

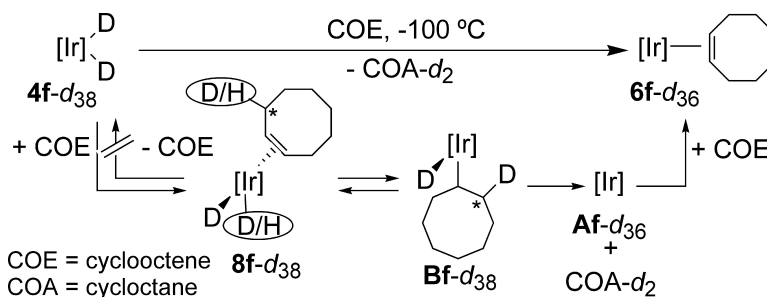
Article

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Mechanistic Studies of the Transfer Dehydrogenation of Cyclooctane Catalyzed by Iridium Bis(phosphinite) *p*-XPCP Pincer Complexes

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Abstract: Reaction of bis(phosphinite) PCP iridium pincer complexes (*p*-XPCP)IrHCl (**5a–f**) [*X* = MeO (**5a**), Me (**5b**), H (**5c**), F (**5d**), C₆F₅ (**5e**), Ar^F(= 3,5-bis(trifluoromethyl)phenyl) (**5f**)] with NaOtBu in neat cyclooctane (COA) generates 1:1 mixtures of the respective (*p*-XPCP)IrH₂ complexes **4a–f** and the cyclooctene (COE) olefin complexes (*p*-XPCP)Ir(COE) (**6a–f**) at 23 °C. At higher temperatures, complexes **4** and **6** are equilibrated because of the degenerate transfer dehydrogenation of COA with free COE (**6** + COA ⇌ **4** + 2COE), as was shown by temperature-dependent equilibrium constants and spin saturation transfer experiments at 80 °C. At this temperature, the COE complexes **6** exchange with free COE on the NMR time scale with the more electron-deficient complexes **6** exchanging COE faster. The exchange is dissociative and zero order in [COE]. Further analysis reveals that the stoichiometric hydrogenation of COE by complex **4f**, and thus the separated back reaction **4f** + 2COE → **6f** + COA proceeds at temperatures as low as –100 °C with the intermediacy of two isomeric complexes (*p*-Ar^FPCP)Ir(H)₂(COE) (**8f**, **8f'**). COE deuteration with the perdeuterated complex **4f-d₃₈** at –100 °C results in hydrogen incorporation into the hydridic sites of complexes **8f,8f'-d₃₈** but not in the hydridic sites of complex **4f-d₃₈**, thus rendering COE migratory insertion in complexes **8f,8f'** reversible and COE coordination by complex **4f** rate-determining for the overall COE deuteration.

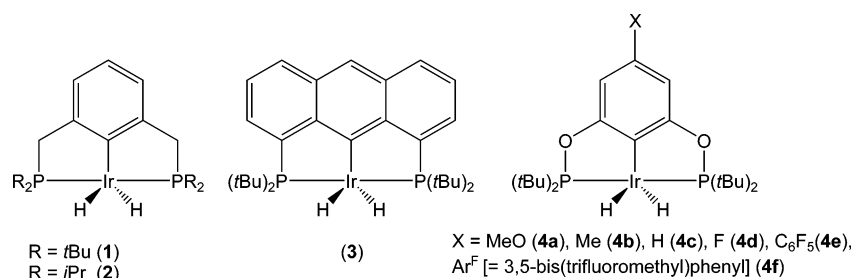
Introduction

Invention of catalytic processes for conversion of abundant alkane feedstocks to higher value products based on transition-metal-mediated C–H bond activations remains a challenging task.¹ Heterogeneous alkane dehydrogenation processes such as (hydro)cracking or catalytic reforming are the most important industrial source of olefins and arenes.² Development of analogous homogeneous processes, due to drastically decreased reaction temperatures (typically heterogeneous processes operate at 400–600 °C), is expected to provide higher selectivities and higher energy efficiency. In addition, such studies might lead to a better understanding of the requirements for efficient alkane C–H functionalization.

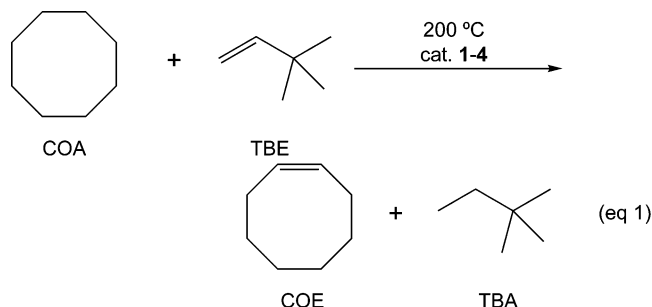
Since the first examples of homogeneous alkane dehydrogenation stoichiometric and substoichiometric in transition metal,³ much progress has been made providing effective photo-⁴ and

thermocatalytic^{4a,b,5} dehydrogenation of alkanes, though industrial applications are far from realized. As the reverse of olefin hydrogenation, homogeneous hydrogenation catalysts in principle should accomplish the alkane dehydrogenation.^{3a,6} The endothermicity of this reaction however,⁷ requires very high-temperature conditions (> 150 °C), which are often not compatible with the thermal stability of potential catalysts. Partly because of their improved thermal stability, bis(phosphine) and bis(phosphinite) PCP iridium pincer complexes **1–4** (Chart 1) have been shown to be the most active homogeneous catalysts

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Chart 1. Active PCP Iridium Pincer Catalysts for the Transfer Dehydrogenation of COA with TBE

for the thermochemical transfer dehydrogenation of, for example, cyclooctane (COA) in the presence of *tert*-butylethylene (TBE), as shown in eq 1.^{1e,8–11}



Initial turnover frequencies (TOF) of 0.2 s^{-1} and turnover numbers (TON) up to 1000 have been observed with catalyst **1** at $200\text{ }^{\circ}\text{C}$. Inhibition of catalysis using **1** by TBE and the formed cyclooctene (COE) was shown to restrict higher TON and required the portionwise addition of TBE to obtain the reported TON.⁸ Mechanistic studies by Goldman et al. reveal a first-order dependence of this reaction in TBE at low [TBE], which becomes inverse first-order at high [TBE] because of the pre-equilibrium formation of the Ir(III) complex (PCP)Ir(H)(*tert*-butylvinyl), the catalyst resting state under these conditions.^{11a} Furthermore, under conditions where [TBE] < 0.3 M, hydrogenation of TBE, and more specifically reductive elimination of TBA from the (PCP)Ir(H)(*neo*-hexyl) complex, was found to be the rate-determining step for the overall reaction in the same study. Recently, we have shown that complexes **4a–f** exhibit a catalytic activity for the reaction of eq 1 up to 1 order of magnitude higher than that of complex **1** under standard conditions without the need of maintaining relatively low TBE

concentrations. Furthermore, catalytically active species can be easily generated in situ by addition of NaOtBu to a solution of the respective air stable hydrido-chloro precursor (*p*-XPCP)IrHCl (**5a–f**) in 1:1 mixtures of COA and TBE.¹² We now wish to report the nature of the catalytically active species generated from the hydrido-chloro precursors **5a–f** as well as mechanistic results with relevance to the catalytic transfer dehydrogenation of COA.

Results and Discussion

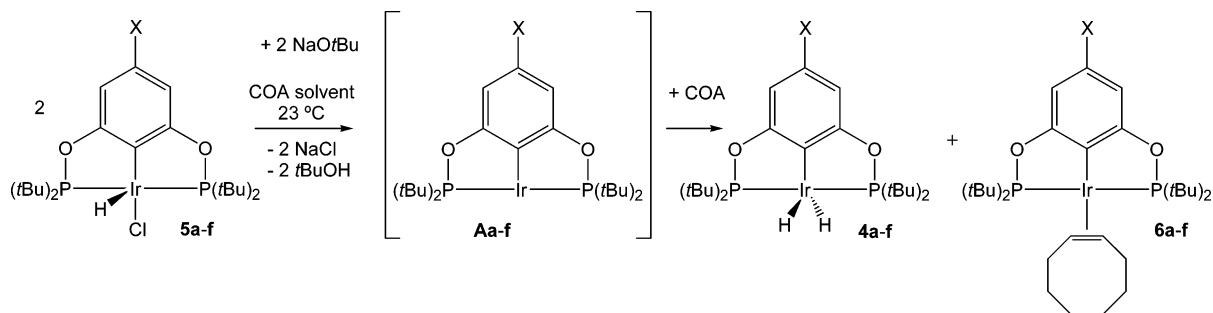
Oxidative Addition/C–H Activation of COA by the Fragment (*p*-XPCP)Ir (A). In recent studies, we have shown that C–H oxidative addition of toluene and other arenes can be easily accomplished by reaction of hydrido-chloro complexes **5a–f** with NaOtBu in the arene solvent.¹³ Furthermore, a dissociative exchange of arene from the formed (*p*-XPCP)Ir–(H)(aryl) complexes comprising a reductive elimination/oxidative addition sequence through the (presumed) intermediacy of a $14e^-$ species (*p*-XPCP)Ir (**Aa–f**) was established by line-broadening techniques at temperatures above $-30\text{ }^{\circ}\text{C}$.¹³ Since alkane C–H activation is one prerequisite step in the transfer dehydrogenation of COA with *tert*-butylethylene (TBE) catalyzed by complexes **4a–f**, or by **5a–f** in the presence of NaOtBu, we have chosen to examine the stoichiometric reaction of **5a–f**, NaOtBu, and COA. Thus, reaction of complexes **5a–f** with 1.1 equiv of NaOtBu in neat COA forms within ca. 30 min at $23\text{ }^{\circ}\text{C}$ the respective (*p*-XPCP)IrH₂ complexes **4a–f** as was proven by matching the $^{31}\text{P}\{^1\text{H}\}$ NMR signals and the hydridic IrH₂ resonances in neat COA to independently prepared complexes.¹³ A second Ir complex was formed in each case with a characteristic $^{31}\text{P}\{^1\text{H}\}$ NMR resonance in the range between 173 and 180 ppm. Additionally, for these species a second set of signals for the ligand backbone of each *p*-XPCP ligand as well as a broad multiplet in the narrow range of 4.2–4.3 ppm could be detected in the ^1H NMR spectra. The ratio of the (*p*-XPCP)IrH₂ (**4a–f**) and the new complexes is 1:1, as determined by integration of the corresponding signals in the ^1H NMR spectrum as well as integration of the $^{31}\text{P}\{^1\text{H}\}$ NMR signals. No other complexes are formed in these reactions. We have assigned the new Ir complexes as (*p*-XPCP)Ir(COE) (**6a–f**) on the basis of matching $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR resonances to those species formed by reacting (*p*-HPCP)IrH₂ (**4c**) or (*p*-Ar^FPCP)IrH₂ (**4f**) with 2.5 equiv of COE in neat COA. We have been unable to isolate complexes **6c,f** in a pure form. Generation of complexes **4a–f** and **6a–f** from the hydrido-chloro precursors **5a–f** and NaOtBu in COA can be rationalized by dehydro-

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Scheme 1. Generation of (*p*-XPCP)IrH₂ (**4**) and (*p*-XPCP)Ir(COE) (**6**) by Dehydrochlorination of Complexes **5** with NaOtBu in Neat COA



Scheme 2. Equilibrium Reaction of Complexes **4** and **6** Generated from Complexes **5**

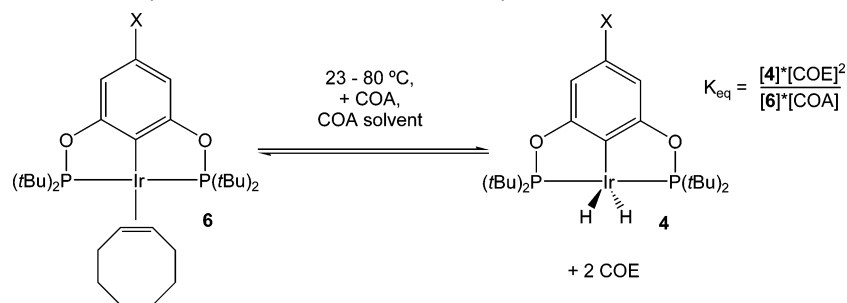


Table 1. ³¹P NMR Spin Saturation Transfer Data for the Equilibrium **6** + COA ⇌ **4** + 2COE at 80 °C

4,6	<i>I</i> _{35 dB} (4) ^a (%)	<i>I</i> _{35 dB} (6) ^b (%)	<i>T</i> ₁ (4) ^c (s)	<i>T</i> ₁ (6) ^c (s)	<i>R</i> _{obs1} ^d (s ⁻¹)	<i>R</i> _{obs-1} ^e (s ⁻¹)	<i>R</i> _{obs1} / <i>R</i> _{obs-1}	[4/6] (from <i>K</i> _{eq} measurement)
a	84.5	74.5	2.1	1.8	0.19	0.09	2.18	2.23
b	64.6	52.5	2.2	2.0	0.45	0.25	1.82	1.92
c	47.8	39.2	2.7	2.3	0.67	0.40	1.67	1.78
f	51.5	42.8	1.6	1.5	0.89	0.59	1.51	1.62

^a Relative integration of the ³¹P NMR signal of **4** obtained for complete versus no saturation of **6**. ^b Relative integration of the ³¹P NMR signal of **6** obtained from complete versus no saturation of **4**. ^c Obtained by the inversion recovery method. Based on the observed *T*₁ values, the relaxation delay in each SST experiment was uniformly set to 15 s. ^d Rate for the conversion of **6** to **4**. ^e Rate for the conversion of **4** to **6**.

chlorination of **5a–f** to give an undetected 14e⁻ fragment (*p*-XPCP)Ir(**Aa–f**). Oxidative addition of COA to **Aa–f** followed by β-hydride elimination generates compounds **4a–f** and 1 equiv of COE, which traps another 14e⁻ fragment (*p*-XPCP)Ir to yield **6a–f** (Scheme 1).

Significantly, we find here that the methylene-bridged pincer complex {C₆H₃-2,6-[CH₂P(*t*Bu)₂]₂}IrHCl¹⁴ undergoes the same reaction with NaOtBu in neat COA, but the ratio of the generated complexes {C₆H₃-2,6-[CH₂P(*t*Bu)₂]₂}IrH₂ (**1**):{C₆H₃-2,6-[CH₂P(*t*Bu)₂]₂}Ir(COE) is ca. 8–9:1 at 23 °C, and free COE is detected by ¹H NMR experiments. Furthermore, we find that the ratio of each **4a–c/f/6a–c,f** pair gradually increases as temperature is raised with concomitant liberation of free COE.¹⁵ More electron-rich ligand backbones *p*-XPCP result in larger **4/6** ratios (and larger amounts of free COE) at a given temperature, for example: **4a/6a** = 2.23, **4b/6b** = 1.92, **4c/6c** = 1.78, and **4f/6f** = 1.62 at 80 °C. The ratios **4a–c/f/6a–c,f** return to 1:1 again when the temperature is lowered back to 23 °C. These observations strongly suggest that an equilibrium is established between complexes **4** and **6** by the reaction (*p*-XPCP)Ir(COE) (**6**) + COA ⇌ (*p*-XPCP)IrH₂ (**4**) + 2COE (Scheme 2). It is noteworthy that more electron-rich ligand backbones *p*-XPCP thermodynamically favor the formation of

free COE and the iridium(III) complexes **4** from their iridium(I) precursors **6** and COA.

The ³¹P NMR resonances of **6** and **4** are sharp in the range of 25–80 °C and give no indication of the interchange of **6** and **4** as shown in Scheme 2. However, ³¹P NMR spin saturation transfer (SST) experiments at 80 °C provide clear evidence for the equilibrium as well as quantitative rates for the interchange of the **6a–c,f** and **4a–c,f** pairs. In a typical set of experiments, a 1:1 mixture of complexes **4f** and **6f**, obtained by reaction of 20 μmol complex **5f** and 1.1 equiv of NaOtBu in 300 mg of COA in a J. Young NMR tube at 23 °C, was heated to 80 °C, while equilibration resulted in generation of free COE and increase of the **4f/6f** ratio. SST experiments on the well-separated (by ca. 30 ppm) ³¹P NMR resonances were then carried out. Irradiation and saturation of the resonance for **4f** resulted in a decrease of the net magnetization of the ³¹P signal for **6f**, while saturation of the signal for **6f** resulted in decrease of the integral for **4f**. These data, together with *T*₁ measurements for both nuclei, are summarized in Table 1 and can be used to calculate the rate of formation (not rate constants) of **4f** from **6f** (*R*_{obs1}) as well as the reverse rate, formation of **6f** from **4f** (*R*_{obs-1}). Similar data for the **4a–c/6a–c** pairs are also summarized in Table 1.

As a check on the accuracy of the SST experiments, the ratio of *R*_{obs}/*R*_{obs-1} should correspond to the independently measured equilibrium ratio of the **4/6** pairs. These ratios and the *K*_{eq} values

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(15) The olefinic signal at 5.6 ppm (calibrated to the COA signal at 1.57 ppm) is dynamically broadened.

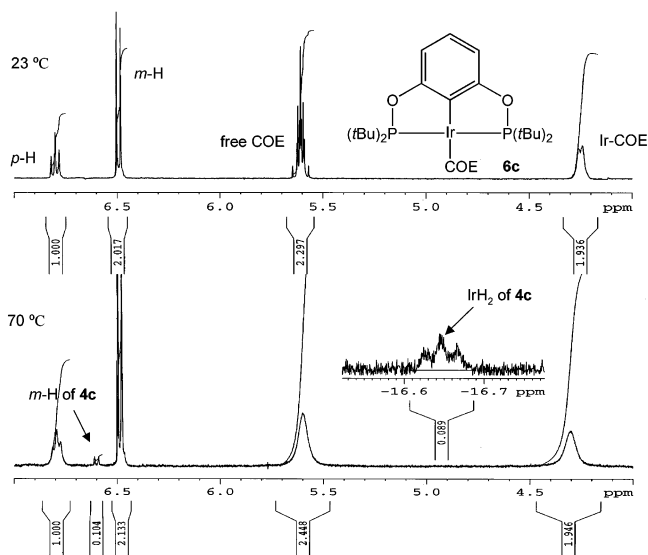


Figure 1. Temperature-dependent equilibrium $6c + COA \rightleftharpoons 4c + 2COE$ in the aromatic and olefinic region of the 1H NMR spectrum. Sample obtained from reaction of $5c$ and ca. 2.2 equiv of COE in neat COA.

are summarized in the last two columns and are clearly in close agreement. It is significant to note that the rates of interchange of species 4 and 6 increase as the electron-withdrawing ability of para-substituent increases. For example, the rate of conversion of $6f$ to $4f$ is 0.89 s^{-1} compared to 0.19 s^{-1} for conversion of $6a$ to $4a$. The reverse rate is similarly accelerated, with the rate of $4f$ to $6f$ equal to 0.59 s^{-1} compared to 0.09 s^{-1} for $4a$ to $6a$.

Additional details concerning the $4/6$ equilibration were revealed by reacting (*p*-HPCP)IrHCl ($5c$) with 1.1 equiv of NaOtBu in neat COA in the presence of ca. 2.2 equiv of COE. Quantitative conversion of $5c$ into $6c$ is complete within ca. 40 min at $23\text{ }^\circ\text{C}$, and a ca. 1:1.2 mixture of $6c$ /COE (sharp multiplet at 5.61 ppm) results. Heating this reaction mixture to $70\text{ }^\circ\text{C}$ causes the appearance of the iridium dihydride complex $4c$ (ca 5% with respect to $6c$). In the same experiment, increasing line-broadening of the signals for free COE at 5.61 ppm and coordinated COE (slightly shifted downfield by ca. 0.05 ppm) can be observed upon heating the sample gradually to $70\text{ }^\circ\text{C}$ (Figure 1).

Upon addition of COE (12, 41 equiv), the disappearance of $4c$ at $70\text{ }^\circ\text{C}$ is observed. Furthermore, we find that the olefinic signal for free COE becomes increasingly sharp with COE addition, while the width at half-height ($\Delta\nu_{1/2}^*$) of the olefinic signal of complex $6c$ remains at ca. 25.0 Hz. Similar results have been obtained for the olefinic resonance of complexes $6a,f$. At $75\text{ }^\circ\text{C}$, $\Delta\nu_{1/2}^*(6a) = \text{ca. } 19 \pm 1\text{ Hz}$, $\Delta\nu_{1/2}^*(6c) = \text{ca. } 34 \pm 1\text{ Hz}$, and $\Delta\nu_{1/2}^*(6f) = \text{ca. } 48 \pm 1\text{ Hz}$ in the presence of 2–40 equiv of free COE. Upon heating a solution of 5 equiv of free COE and $6f$ in neat COA from 70 to $100\text{ }^\circ\text{C}$, the olefinic COE signal of $6f$ gradually broadens into the baseline while the signal for free COE reaches $\Delta\nu_{1/2}^* = \text{ca. } 72\text{ Hz}$ at $\delta = 5.55\text{ ppm}$ (instead of 5.61 ppm at $23\text{ }^\circ\text{C}$). Further heating to $120\text{ }^\circ\text{C}$ results in a diminished signal width $\Delta\nu_{1/2}^* = \text{ca. } 64\text{ Hz}$ and $\delta = 5.45\text{ ppm}$ (the weighted average position for fast exchange is 5.41 ppm). The lack of dependence of line-broadening of the olefinic resonances of $6a,c,f$ on $[COE]$ clearly indicates the exchange is zero-order in $[COE]$ with COE dissociation from complexes 6 as the rate-limiting step.¹⁶ As was quantitatively shown for the dissociative arene exchange (via reductive elimination/

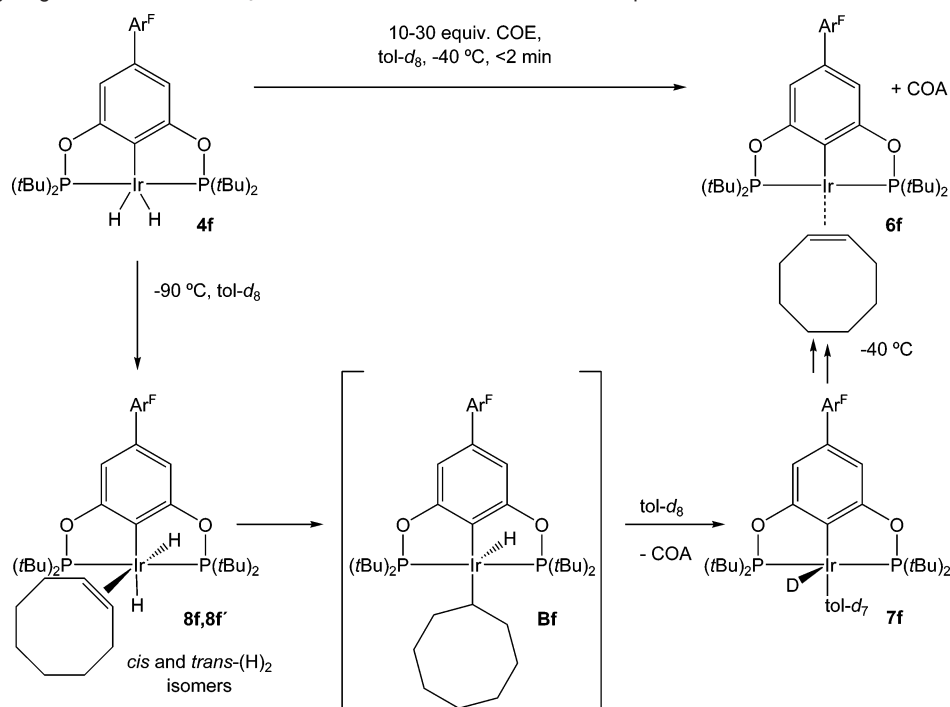
oxidative addition) in the respective (*p*-XPCP)Ir(H)(aryl) complexes,¹³ exchange of COE in complexes 6 , as judged by the signal width " $\Delta\nu_{1/2}^*$ " of the olefinic resonances, qualitatively proceeds faster for the more electron-deficient (*p*-XPCP)Ir fragments ($6a-f$). This is also in accordance with the quantitative SST experiments that revealed that electron-deficient *p*-XPCP ligand backbones result in enhanced rates for the transformation of 6 to 4 (vide supra). A faster dissociative ligand exchange with increasing electron deficiency at the metal center is not unprecedented.¹⁷

The equilibria of Scheme 2 constitute a full catalytic cycle of a putative transfer dehydrogenation, since the COE/COA couple can be considered as a degenerate hydrogen acceptor/donor system. At "low" temperature ($23\text{ }^\circ\text{C}$) and "low" $[COE]$, both complexes 4 and 6 are resting states of the catalytic cycle, while at "high" $[COE]$ (i.e., in the presence of an additional 1.2 equiv of COE with respect to the catalyst) the sole resting state is COE complex 6 (Figure 1, $23\text{ }^\circ\text{C}$ spectrum). Increasing temperature, however, entropically favors the formation of three species (4 and two COE molecules) from two species (6 and COA) and shifts the equilibrium of Scheme 2 to the right (Figure 1, $70\text{ }^\circ\text{C}$ spectrum). Pre-equilibrium COE dissociation from the resting state 6 presumably generates the $14e^-$ species A , which is capable of COA C–H oxidative addition and subsequent β -hydride elimination to generate dihydride 4 and COE.

Stoichiometric COE Hydrogenation by Complex $4f$. To gain a better understanding of the equilibrium described in Scheme 2, we have studied the stoichiometric reaction of dihydride $4f$ with COE to generate COA and $6f$ (and thus the separated back reaction of Scheme 2). While similar studies have been conducted for the hydrogenation of TBE with methylene-bridged complex 1 at $55\text{ }^\circ\text{C}$ to obtain kinetic data,^{11a} reaction of complex $4f$ with COE (11–37 equiv) in neat COA solvent is instantaneous at $23\text{ }^\circ\text{C}$ and produces complex $6f$ as the sole product. Low-temperature hydrogenation of COE was therefore conducted in toluene- d_8 and, surprisingly, proceeds too fast for NMR monitoring even at $-40\text{ }^\circ\text{C}$. At $-90\text{ }^\circ\text{C}$, however, it was possible to follow the consumption of $4f$ in the presence of 11 equiv of COE over the course of ca. 3 h (ca. 4 to 5 half-lives) by 1H and $^{31}P\{^1H\}$ NMR experiments. Significantly, the final product $6f$ is not formed at $-90\text{ }^\circ\text{C}$, but the buildup of two new species with characteristic resonances at $\delta = 181.5$ and 167.7 in the $^{31}P\{^1H\}$ NMR and at -9.86 , 3.61 , and 2.95 ppm (in a 1:1:1 ratio) in the 1H NMR spectra can be observed. While the ^{31}P NMR resonance at 181.5 ppm at $-90\text{ }^\circ\text{C}$ matches that of (*p*-Ar^FPCP)Ir(D)(tolyl- d_7) ($7f$),¹³ the ^{31}P NMR resonance at 167.7 ppm and the 1H NMR resonances are indicative of a six-coordinate Ir complex containing a coordinated COE double bond (3.61 ppm), the allylic signals of coordinated COE (2.95 ppm), and two averaged hydride ligands (-9.86 ppm). Over time, a minor isomer characterized by a hydridic resonance at -9.41 ppm can also be observed by 1H NMR experiments. However, disappearance of these isomers and further buildup of $7f$ can be monitored by $^{31}P\{^1H\}$ and 2D NMR (characteristic resonance at -43.1 ppm) at $-90\text{ }^\circ\text{C}$. We tentatively assign the aforementioned Ir(H_2)(COE) complexes

(16) In principle, the dissociation of COE could be induced by association of COA C–H bonds which are present in ca. 100–10 000-fold excess with respect to the olefinic C=C bond of free COE in this study.

(17) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378–1399.

Scheme 3. COE Hydrogenation in Toluene- d_8 at -90 °C and Formation of COE Complex **6f** at -40 °C

as *cis*- and *trans*-isomers of $(p\text{-Ar}^{\text{F}}\text{PCP})\text{Ir}(\text{H})_2(\text{COE})$ **8f,8f'**,¹⁸ which upon insertion of coordinated COE into one Ir–H bond generates the $(p\text{-Ar}^{\text{F}}\text{PCP})\text{Ir}(\text{H})(\text{cyclooctyl})$ complex **Bf**. Reductive elimination of COA from **Bf** generates the $14e^-$ species **Af**, which C–D activates the toluene- d_8 solvent and results in formation of $(p\text{-Ar}^{\text{F}}\text{PCP})\text{Ir}(\text{D})(\text{tol-}d_7)$ (**7f**) (Scheme 3).

While aromatic and aliphatic C–H(C–D) activations at very low temperatures are not unprecedented, the generation of coordinatively unsaturated species capable of accomplishing this reaction usually requires photolytic conditions¹⁹ rather than “low-temperature” thermochemical conditions.²⁰ Oxidative addition of toluene at -90 °C starting from **4f** and COE implies that the activation barriers for the hydrogenation of COE, including reductive elimination of COA from complex **Bf** to form the $14e^-$ species **Af**, are remarkably low. The observed $\text{Ir}(\text{D})(\text{tolyl-}d_7)$ complex **7f** is kinetically stable at -90 °C. Its protio analogue $(p\text{-Ar}^{\text{F}}\text{PCP})\text{Ir}(\text{H})(\text{tolyl})$ was shown by line-broadening techniques to exchange toluene by a dissociative mechanism at temperatures above -30 °C.¹³ Heating the sample to -40 °C results in reductive elimination of toluene- d_8 and finally in quantitative generation of the $(p\text{-Ar}^{\text{F}}\text{PCP})\text{Ir}(\text{COE})$ (**6f**) as the thermodynamic product within minutes (Scheme 3). Complex **6f** exhibits no detectable ^{31}P NMR resonance at -40 °C (400 MHz) because of the exchange of two diastereotopic ^{31}P nuclei, which occurs at a rate that broadens signals into the baseline. At -90 °C, the ^{31}P NMR resonances appear as two doublets ($^2J_{\text{PP}} = 345$ Hz) at 184.8 and 169.2 ppm, while the fast exchange singlet is detected at 177.0 ppm above 0 °C.

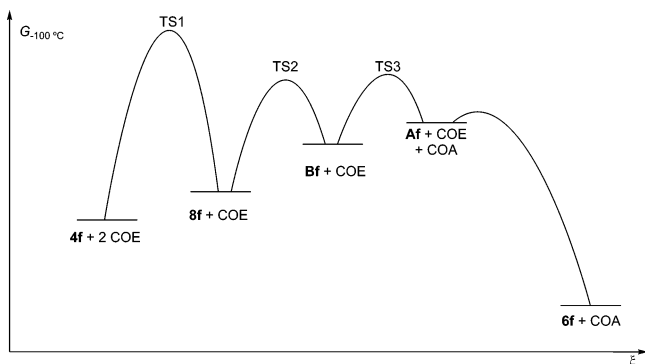
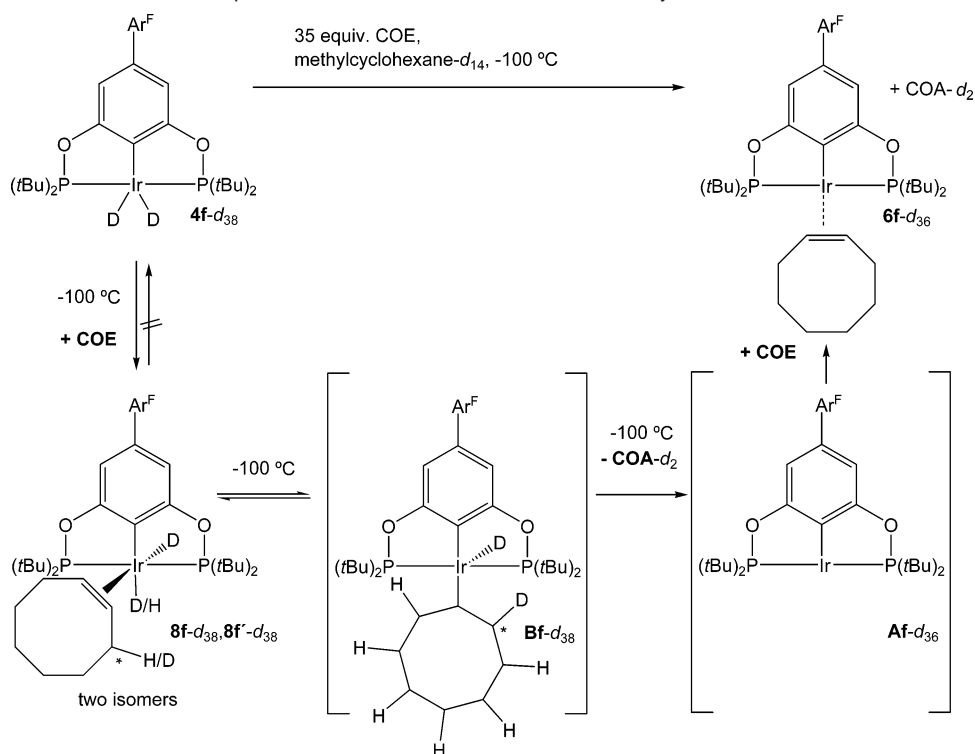
When complex **4f** is treated with COE in methylcyclohexane- d_{14} (in place of toluene- d_8) at -90 °C, formation of both isomeric complexes **8f,8f'** and the final product **6f** is observed by ^1H NMR experiments. By warming samples of **4f** and COE from -110 °C to -70 °C in the NMR spectrometer, there is a small buildup of complexes **8f,8f'** up to 10% (10.5 equiv of COE), 12% (14 equiv of COE), and 15% (20.5 equiv of COE) during the heating period. At -70 °C, species **8f,8f'** are consumed faster than they are generated to leave **6f** as the sole product. The half-life of dihydride complex **4f** in these reactions was determined to be ca. 17 min (10.5 equiv of COE) and ca. 9 min (20.5 equiv of COE) at -70 °C. Finally, when the perdeuterio complex $(p\text{-Ar}^{\text{F}}\text{PCP})\text{IrD}_2$ (**4f-}d_{38})²¹ in methylcyclohexane- d_{14} is treated at -100 °C with 35 equiv of COE (conditions chosen to build up complexes **8f-}d_{38}**, **8f'-}d_{38}** in substantial amounts), an exchange of Ir–deuteride by hydride is observed in complexes **8f-}d_{38}**, **8f'-}d_{38}**. On the basis of the integrals for both the Ir–H and olefinic resonances of **8f,8f'**, H/D exchange is not complete prior to formation of **6f**. These experiments indicate that the insertion of coordinated COE into one of the Ir–D bonds of **8f-}d_{38}**, **8f'-}d_{38}** and β -hydride (β -deuteride) elimination in **Bf** are reversible and competitive with reductive elimination of COA from the unobserved $(p\text{-Ar}^{\text{F}}\text{PCP})\text{Ir}(\text{D})(\text{cyclooctyl-}d_1)$ complex (**Bf-}d_{38}**). Remarkably, no protio label is transferred into the hydridic sites of the starting $(p\text{-Ar}^{\text{F}}\text{PCP})\text{IrD}_2$ complex **4f-}d_{38}** at -100 °C (Scheme 4). Thus, COE coordination to **4f-}d_{38}** is irreversible. This step must be the rate-limiting step for overall COE hydrogenation at low [COE] where little **8f,8f'** grow in during reaction. Figure 2 shows a qualitative free-energy diagram for the overall reaction. To accommodate the H/D exchange results, transition-state 1 (TS1) must be higher in energy than transition-states 2 (TS2) and 3 (TS3) and transition-states 2 and 3 must be comparable in energy.**

(18) We believe that the *cis*-dihydride gives rise to one hydridic resonance because of fast exchange presumably through an $\text{Ir}(\eta^2\text{-H}_2)$ species.

(19) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352–354. (b) Arndtsen, B. A.; Bergman, R.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154–162 and references cited herein.

(20) A few examples of oxidative C–H addition after thermochemical generation of coordinatively unsaturated species at -86 to -60 °C are known: (a) Periana, R.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332–7346. (b) Golden, J. T.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 5837–5838.

(21) Deuteration of all *tert*-butyl and hydridic positions of compound **4f-}d_{38}** is achieved by heating **4f** in benzene- d_6 for 12 h to 150 °C.

Scheme 4. Reversible and Irreversible Steps of COE Deuteration at $-100\text{ }^{\circ}\text{C}$ in Methylcyclohexane- d_{14} **Figure 2.** Free-energy G versus reaction coordinate ξ for the hydrogenation of COE by **4f**, **4f-d₃₈** at $-100\text{ }^{\circ}\text{C}$ (the intermediacy of **Bf** and **Af** is postulated).

Increasing temperature should accelerate the first-order conversion of **8f**, **8f'** to **6f** relative to the second-order formation (negative ΔS^{\ddagger}) of **8f**, **8f'** from **4f**. Thus, it is not surprising that at higher temperatures, i.e., $-70\text{ }^{\circ}\text{C}$, it becomes increasingly difficult to detect **8f**, **8f'** in the reaction of COE with **4f**.

TBE Hydrogenation. The hydrogenation of TBE by complex **4f** requires slightly higher temperatures than COE hydrogenation but is still several orders of magnitude faster than with the standard Kaska/Jensen/Goldman pincer complex **1**. Thus **4f** disappears with $t_{1/2} = \text{ca. } 70\text{ min}$ in the presence of 12 equiv of TBE in methylcyclohexane- d_{14} solution at $-80\text{ }^{\circ}\text{C}$, which compares to the reported disappearance of complex **1** with $t_{1/2} = \text{ca. } 10\text{ min}$ in the presence of 12 equiv of TBE at $55\text{ }^{\circ}\text{C}$.^{11a} No complexes other than **4f** and the product olefin complex ($p\text{-Ar}^{\text{F}}\text{PCP}$)Ir(TBE) (**9f**) are observed in this reaction.²² It is

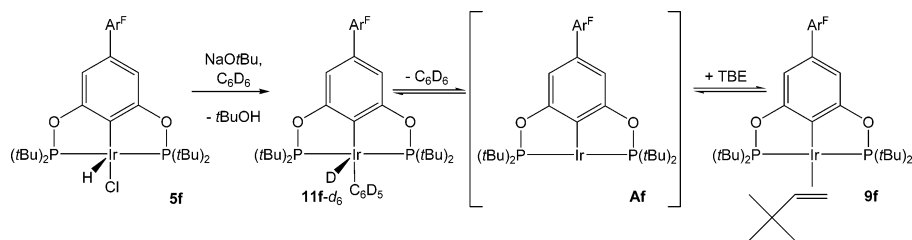
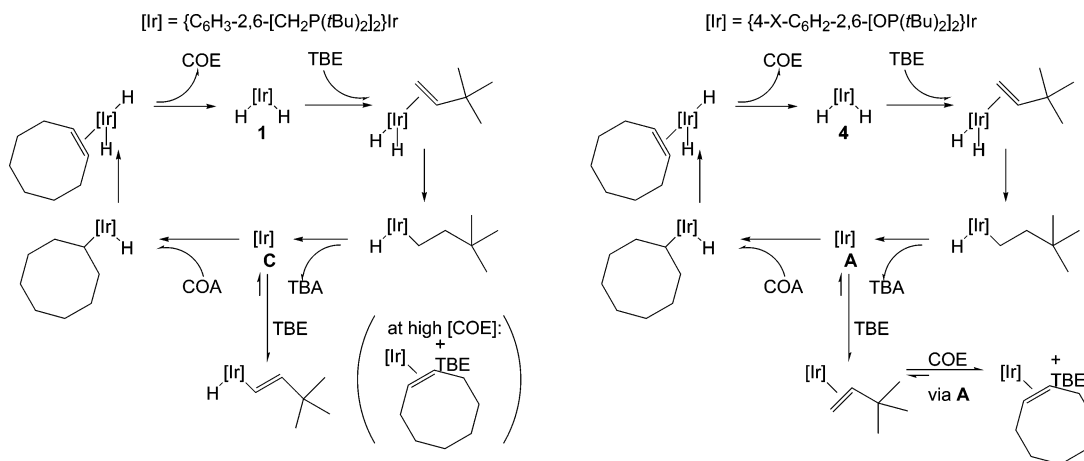
significant to note that in the case of **1** the Ir(III) vinyl hydride, $\{\text{C}_6\text{H}_3\text{-2,6-}[\text{CH}_2\text{P}(\text{tBu})_2]_2\}\text{Ir}(\text{H})[\text{CH}=\text{CHC}(\text{CH}_3)_3]$, is formed rather than the olefin complex.^{11a,g,k} Similar to the case of COE, no hydride label is transferred into the deuterio sites of **4f-d₃₈** upon reaction with TBE over the course of 160 min at $-80\text{ }^{\circ}\text{C}$, thus implying an irreversible step between **4f** and the ($p\text{-Ar}^{\text{F}}\text{PCP}$)Ir(H)(*neo*-hexyl) complex (**Cf**). Given the increased steric bulk of TBE relative to COE, it seems likely that TBE coordination to form the (unobserved) *cis*- and *trans*-($p\text{-Ar}^{\text{F}}\text{PCP}$)Ir(H)₂(TBE) complexes requires a higher activation barrier than COE coordination. This suggests that coordination of TBE is the rate-determining step in the hydrogenation.

The transfer dehydrogenation of COA by TBE was studied by ^1H and ^{31}P NMR spectroscopy in COA solution at $70\text{ }^{\circ}\text{C}$. Treatment of a mixture of COA/**6f** (330:1) (obtained by reaction of **4f** with 2 equiv of COE in neat COA solvent at $23\text{ }^{\circ}\text{C}$) with 20 equiv of TBE resulted in one turnover after ca. 20 min, as shown by generation of 1 equiv of TBA. At this stage, the major iridium species is the COE complex **6f**, but a small amount of TBE complex **9f** (ca. 10%) can be detected. After 5.5 turnovers (ca. 190 min), **6f** is the sole iridium complex present, even though a large excess of TBE is still present.

TBE is therefore much more weakly bound to the fragment **Af** than COE. These experiments show that under transfer dehydrogenation conditions previously reported once [COE] begins to rise, the catalyst resting state is the COE complex **6f**, and as observed, free COE inhibits turnover to a much higher degree than TBE.^{12,13}

The higher binding affinity of COE relative to TBE was independently proved by reaction of precatalyst **5f** with NaOrBu and 2.7 or 12.7 equiv of TBE in benzene- d_6 at $23\text{ }^{\circ}\text{C}$. These reactions do not give quantitative conversion of **5f** to **9f** but give mixtures of ($p\text{-Ar}^{\text{F}}\text{PCP}$)Ir(TBE) (**9f**) and ($p\text{-Ar}^{\text{F}}\text{PCP}$)Ir-(D)(C₆D₅) (**11f-d₆**)¹³ [2.7 equiv of TBE: **9f**/**11f-d₆** = 1:4, 12.7

(22) The assignment of complex **9f** is based on the absence of any hydridic resonances down to $-100\text{ }^{\circ}\text{C}$ as well as on the appearance of three multiplets in the ^1H NMR spectrum in a 1:1:1 ratio at 4.98, 4.03, and 3.15 ppm.

Scheme 5. Equilibration of Complexes **11f-d₆** and **9f** by Dissociative Ligand Exchange**Chart 2.** Catalytic Cycles for the Transfer Dehydrogenation of COA with TBE by Complexes **1** (left side)^a or **4** (right side)

^a Resembling the results obtained by Goldman et al. according to ref 11a.

equiv of TBE: **9f/11f-d₆** = 1.4:1]. In contrast, reaction of **5f** with NaOtBu with 2 equiv of COE in benzene-d₆ already results in quantitative generation of COE complex **6f** at 23 °C. Since complexes **9f** and **11f-d₆** are equilibrated through a dissociative ligand exchange (see Scheme 5) in a manner similar to that found for complexes (*p*-XPCP)Ir(H)(aryl)¹³ and complexes **6**, it is clear COE has a substantially higher binding affinity than TBE.

Summary

Reaction of (*p*-XPCP)IrHCl complexes **5a–f** with NaOtBu in neat cyclooctane at 23 °C generates 1:1 mixtures of complexes **4a–f**, (*p*-XPCP)IrH₂, and complexes **6a–f**, (*p*-XPCP)Ir(COE). At 70 °C, complexes **4a–f** and **6a–f** are equilibrated by the degenerate transfer dehydrogenation of COA with COE. At higher [COE], the equilibria **6** + COA ⇌ **4** + 2COE are shifted to the (*p*-XPCP)Ir(COE) complexes **6**, while a degenerate COE exchange in complexes **6** was found to be independent of [COE] and faster for the more electron-deficient ligand backbones *p*-XPCP. The separated back reaction **4f** + 2COE → **6f** + COA already proceeds at –100 °C via the intermediacy of two observable isomeric (*p*-Ar^FPCP)Ir(H)₂(COE) complexes **8f,8f'**. At –70 °C, complexes **8f,8f'** are consumed faster than they are generated under pseudo-first-order conditions, and *t*_{1/2} = ca. 9 min (20.5 equiv of COE) and ca. 17 min (10.5 equiv of COE) for the overall COE hydrogenation. Deuteration of COE (35 equiv) by **4f-d₃₈** at –100 °C reveals that coordination of COE to **4f-d₃₈** is rate-limiting for the overall hydrogenation reaction and that migratory insertion of (*p*-Ar^FPCP)Ir(H)₂(COE) **8f,8f'** is partially reversible, indicating that the reductive elimination of (*p*-Ar^FPCP)Ir(cyclooctyl)(H) is competitive with β-elimination to reform the dihydride **8f,8f'**. Hydrogenation of TBE by **4f** proceeds somewhat slower

than COE hydrogenation although still several orders of magnitude faster than with complex {C₆H₃-2,6-[CH₂P(*t*Bu)₂]₂}Ir(H)₂ (**1**).

The results reported permit a detailed comparison of the catalytic cycles for the Kaska/Jensen/Goldman system based on a pincer complex of the phosphine {C₆H₄-1,3-[CH₂P(*t*Bu)₂]₂} and the pincer catalysts studied here employing the more electron-deficient phosphinites {5-X-C₆H₄-1,3-[OP(*t*Bu)₂]₂}.¹³ Although very similar at first glance, the catalytic cycles for the transfer dehydrogenation of COA with TBE by complexes **1** or **4** exhibit some remarkably different characteristics. Catalytic cycles for the two systems are shown separately in Chart 2. Both systems C–H activate COA via a 14e⁻ fragment, {4-X-C₆H₂-2,6-[OP(*t*Bu)₂]₂}Ir [= (*p*-XPCP)Ir] (**Aa–f**) or {C₆H₃-2,6-[CH₂P(*t*Bu)₂]₂}Ir (**C**), respectively, while generation of the 14e⁻ fragment results from hydrogenation of TBE by the dihydride complexes **1** or **4**. β-Hydride elimination from unobserved Ir(H)(cyclooctyl) complexes generates COE and the catalytically active Ir(H)₂ complexes **1** or **4**. Under typical catalysis condition, that is, at high [TBE] or high [COE] relative to [Ir], the catalyst resting states are predominantly controlled by strong olefin to Ir interactions, while under more stoichiometric conditions (low [olefin]:[Ir] ratios) **1** or **4** are competitive resting states relative to the iridium olefin complexes (Chart 2).

A striking difference between catalysts derived from **1** and **4** is the interaction of their 14e⁻ fragments with olefins. {C₆H₃-2,6-[CH₂P(*t*Bu)₂]₂}Ir (**C**) has a high affinity for TBE because of formation of the oxidative addition product {C₆H₃-2,6-[CH₂P(*t*Bu)₂]₂}Ir(H)[CH=CHC(CH₃)₃]. The thermodynamic stability of this Ir(III)(vinyl)(hydride) complex results in its dominance at [TBE] > 0.3 M and strong inhibition of catalysis. Goldman's

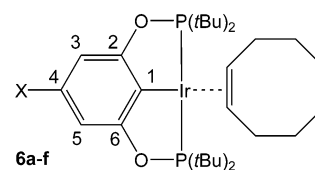
kinetic studies established an inverse first-order dependence of the catalytic turnover frequency on [TBE] because of the unfavorable equilibrium between **C** + TBE and the vinyl hydride complex, $\{C_6H_3-2,6-[CH_2P(tBu)_2]_2\}Ir(H)[CH=CHC(CH_3)_3]$.^{11a} In contrast, the affinity of $\{4-X-C_6H_2-2,6-[OP(tBu)_2]_2\}Ir$ (**A**) for TBE is rather low; TBE is not oxidatively added but simply π -coordinated to the metal. Such a different binding mode of TBE, despite the very similar geometric environment at the Ir centers in **A** and **C**, is clearly electronic in nature considering that **A** is much more electron-deficient than **C** and therefore prefers substrate interactions which do not increase its oxidation state from Ir(I). Furthermore, the steric requirements for coordination (instead of oxidative addition) of TBE or COE at **A** are rather different, radically disfavoring TBE coordination. Consequently, TBE is only a weak inhibitor of the catalytically active fragment **A**, and high TONs and TOFs can be achieved even at high [TBE] (~ 5.5 M). However, the much higher affinity of **A** for COE compared to TBE causes the catalytic inhibition after ca. 2200 TON for the best performing fragment **Af** due to pre-equilibrium formation of **6f**.

The second, and truly striking, difference between catalysts **1** and **4** is that **4f** hydrogenates TBE or COE at much lower temperatures (-70 °C) than **1** (55 °C) with comparable rate constants. Significantly, the rate-determining step for the hydrogenation of COE, and probably of TBE, by **4f** is the coordination of the olefin to **4f** rather than reductive elimination of *neo*-hexane, for example, from the intermediate (pincer)Ir(H)(*neo*-hexyl) complex, as was demonstrated by Goldman for the Kaska/Jensen/Goldman system.^{11a} Once again, the higher stability of the Ir(III) oxidation state in complexes derived from $\{C_6H_3-2,6-[CH_2P(tBu)_2]_2\}Ir$ (**C**) might account for this behavior when compared to a higher stability of Ir(I) oxidation states in complexes derived from (*p*-XPCP)Ir (**A**). Furthermore, the increased electrophilicity in these bis(phosphinite) complexes suggests a higher rate of insertion of the olefin dihydride complex.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk, high vacuum, and glovebox techniques. Argon was purified by passage through columns of BASF R3-11 (Chemalog) and 4 Å molecular sieves. Toluene-*d*₈, benzene-*d*₆, and methylcyclohexane-*d*₁₄ were degassed, vacuum-transferred, and stored over mol sieves in an argon atmosphere glovebox. COA was stirred with concentrated H₂SO₄ for several hours until it was olefin- and arene-free (GC and NMR analysis), and then it was distilled under vacuum and stored in an argon atmosphere glovebox. Cyclooctene was degassed and distilled under vacuum and stored in an argon atmosphere glovebox prior to use. TBE as received from Aldrich was degassed, vacuum-transferred, and stored in an argon atmosphere glovebox. Complexes **4** and **5** were synthesized by known procedures,^{12,13} and complex **4f-d**₃₈ (deuterated in all *tert*-butyl and hydridic positions) was obtained by heating a benzene-*d*₆ solution of **4f** for 12 h to 150 °C followed by high vacuum sublimation of the frozen solvent at 0 °C.²³ NMR spectra were recorded on a Bruker DRX 400 MHz instrument and are referenced either to residual protio solvent or to TMS as internal standard. Samples in neat protio solvent were shimmed by optimizing the intensity of the FID and referenced to the solvent chemical shift in CDCl₃. ³¹P chemical shifts are referenced to an external H₃PO₄ standard.

General Procedure for in Situ Generation of COE Complexes 6a–d,f. To a mixture of complex **5a** and 1.1 equiv of NaOtBu in a medium-walled J. Young NMR tube was added ca. 330 mg of COA containing the appropriate amount of COE in an argon atmosphere glovebox. The tube was occasionally shaken and treated with ultrasound until **5a** was completely dissolved. After 30–60 min at 23 °C, the starting complex had disappeared, and the solution was deep red colored. If no COE was added to the reaction mixture, 1:1 mixtures of **4a/6a** were obtained at 23 °C. A similar technique was used to generate 1:1 mixtures of **4b,c,f/6b,c,f**. Complexes **6c** and **6f** were alternatively generated by reaction of complexes **4c** and **4f**, respectively, with 2 to 2.5 equiv of COE in neat COA at 23 °C. ¹H NMR spectra in neat COA were referenced to the COA signal ($\delta = 1.57$ ppm). NMR data for **6a–d,f** are reported in neat COA. The ³¹P resonances are temperature-dependent. Samples for ³¹P {¹H}NMR spin saturation transfer experiments were prepared by an identical procedure in the absence of COE. Capillaries containing a toluene-*d*₈ solution of the *p*-HPCP ligand of complex **4c** $\{=C_6H_4-1,3-[OP(tBu)_2]_2\}$ were used as internal integration standards and gave identical results when compared to the software calibration routine provided by the Bruker XWinNMR package. *T*₁ relaxation times for the ³¹P NMR resonances were determined by the inversion recovery method. The relaxation delay was uniformly set to 15 s ($> 5 \times T_1$) for each SST experiment. Five independent SST experiments at 80 °C were conducted with 64 transients each, to obtain accurate rate data for the equilibrium of Scheme 2. Irradiation of the ³¹P{¹H} NMR resonance of complexes **4** or **6** with dB = 120 gave no changes of the integrals of **4** and **6**. Irradiation of the ³¹P{¹H} NMR resonance of complexes **4** with dB = 35 gave complete saturation of complex **4** and signal depletion of the respective complex **6**. Irradiation of the ³¹P{¹H} NMR resonance of complexes **6** with dB = 35 gave complete saturation of complex **6** and signal depletion of the respective complex **4**. Finally, irradiation in the middle of both resonances with dB = 35 gave no signal depletion of **4** or **6**. The *T*₁ relaxation times, in combination with the degree of signal depletion (and the thermodynamic ratio of **4/6** as a crosscheck), allowed for a quantitative analysis of the rates of the separated forward and back reactions of the equilibrium $6 + COA \rightleftharpoons 4 + 2COE$. Rates *R*_{obs1} for the half reaction $6 + COA \rightarrow 4 + 2COE$ were obtained by the algorithm $R_{obs1} = T_1(6)^{-1} \times [(1/I(6)) - 1]$ after irradiation of the ³¹P NMR signal of **4**, where *I*(**6**) is the relative integral of **6** obtained by complete versus no saturation of **4**. Rates *R*_{obs-1} for the back reaction were obtained by the respective algorithm $R_{obs-1} = T_1(4)^{-1} \times [(1/I(4)) - 1]$ after irradiation of the ³¹P NMR signal of **6**, where *I*(**4**) is the relative integral of **4** obtained by complete versus no saturation of **6**.



6a: ¹H NMR (400.1 MHz, 80 °C, neat COA): δ 6.11 (s, 2 H, 3- and 5-H), 4.18 [m br, 2 H, Ir(COE)], 3.67 (s, 3 H, OCH₃), remaining signals not observed because of COA. ³¹P{¹H} NMR (162 MHz, 80 °C, neat COA): δ 171.4. **6b:** ¹H NMR (400.1 MHz, 80 °C, neat COA): δ 6.33 (s, 2 H, 3- and 5-H), 4.22 [m br, 2 H, Ir(COE)], remaining signals not observed because of COA. ³¹P{¹H} NMR (162 MHz, 80 °C, neat COA): δ 171.2. **6c:** ¹H NMR (400.1 MHz, 80 °C, neat COA): δ 6.78 (t br, 1 H, 4-H), 6.47 (d, ²*J*_{H-H} = 8.0 Hz, 2 H, 3- and 5-H), 4.28 [m br, 2 H, Ir(COE)], remaining signals not observed because of COA. ³¹P{¹H} NMR (162 MHz, 80 °C, neat COA): δ 170.5. **6d:** ¹H NMR (400.1 MHz, 80 °C, neat COA): δ 6.2 (d, ²*J*_{F-H} = 10.3 Hz, 2 H, 3- and 5-H), 4.25 [m br, 2 H, Ir(COE)], remaining signals not observed because of COA. ³¹P{¹H} NMR (162 MHz, 80 °C, neat COA): δ 174.5. **6f:** ¹H NMR (400.1 MHz, 80 °C, neat COA): δ 7.79 (s, 2 H, 2'- and 6'-H), 7.52 (s, 1 H, 4'-H), 6.59 (s, 2 H, 3- and 5-H),

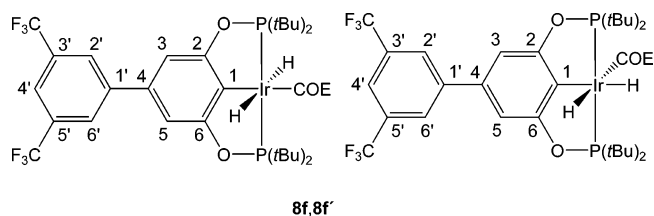
(23) In analogy to complex **1**, complexes **4** exchange their protio or deuterio label in the hydridic positions with the *tert*-butyl groups. See also ref 11k.

4.21 [m br, 2 H, Ir(COE)], remaining signals not observed because of COA. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, 80 °C, neat COA): δ 179.0.

Low-Temperature Hydrogenation of COE by Complex 4f in Toluene- d_8 and Methylcyclohexane- d_{14} and by Complex 4f- d_{38} in Methylcyclohexane- d_{14} . A solution of **4f** (8.1 mg, 10 μmol) and 300 μL toluene- d_8 in a septum-capped NMR tube was cooled to ca. -110 °C in a toluene/liquid nitrogen slush. A solution of COE (12.1 mg, 110 μmol , 11 equiv; 20.6 mg, 187 μmol , 18.7 equiv; 40.8 mg, 370 μmol , 37 equiv) in 100 μL toluene- d_8 was slowly added via syringe, and the content was carefully mixed while the tube remained in the toluene/liquid nitrogen slush. The tube was then inserted into the precooled (-105 °C) probe of the NMR spectrometer and shimmed before being heated to -90 °C and reshimmed. Formation of complexes **8f,8f'** and traces of **7f- d_8** were already evidenced by the first acquired experiment at -90 °C (after ca. 5 min). The buildup of complexes **8f,8f'** and **7f- d_8** was monitored over the course of 3 h (11 equiv of COE), while $>95\%$ (4 to 5 half-lives) of **4f** and **8f,8f'** was consumed to leave **7f- d_8** . Warming of the sample to -40 °C (within ca. 2 min) resulted in quantitative generation of the COE complex **6f**. Increasing amounts of COE added to complex **4f** resulted in higher buildup of complexes **8f,8f'**.

A solution of **4f** (8.1 mg, 10 μmol) and 280 μL methylcyclohexane- d_{14} in a septum-capped NMR tube was cooled to ca. -125 °C in an *n*-hexane/liquid nitrogen slush. A solution of COE (11.6 mg, 105 μmol , 10.5 equiv; 15.4 mg, 140 μmol , 14 equiv; 22.6 mg, 205 μmol , 20.5 equiv) in 100 μL methylcyclohexane- d_{14} was slowly added via syringe, and the content was carefully mixed while the tube remained in the *n*-hexane/liquid nitrogen slush. The tube was then inserted into the precooled (-110 °C) probe of the NMR spectrometer, and the sample was shimmed. An ^1H NMR experiment at -110 °C indicated no consumption of complex **4f**. The sample was then heated to -70 °C in the probe and reshimmed. Substantial amounts of complexes **8f,8f'** (10–15%, depending on the equivalents of COE added) and **6f** (10–16%) were already formed by the time the first experiment was acquired (ca. 4 min). The consumption of **4f** and **8f,8f'** as well as the buildup of complex **6f** was monitored by ^1H NMR experiments. The well-separated signals of 3- and 5-H of complexes **4f** (6.83 ppm), **8f,8f'** (6.58 ppm), and **6f** (6.73 ppm) were suitable for accurate integration and allowed for the determination of $t_{1/2}$ of complex **4f** = ca. 17 min (10.5 equiv of COE) and ca. 9 min (20.5 equiv of COE). Similar experiments were conducted with **4f- d_{38}** and 35 equiv of COE in methylcyclohexane- d_{14} at -100 °C. In these experiments, the buildup of hydridic resonances for complexes **8f,8f'- d_{38}** was observed, while no hydridic label in complex **4f- d_{38}** was detectable. **4f** ^1H NMR (400.1 MHz, -70 °C, methylcyclohexane- d_{14}): δ 7.94 (s, 2 H, 2'- and 6'-H), 7.69 (s, 1 H, 4'-H), 6.83 (s, 2 H, 3- and 5-H), *t*Bu not observed because of excess COE, -15.80 (t br, 2 H, IrH₂). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -70 °C, methylcyclohexane- d_{14}): δ 205.4.

8f,8f': ^1H NMR (400.1 MHz, -70 °C, methylcyclohexane- d_{14} , second isomer in {}): δ 7.85 {7.85} (s, 2 H, 2'- and 6'-H), 7.60 {7.60} (s, 1 H, 4'-H), 6.58 {6.58} (s, 2 H, 3- and 5-H), 3.86 {3.42} (m, COE), 2.69 {2.69} (m, COE), *t*Bu not observed because of excess COE, -9.80 {-10.23} (t br, $^2J_{\text{PH}} = 15.5$ Hz 2 H, IrH₂). $^{31}\text{P}\{^1\text{H}\}$ NMR (162.1 MHz, -70 °C, methylcyclohexane- d_{14}): δ 167.2 {167.1} (br).



6f: ^1H NMR (400.1 MHz, -70 °C, methylcyclohexane- d_{14}): δ 7.92 (s, 2 H, 2'- and 6'-H), 7.65 (s, 1 H, 4'-H), 6.73 (s, 2 H, 3- and 5-H), 4.23 (m), 2.48 (m), *t*Bu not observed because of excess COE. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -70 °C, methylcyclohexane- d_{14}): δ . 184.2 and 168.6 (d each, $^2J_{\text{PP}} = 348$ Hz).

Low-Temperature Hydrogenation of TBE by Complexes 4f and 4f- d_{38} . A solution of **4f** (8.1 mg, 10 μmol) and 280 μL methylcyclohexane- d_{14} in a septum-capped NMR tube was cooled to ca. -125 °C in an *n*-hexane/liquid nitrogen slush. A solution of TBE (10.1 mg, 120 μmol , 12 equiv; 29.5 mg, 350 μmol , 35 equiv) in 100 μL methylcyclohexane- d_{14} was slowly added via syringe, and the content was carefully mixed while the tube remained in the *n*-hexane/liquid nitrogen slush. The tube was then inserted into the precooled (-110 °C) probe of the NMR spectrometer and shimmed before heating to -80 °C and reshimming. With 12 equiv of TBE, slow formation of the TBE complex **9f** was observed with a $t_{1/2} =$ ca. 70 min at -80 °C. Deuteriation of TBE (35 equiv) with **4f- d_{38}** at -80 °C resulted in observation only of complexes **4f- d_{38}** and **9f- d_{36}** . **9f**: ^1H NMR (400.1 MHz, -80 °C, methylcyclohexane- d_{14}): δ 7.93 (s, 2 H, 2'- and 6'-H), 7.66 (s, 1 H, 4'-H), 6.72 (s, 2 H, 3- and 5-H), 4.83 (m, 1 H), 3.81 (m, 1 H), 3.22 (m, 1 H), *t*Bu not observed because of residual protiomethylcyclohexane/excess TBE. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -80 °C, methylcyclohexane- d_{14}): δ 180.5 and 170.3 (d each, $^2J_{\text{PP}} = 342$ Hz each, 1:1 P).

In Situ Generation of the TBE Complex (Ar^FPCP)Ir(TBE) (9f) from 5f. Mixtures of complexes **9f** and **11f- d_6** were obtained by reacting complex **5f** and NaOtBu with variable amounts of TBE in benzene- d_6 solution (see Scheme 5). **9f**: ^1H NMR (400.1 MHz, 23 °C, benzene- d_6): δ 7.87 (s, 2 H, 2'- and 6'-H), 7.67 (s, 1 H, 4'-H), 7.02 (s, 2 H, 3- and 5-H); 4.99, 4.07, and 3.15 (m each, 1 H each, TBE), 1.28 (s, 9 H, TBE), 1.13 (vt, $J_{\text{PH}} = 7.0$ Hz, 36 H, 4 × *t*Bu). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, 23 °C, benzene- d_6): δ 176.9. **11f- d_6** : ^1H NMR (400.1 MHz, 23 °C, benzene- d_6): δ 7.87 (s, 2 H, 2'- and 6'-H), 7.67 (s, 1 H, 4'-H), 6.97 (s, 2 H, 3- and 5-H), 1.34 (vt, $J_{\text{PH}} = 7.0$ Hz, 36 H, 4 × *t*Bu). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, 23 °C, benzene- d_6): δ 182.0.

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