaction between Cp*Rh(PMe₃)(H)₂ and PMe₃.^{9c}

Scheme III depicts a stepwise reaction in which consecutive acetonitrile attacks reduce the Cp* hapticity. The steady-state approximation is assumed to hold for the η³-bonded intermediate. This results in rate law 2 for the overall reaction. Provided that the magnitudes of *k*₋₃ and

(14) (a) Cp*Ir(PPh₃)(NCMe)H⁺: ¹H NMR (acetonitrile-*d*₃) δ -13.93 (d, *J* = 34.3 Hz, 1 H), 1.64 (d, *J* = 2.0 Hz, 15 H), 2.01 (s, 3 H), 7.4–7.6 (m, 18 H). This complex may be conveniently prepared by treatment of Cp*Ir(PPh₃)(CH₃)H with HBF₄·Et₂O in acetonitrile.^{14b} (b) Pedersen, A.; Tilset, M. Unpublished results.

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k_4 [MeCN] are comparable, the acetonitrile concentration can actually determine whether a first-order or a second-order dependence on [MeCN] will be observed. Rate law 2 predicts a first-order dependence on [MeCN] at high concentrations and a second-order behavior at low concentrations, and this leads to a curvature of the kind seen in Figure 2. The first reaction indicated in Scheme III may well be a two-step process involving slippage followed by capture of acetonitrile, provided that the slippage is truly reversible and that saturation kinetics are not involved.

Attempts were made at evaluating k_3 and k_4/k_{-3} of Scheme III by finding the best fit between the calculated (from eq 2) and the experimentally observed pseudo-first-order rate constants. Reasonable fits were found (by visual inspection of calculated and observed data, as well as by a least-squares analysis) over a relatively wide range of values for k_3 (ca. $(0.4\text{--}1.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1})$) and then for k_4/k_{-3} . The curved line drawn in Figure 2 corresponds to $k_3 = 1.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ and $k_4/k_{-3} = 0.006 \text{ M}^{-1}$. The intercept, accounting for the acetonitrile-independent side reaction as discussed above, has been set to $0.02 \times 10^{-4} \text{ s}^{-1}$, on the basis of ca. 10% reaction of 2 during 18 h in dichloromethane- d_2 . However, the numbers should be viewed with caution because bulk solvent effects are obviously ignored in the analysis.

It is interesting to note that the neutral complex $\text{Cp}^*\text{Ru}(\text{PPh}_3)(\text{H})_3$, which is isoelectronic with 2, shows no sign of Cp^*H loss in acetonitrile.¹⁷ Two factors may contribute to this. First, the cationic species 2 should be more susceptible to nucleophilic attack by acetonitrile than neutral $\text{Cp}^*\text{Ru}(\text{PPh}_3)(\text{H})_3$. Second, the formally Ir(V) species 2 may be more prone to undergo reductive elimination than the formally Ru(IV) species.

On the basis of the available kinetic data, we cannot firmly rule out that migration of a hydride ligand to the endo face of the Cp^* ligand takes place before or during the rate-limiting step. The detection of possible $k_{\text{H}}/k_{\text{D}}$ kinetic isotope effects has been frustrated by difficulties with preparing 2- d_3 with a sufficient degree of D incorporation, combined with a tendency to lose the D label due to exchange with trace sources of protons. While emphasizing that this ambiguity exists, we conclude that the kinetics of the reaction is best accommodated by the steps depicted in Scheme III. To our knowledge, the apparent contribution of second-order kinetics for the incoming ligand has not previously been noted for Cp or Cp^* slippage reactions.

Experimental Section

General Procedures. All manipulations involving organometallic compounds were carried out with use of vacuum-line, Schlenk, syringe, or drybox techniques. Acetonitrile was distilled from P_2O_5 , and acetonitrile- d_3 , dichloromethane, and dichloromethane- d_2 were distilled from CaH_2 . ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Varian XL-300 or Varian Gemini-200 instrument. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as internal standards (^1H NMR δ 1.93; $^{13}\text{C}\{^1\text{H}\}$ NMR δ 1.3 for acetonitrile). Melting points were measured on a Büchi melting point apparatus in capillary tubes sealed under vacuum. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

$\text{Cp}^*\text{Ir}(\text{PPh}_3)\text{Cl}_2$ ¹⁸ was prepared according to a published procedure. Other chemicals were used as received from commercial suppliers.

$\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_2$ (1). The previously published procedure¹¹ has been modified to give a slightly improved yield. A 50-mL Schlenk flask was charged with $\text{Cp}^*\text{Ir}(\text{PPh}_3)\text{Cl}_2$ (100 mg, 0.015 mmol) and methanol (4 mL). To the orange slurry were added Zn (126 mg, 1.93 mmol) and glacial acetic acid (0.3 mL). The resulting mixture was heated at reflux for 2 h, giving a brown-yellow solution. A saturated aqueous NaCl solution (3 mL) was added at 0 °C. The organic phase was separated from the mixture, and the aqueous phase was extracted with toluene ($3 \times 5 \text{ mL}$). The organic extracts were combined, and the solvent was removed in vacuo. The crude product was transferred to the glovebox and dissolved in benzene, and the solution was filtered through alumina (5% H_2O , $1 \times 3 \text{ cm}$) on a fritted glass filter. This gave a pale yellow solution. The solution was concentrated by vacuum-transfer, dissolved in a minimum amount of warm ether, and crystallized as an air-sensitive white/yellow solid (180 mg, 50%) by cooling at -35 °C. ^1H NMR (200 MHz, acetonitrile- d_3): δ -16.47 (d, $J = 31.7 \text{ Hz}$, 2 H), 1.91 (d, $J = 1.7 \text{ Hz}$, 15 H), 7.00–7.20 and 7.52–7.81 (m, 15 H).

$\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+\text{BF}_4^-$ (2(BF_4^-)). A solution of $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_2$ (192 mg, 0.324 mmol) in ether (12 mL) was stirred vigorously at -20 °C. To this solution was added $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ dropwise, resulting in the formation of a white precipitate. The solvent was decanted, and the precipitate was washed with ether ($3 \times 20 \text{ mL}$) and dried in vacuo to give the product as an air-sensitive white powder (150 mg, 68%). Mp: 150–153 °C slow dec. ^1H NMR (300 MHz, acetonitrile- d_3): δ -12.65 (br s, 3 H), 1.94 (d, $J = 2.3 \text{ Hz}$, 15 H), 7.3–7.7 (m, 15 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, acetonitrile- d_3): δ 9.7, 104.0, 129.7, 131.4, 132.7, 133.6. Anal. Calcd for $\text{C}_{28}\text{H}_{33}\text{BF}_4\text{IrP}$: C, 49.49; H, 4.89. Found: C, 49.40; H, 4.84.

$\text{Ir}(\text{H})_2(\text{PPh}_3)(\text{NCMe})_3^+\text{BF}_4^-$. A solution of $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+\text{BF}_4^-$ (prepared from 50 mg (0.085 mmol) of 1) in acetonitrile (1.0 mL) was stirred at ambient temperature for 4 h. The product (28.1 mg, 50% based on 1) was obtained as glossy white needles by the slow diffusion of ether vapors into the solution. Mp: 164–167 °C. ^1H NMR (200 MHz, dichloromethane- d_2): δ -21.62 (d, $J = 21.9 \text{ Hz}$, 2 H), 2.00 (s, 6 H), 2.52 (s, 3 H), 7.38–7.55 (m, 15 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, acetonitrile- d_3): δ 129.2, 131.8, 134.6. Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{BF}_4\text{IrN}_3\text{P}$: C, 43.25; H, 3.93; N, 6.30. Found: C, 43.32; H, 3.39; N, 6.42.

Quantitative Analysis of the Elimination of Cp^*H from $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+\text{BF}_4^-$ in Acetonitrile- d_3 . A mixture of $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+(\text{BF}_4^-)$ (5.0 mg, 0.0074 mmol) and hexamethylbenzene (1.0 mg, 0.0062 mmol) was added to an NMR tube equipped with a ground-glass joint. Acetonitrile- d_3 (0.7 mL) was added by syringe in the drybox, and the tube was sealed under vacuum. Immediate recording of an ^1H NMR spectrum at ambient temperature revealed the presence of only traces of the reaction products. The hexamethylbenzene internal standard allowed for determination of the yield of the product as time progressed, and it was established that the yield exceeded 95% based on consumed substrate.

Kinetics of the Elimination of Cp^*H from $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+\text{BF}_4^-$ in Acetonitrile- d_3 . In order to ensure identical substrate concentrations and solvent compositions for all the kinetic runs, the following procedure was employed for sample preparation. In the drybox, $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+\text{BF}_4^-$ (35 mg, 0.0515 mmol) was dissolved in acetonitrile- d_3 (4.9 mL). The solution was portioned into seven NMR tubes that were equipped with ground-glass joints. The tubes were attached to the vacuum line via adapters, cooled at -196 °C, evacuated, and sealed. The tubes were stored in at -196 °C until the start of each kinetic run. Kinetic runs were performed at the temperatures 10.9, 21.6, 30.6, and 36.1 °C by inserting the tubes into the preheated or precooled

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spectrometer probe. Earlier experiments had established that the reaction was quantitative, and it was decided that the addition of an internal standard for quantification purposes was not necessary. Therefore, the progress of the reaction was followed by monitoring the concentration $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+\text{BF}_4^-$ relative to the combined concentrations of $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+\text{BF}_4^-$ and $\text{Ir}(\text{H})_2(\text{PPh}_3)(\text{NCMe})_3^+$, based on the intensities of their hydride resonances. The kinetic data are presented under Results and Discussion.

Effect of Added $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_2$ on the Rate of Cp^*H Elimination from $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+\text{BF}_4^-$. In the drybox, $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+\text{BF}_4^-$ (10.0 mg, 0.0147 mmol) was dissolved in acetonitrile- d_3 (1.4 mL). The solution was portioned into two NMR tubes that were equipped with ground-glass joints. One of the tubes was charged with $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_2$ (0.9 mg, 0.0015 mmol). The tubes were attached to the vacuum line via adapters, cooled at -196°C , evacuated, and sealed. The tubes were kept at -196°C until the start of each kinetic run. Kinetic runs were performed at 21.6°C for ca. 4 half-lives. The pseudo-first-order rate constants obtained for this pair of experiments were $k = (2.0 \pm 0.02) \times 10^{-4} \text{ s}^{-1}$ for reaction in the presence of $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_2$ and $(1.8 \pm 0.07) \times 10^{-4} \text{ s}^{-1}$ in its absence.

Kinetics of the Reaction of $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+\text{BF}_4^-$ in Acetonitrile- d_3 /Dichloromethane- d_2 Mixtures Followed by ^1H NMR Spectroscopy. In the drybox, $\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})_3^+\text{BF}_4^-$ (5.0 mg, 0.0085 mmol) was loaded into an NMR tube that was equipped with a ground-glass joint. A mixture of acetonitrile- d_3 and dichloromethane- d_2 (10, 20, 50, 70, 83.3, 91.7, and 100% acetonitrile by volume) was added. The tube was attached to the vacuum line via an adapter, cooled at -196°C , evacuated, and sealed. The tubes were kept at -196°C until the start of each kinetic run. The kinetic runs were performed at 21.6°C , and the progress of the reaction was monitored as described for the previous experiment. The results are presented under Results and Discussion.

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