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Catalytic Dehydrogenation of Alkanes by PCP−Pincer Iridium Complexes Using Proton and Electron Acceptors

Arun Dixith Reddy Shada, Alexander J. M. Miller, Thomas J. Emge, and Alan S. Goldman*

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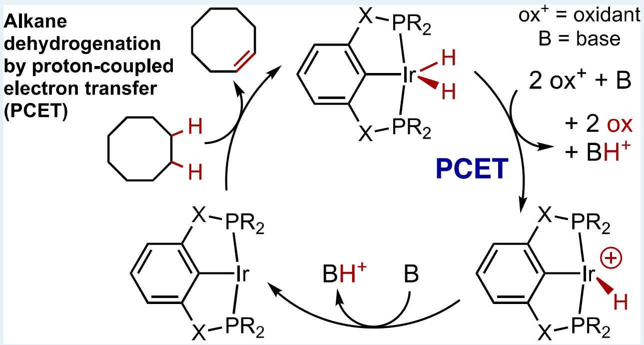
ABSTRACT: Dehydrogenation to give olefins offers the most broadly applicable route to the chemical transformation of alkanes. Transition-metal-based catalysts can selectively dehydrogenate alkanes using either olefinic sacrificial acceptors or a purge mechanism to remove H_2; both of these approaches have significant practical limitations. Here, we report the use of pincer-ligated iridium complexes to achieve alkane dehydrogenation by proton-coupled electron transfer, using pairs of oxidants and bases as proton and electron acceptors. Up to 97% yield was achieved with respect to oxidant and base, and up to 15 catalytic turnovers with respect to iridium, using *t*-butoxide as base coupled with various oxidants, including oxidants with very low reduction potentials. Mechanistic studies indicate that (pincer)IrH$_2$ complexes react with oxidants and base to give the corresponding cationic (pincer)IrH$^+$ complex, which is subsequently deprotonated by a second equivalent of base; this affords (pincer)Ir which is known to dehydrogenate alkanes and thereby regenerates (pincer)IrH$_2$.



KEYWORDS: *alkane dehydrogenation, C−H activation, pincer complexes, proton-coupled electron transfer, iridium catalysis*

■ INTRODUCTION

The dehydrogenation of alkanes to give olefins offers almost unlimited potential as a route to their catalytic conversion to commodity chemicals or to alkanes of higher fuel value, e.g., through olefin coupling after dehydrogenation.[1,2] Over the past decades, great progress has been made toward the use of molecular transition-metal catalysts for alkane dehydrogenation.[3−7] They offer highly attractive regioselectivity for the terminal position of *n*-alkanes in some cases[6,8−10] and operating temperatures much lower than required with conventional heterogeneous catalysts.[11,12] The most widely studied class of such catalysts has been pincer-ligated iridium complexes.[1,13−32]

Alkane dehydrogenation to give olefins and H_2 is highly endothermic.[33] Two general approaches have been developed to address the challenge thus presented in the application of transition-metal-based molecular catalysts. Most commonly, a sacrificial olefinic hydrogen acceptor is used, in which case the overall reaction is approximately thermoneutral. Not only does this introduce the cost of the olefin, however, it also raises the need for separation of hydrogenated and any unreacted acceptor.

An alternative approach to the use of sacrificial acceptors is simply to purge the hydrogen byproduct of dehydrogenation from the solution, typically by refluxing.[34,35] However, at the relatively low temperatures compatible with molecular catalysts, the steady-state concentration of H_2 is extremely low even at low concentration of olefin product and becomes increasingly lower as olefin accrues. Such acceptorless dehydrogenation requires significant energy input and the rate of H_2 expulsion is proportional to the low H_2 concentrations. The long reaction times allow for undesirable secondary reactions such as isomerization, resulting in the loss of valuable regioselectivity.[5−7] Moreover, the partial pressure of the hydrogen produced is necessarily extremely low, rendering it very difficult to realize its significant potential value as a byproduct.

An approach that is very distinct from the transfer of hydrogen to an olefin or purging H_2 from the solution would be the separate removal of electrons and protons. In contrast with the sacrifice of an olefin or the high energy input required for acceptorless dehydrogenation, the transfer of electrons and protons could proceed as in a fuel cell,[36−40] yielding useful energy. Alternatively, in the absence of O_2 at the cathode, the protons could be reduced to give hydrogen. Although this would require the input of electrical energy, it could yield H_2 at a very low energetic cost compared with the electrolysis of water—and the "byproduct" would be a valuable olefin instead of dioxygen.[41,42]

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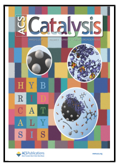

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Nonelectrochemical approaches to dehydrogenation based on the transfer of electrons and protons are also potentially very attractive. Dioxygen is the most obviously favorable acceptor based on thermodynamic and economic considerations, while the byproduct, water, could be easily separated from the mixture. The use of dioxygen for alkane dehydrogenation presents challenges, including oxidative decomposition of the catalyst, unwanted oxidation reactions of the alkane and olefin products, and safety issues in dealing with alkanes, oxygen, and catalysts.[43−45] These problems, however, can be circumvented via a system for electron and proton transfer in which O_2 does not need to come into contact with either a catalyst or a reagent. This approach is exemplified most famously in the case of the Wacker oxidation of ethylene,[46] in which case electrons are ultimately transferred to O_2 by Cu(I), which is returned to solution as Cu(II).

Evidence for the viability of separated proton-coupled electron-transfer (PCET) reactions[47,48] for the activation of C−H bonds in general[41,48−50] and by pincer-iridium systems in particular[51,52] has been demonstrated recently. In this paper, we report this approach, using one-electron oxidants and Brønsted bases,[47,49] for the catalytic dehydrogenation of alkanes. Incorporation of such reactions into either electrochemical or nonelectrochemical systems offers the possibility of a fundamentally different and highly attractive class of alkane dehydrogenation reactions.

■ RESULTS AND DISCUSSION

Dehydrogenation of cyclooctane (COA) is somewhat less endothermic than dehydrogenation of typical alkanes,[33] and cycloalkane dehydrogenation does not introduce complications due to the formation of various double-bond isomers. Additionally, the resulting olefin, cyclooctene (COE), tends to bind to metal centers less strongly than linear olefins[53] and has less tendency to form allyl complexes;[54] for both reasons, it is therefore less likely to inhibit catalysis. COA has therefore long been the standard substrate of choice for studies of alkane dehydrogenation catalysis, at least at the early stages of catalyst development.[3−7,55]

The free energy of dehydrogenation of COA, to give COE and H_2, is $\Delta G° = 15.5$ kcal/mol, while $\Delta G° = 97.2$ kcal/mol for the formation of $2H^\bullet$ from H_2.[33] Therefore, for the formation of COE and two hydrogen atoms from COA, $\Delta G° = 112.7$ kcal/mol (eqs 1−3).

$$\text{COA} \rightarrow \text{COE} + \text{H}_2 \quad \Delta G° = 15.5\ \text{kcal/mol} \tag{1}$$

$$\text{H}_2 \rightarrow 2\text{H}^\bullet \quad \Delta G° = 97.2\ \text{kcal/mol} \tag{2}$$

$$\text{COA} \rightarrow \text{COE} + 2\text{H}^\bullet \quad \Delta G° = 112.7\ \text{kcal/mol} \tag{3}$$

The effective bond dissociation free energy (BDFE_{eff}) of an oxidant/base pair is the free energy of the reaction of a free H atom with that pair, to give the respective reduced and protonated species.[47,56] For reaction 4 to be ergoneutral ($\Delta G° = 0$), therefore, the BDFE_{eff} for the oxidant/base couple must be (112.7 kcal/mol)/2 or 56.35 kcal/mol. It is perhaps worth noting that this required BDFE_{eff} is much less than the BDFE of an alkane C−H bond.

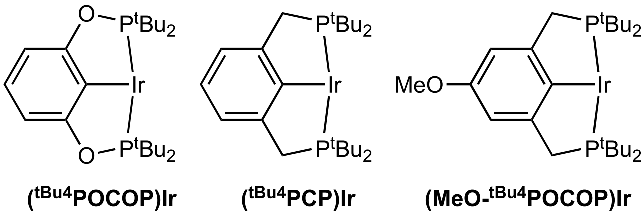
$$\text{COA} + 2\text{Ox}^+ + 2\text{B} \rightarrow \text{COE} + 2\text{Ox} + 2\text{BH}^+ \tag{4}$$

Equation 5 gives the value of BDFE_{eff} for any oxidant/base couple (for acetonitrile), where $\text{p}K_\text{a}(\text{BH}^+)$ is the $\text{p}K_\text{a}$ of the conjugate acid of B and $E°(\text{A}^{+/0})$ is the reduction potential relative to Cp_2Fe^+.[49] For example, for KO^tBu, the $\text{p}K_\text{a}$ of the conjugate acid in acetonitrile is reportedly 40,[47] while $E°$ for Cp_2Fe^+ is by definition zero. Thus, the $\text{Cp}_2\text{Fe}^+/\text{KO}^t\text{Bu}$ couple has a BDFE_{eff} of 109.7 kcal/mol, which is much greater than is thermodynamically required for COA dehydrogenation.

$$\begin{aligned}&\text{BDFE}_{\text{eff}}(\text{Ox} + \text{BH}^+)\\&\quad = 1.37\text{p}K_\text{a}(\text{BH}^+) + 23.1E°(\text{A}^{+/0}) + 54.9\ \text{kcal/mol}\end{aligned} \tag{5}$$

Our initial choices of an oxidant and Brønsted base, respectively, were Ag^+ and the *t*-butoxide anion.[57] Its very high basicity notwithstanding, *t*-butoxide has been demonstrated to be surprisingly compatible with various oxidants.[47] To a *p*-xylene-d_{10} solution of $(^{t\text{Bu}4}\text{POCOP})\text{IrH}_2$ (20 mM; Scheme 1) and COA (300 mM), 2.0 equivalents (based on Ir) of $\text{Ag}[\text{BF}_4]$ and 2.0 equivalents of KO^tBu were added. Heating to 120 °C rapidly resulted in a color change from dark brown to orange-brown and the formation of silver mirror on the wall of the NMR tube (Scheme 2, first reaction). The ^{31}P NMR spectrum showed a single signal at δ 177.2. The ^{1}H NMR spectrum revealed a triplet at δ −42.96 ($^2J_{\text{P-H}} = 13.1$ Hz), indicative of a hydride ligand trans to a vacant coordination site, and inequivalent ^{t}Bu groups.[58] These NMR spectroscopic features are very similar to those of $[(^{t\text{Bu}4}\text{POCOP})\text{Ir(H)(acetone)}][\text{B}(\text{C}_6\text{F}_5)_4]$ (^{31}P NMR δ 174.4; ^{1}H NMR δ −42.28, $^2J_{\text{P-H}} = 12.4$ Hz),[59] synthesized by Brookhart via the reaction of $(^{t\text{Bu}4}\text{POCOP})\text{IrH}_2$ with hydride abstraction agent $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. In the absence of any evidence for a ligand other than the hydride and pincer (i.e., a ligand analogous to the acetone in Brookhart's complex) or any obvious source of such ligand, we expect that the BF_4 anion would coordinate weakly at the site trans to the $^{t\text{Bu}4}$POCOP ipso carbon. However, the presence of either a weakly coordinating solvent molecule or an adventitious species cannot be excluded.

Scheme 1. (Pincer)Ir Units Used in This Work

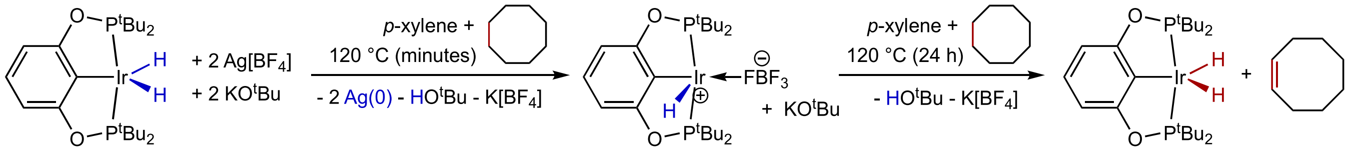


Continued heating of the reaction mixture for 24 h at 120 °C results in the formation of COE (0.9 eq as determined by ^{1}H NMR and gas chromatography) and the reappearance of $(^{t\text{Bu}4}\text{POCOP})\text{IrH}_2$ (Scheme 2, second reaction).[58] This is readily explained in that deprotonation of the cationic hydride (Scheme 3) by the remaining equivalent of KO^tBu should afford the key Ir(I) intermediate, $(^{t\text{Bu}4}\text{POCOP})\text{Ir}$, that is presumed to undergo C−H addition and then β−H elimination to yield olefin in the cycle for catalytic alkane dehydrogenation by $(^{t\text{Bu}4}\text{POCOP})\text{IrH}_2$.[53]

The overall reaction shown in Scheme 2 was also conducted at 150 °C, for 16 h, giving the same yield of COE (90% relative to $\text{Ag}[\text{BF}_4]$ or KO^tBu), as determined by gas chromatography (Table 1, entry 1). The reaction also gave a 90% yield when conducted in neat COA (Table 1, entry 2).

The overall reaction of Scheme 2 comprises a catalytic cycle for dehydrogenation of COA driven by proton-coupled electron

Scheme 2. Reaction of (^{tBu4}POCOP)IrH$_2$ with Ag[BF$_4$] and KO^{t}Bu in Cyclooctane



Scheme 3. Proposed Pathway for the Reaction of [(^{tBu4}POCOP)IrH][BF$_4$] with KO^{t}Bu and Cyclooctane

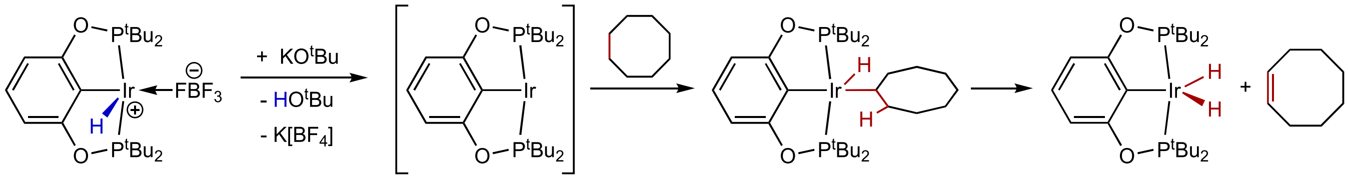


Table 1. Dehydrogenation of Cyclooctane by Pincer Iridium Complexes with [Ag][BF$_4$] and KO^{t}Bu (150 °C, 16 h)

entry	catalyst (concentration)	concentration KO^{t}Bu (mM)	concentration AgBF$_4$ (mM)	concentration COA	concentration product (COE) (mM)	TON (yield)[a]
1	(^{tBu4}POCOP)IrH$_2$ (20 mM)	40	40	300 mM	18	0.9 (90%)
2	(^{tBu4}POCOP)IrH$_2$ (20 mM)	40	40	neat (7.4 M)	18	0.9 (90%)
3	(^{tBu4}POCOP)IrH$_2$ (20 mM)	80	80	neat (7.4 M)	36	1.8 (90%)
4	(^{tBu4}POCOP)IrH$_2$ (4 mM)	120	120	neat (7.4 M)	56	14 (93%)
5	none	80	80	neat (7.4 M)	not detected	0
6	(^{tBu4}POCOP)IrH$_2$ (20 mM)	80	none	neat (7.4 M)	not detected	0
7	(^{tBu4}POCOP)IrH$_2$ (20 mM)	none	80	neat (7.4 M)	not detected	0
8	(MeO-^{tBu4}POCOP)IrH$_2$ (4 mM)	120	120	neat (7.4 M)	58	14.5 (97%)
9	(^{tBu4}PCP)IrH$_2$ (4 mM)	120	120	neat (7.4 M)	58	14.5 (97%)

[a] TON = number of turnovers based on the iridium catalyst; yield based on silver salt or KO^{t}Bu.

transfer. To our knowledge, this is the first reported example of this approach to alkane dehydrogenation.

While Scheme 2 represents a single catalytic turnover for dehydrogenation, multiple turnovers can be achieved. The addition of 4 equiv each of Ag[BF$_4$] and KO^{t}Bu to a COA solution of (^{tBu4}POCOP)IrH$_2$ (20 mM) resulted in the formation of 36 mM COE, a 90% yield, and 1.8 TO (catalytic turnovers; Table 1, entry 3). Much higher quantities of Ag[BF$_4$] and KO^{t}Bu were not feasible, but with a lower concentration of (^{tBu4}POCOP)IrH$_2$ (4 mM) and 30 equiv of Ag[BF$_4$] and KO^{t}Bu, 56 mM COE was produced (14 TO and 93% yield based on oxidant and base; Table 1, entry 4).

Control experiments were conducted in which the conditions given in Table 1, entry 3, were reproduced but with the omission of (^{tBu4}POCOP)IrH$_2$, Ag[BF$_4$], or KO^{t}Bu. No COE formation was observed in these experiments (Table 1, entries 5, 6, and 7).

Comparable results were obtained with the other (pincer)Ir complexes of Scheme 1. With the same conditions as used for the experiment of Table 1, entry 4, but with the use of (MeO-^{tBu4}POCOP)IrH$_2$ or (^{tBu4}PCP)IrH$_2$ (Scheme 1), approximately equal or greater yields of COE were obtained, 58 mM in both cases (14.5 TO, 97% yield; Table 1, entries 8 and 9).

While the use of Ag$^+$ as oxidant serves as proof of principle, it surely does not represent a practical advance over the use of olefinic acceptors. A practical oxidant must be easily reoxidized, ultimately either by oxygen or at an anode of an electrochemical cell, whereas Ag$^+$ forms metallic silver. Turning our attention to such oxidants, we considered metallocenium cations, which also offer the possibility of "tuning" oxidation potentials and thereby the reaction thermodynamics. [Cp$_2$Fe][BF$_4$], [Cp$_2$Fe][PF$_6$], and [Cp$_2$Fe][BAr$_4^F$] (BAr$_4^F$ = B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$) were initially investigated. KO^{t}Bu and the Cp$_2$Fe$^+$ salts were added (30 equiv each) to the COA solutions of (^{tBu4}PCP)IrH$_2$ (4 mM), and the mixture was heated at 150 °C for 16 h. Turnover numbers were very limited (1.2, 0.8, and 2.0 TO, respectively, out of a theoretical limit of 15 TO; Table 2, entries 1−3), but this was considered likely attributable to the very low solubility of these salts in alkane solvent.

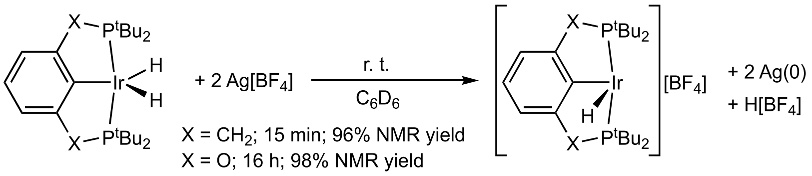
Ferrocenium salts that were expected to be more soluble than those of the parent Cp$_2$Fe$^+$ were then investigated.[65] With BF$_4$ and PF$_6$ salts of bis(acetylcyclopentadienyl)iron(III), 2.0 and

Table 2. Catalytic Dehydrogenation of Cyclooctane by (^{tBu4}PCP)IrH$_2$ with Various Metallocenium Salts as Oxidants[a]

entry	metallocenium salt	$E°$ (vs Fc/Fc+)	TON
1	[Fc][BF$_4$]	0.00	1.2
2	[Fc][PF$_6$]	0.00	0.8
3	[Fc][BArF$_4$]	0.00	2
4	[Ac$_2$Fc][PF$_6$]	0.51[b,c]	2.2
5	[Ac$_2$Fc][BF$_4$]	0.51[b,c]	2
6	[Me$_2$Fc][PF$_6$]	−0.11[d], −0.10[e]	7.4
7	[Me$_2$Fc][BF$_4$]	−0.11[d], −0.10[e]	8
8	[^{i}Pr$_2$Fc][BF$_4$]	−0.11[d]	10
9	[^{i}Pr$_2$Fc][PF$_6$]	−0.11[d]	9
10	[Cp$_2$Co][PF$_6$]	−1.33[d,f]	12
11	[Cp*$_2$Co][PF$_6$]	−1.94[f], −1.91[g]	8

[a] Conditions: (^{tBu4}PCP)IrH$_2$ (4 mM), metallocene (120 mM), KO^{t}Bu (120 mM), COA solvent, 150 °C, and 16 h. [b] CH$_2$Cl$_2$ solvent, ref 60. [c] Acetonitrile solvent, ref 61. [d] CH$_2$Cl$_2$ solvent, ref 62. [e] Acetonitrile solvent, ref 63. [f] CH$_2$Cl$_2$ solvent, ref 64. [g] Acetonitrile solvent, ref 64.

Scheme 4



2.2 TO COE were obtained, respectively (Table 2, entries 4 and 5). The methylcyclopentadienyl derivatives gave better results, 8.0 and 7.4 TO, respectively, and the isopropylcyclopentadienyl derivatives gave 10 and 9 TO, respectively (Table 2, entries 6–9). Note that the solubility of even these salts in alkane solvent is still very limited.

A much weaker oxidant than Cp_2Fe^+ is Cp_2Co^+ ($E° = -1.33$ V). For the Cp_2Co^+/KO^{t}Bu couple, according to eq 5, $BDFE_{eff}$ is equal to 79.0 kcal/mol. Although Cp_2Co^+ is rarely viewed as an oxidant (rather, cobaltocene is prized as a reductant[36]), it is still capable of pairing with *t*-butoxide to provide about 23 kcal/mol of thermodynamic driving force for the dehydrogenation of COA. The use of cobaltocenium as an oxidant was therefore of interest in this context to probe the driving force needed above the theoretical value. Additionally, we were interested to see if an oxidant/base couple with a $BDFE_{eff}$ much less than that of the cyclooctane C–H bond (ca. 87 kcal/mol[66−68]) would be effective.

Surprisingly, the use of cobaltocenium actually gave a higher TON (12) (Table 2 entry 10) than ferrocenium, or any of the ferrocenium derivatives investigated, under the same reaction conditions. The observation of the characteristic chemical shift of cobaltocene at 55 ppm[69] as well as the formation of *t*-butanol confirmed the reaction stoichiometry of eq 4.

Remarkably, even the very weak oxidant decamethylcobaltocenium, $Cp^*_2Co^+$, ($E° = -1.94$ V)[64] was found to be an effective oxidant. A total of 8 TO was obtained with 30 equiv $[Cp^*_2Co][PF_6]$ (Table 2, entry 11; 53% yield), or somewhat less than with $[Cp_2Co][PF_6]$, but equal to the highest values obtained with Cp_2Fe^+ derivatives. The $BDFE_{eff}$ of the $Cp^*_2Co^+$/KO^{t}Bu couple is 64.9 kcal/mol, much less than that of the ferrocenium/KO^{t}Bu couples but still significantly greater than the $BDFE_{eff}$ that is thermodynamically required for COA dehydrogenation. Thus, consistent with a mechanism in which the C–H bonds are cleaved by the Ir center, not directly by the oxidant/base couple, dehydrogenation can proceed even though the $BDFE_{eff}$ of the oxidant/base pair is much less than the BDFE of the cyclooctane C–H bond.

We would exercise caution in drawing mechanistic conclusions based on the above experiments since the metallocenium salts are not fully soluble. Given that caveat, however, we consider that the improved yields from cobaltocenium vs ferrocenium may be attributable to overoxidation by the latter. Notably, the oxidation/deprotonations are proposed to yield the Ir(I) species, (pincer)Ir, and it seems plausible that this species in particular may be susceptible to oxidation in a catalytically unproductive degradation. The same explanation might also apply to the observation that higher TONs were achieved with methyl- and isopropyl-substituted ferrocenium than with the more strongly oxidizing acetyl derivative (Table 2).

Isolation of the Cationic Intermediate. The reaction of either $(^{tBu4}PCP)IrH_2$ or $(^{tBu4}POCOP)IrH_2$ with $Ag[BF_4]$ at room temperature, even in the absence of added base, results in the formation of the corresponding $(pincer)IrH^+$ species with the former dihydride complex reacting rapidly and the latter reacting over the course of 16 h. The cationic complexes were identified by the ^1H NMR chemical shift characteristic of a hydride ligand trans to a vacant coordination site at −44.85 and −42.96 ppm, respectively, Scheme 4.[58]

Thus, 2 equiv of $Ag[BF_4]$ effectively acts to remove a hydride anion.[57,70] The implication that this "oxidative removal of hydride" should be possible electrochemically has already been demonstrated;[52,71] electrochemical oxidation of $(^{tBu4}PCP)IrH_4$ (either preceding or following the loss of H_2) in the presence of lutidine gives $[(^{tBu4}PCP)IrH(lutidine)^+]$.[52]

Slow evaporation of a pentane/benzene (3:1) solution of the cationic ^{tBu4}PCP complex at room temperature afforded orange-brown crystals. Single-crystal X-ray diffraction revealed the presence of a water molecule coordinated to iridium (Figure 1).

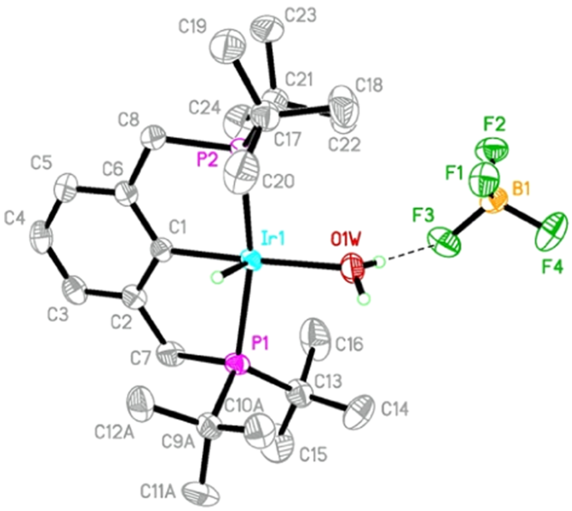
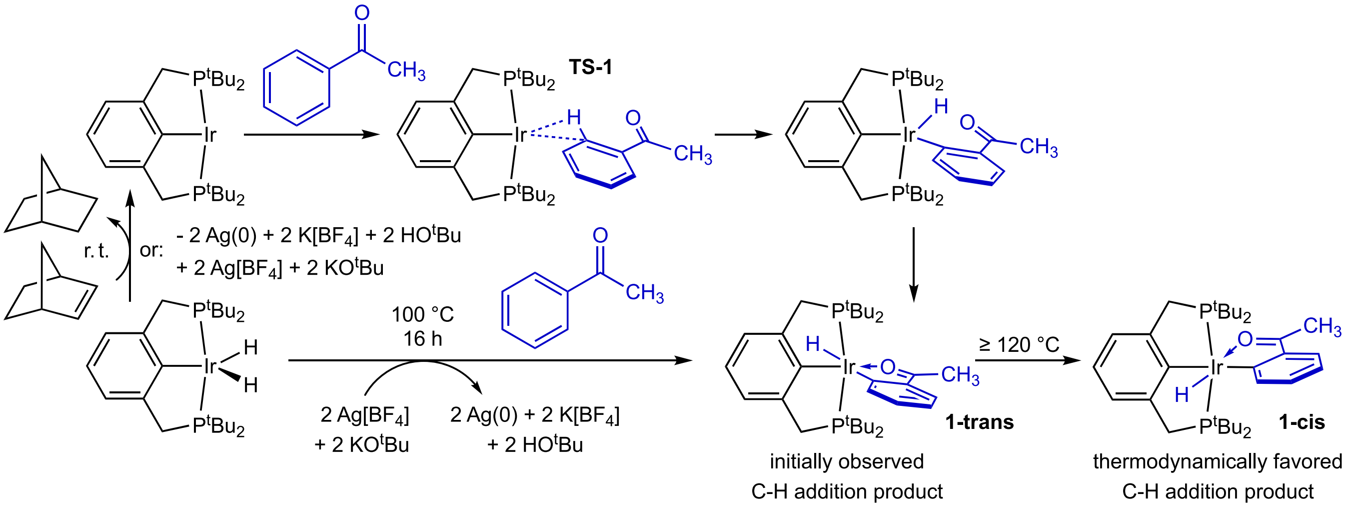


Figure 1. ORTEP structure of $[(^{tBu4}PCP)Ir(H)(H_2O)][BF_4]$ at the 50% probability level (C-bound hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ir(1)–C(1) 2.008(3); Ir(1)–O(1W) 2.207(2); Ir(1)–P(1) 2.3108(8); Ir(1)–P(2) 2.3137(8); Ir(1)–H(1A) 1.599(7); C(1)–Ir(1)–O(1W) 177.57(11); C(1)–Ir(1)–P(1) 83.41(9); O(1W)–Ir(1)–P(1) 98.86(7); O(1W)–Ir(1)–P(2) 94.29(7); P(1)–Ir(1)–P(2) 166.84(3); C(1)–Ir(1)–H(1A) 86.3(3); and O(1W)–Ir(1)–H(1A) 92.8(3).

It is not clear if the major solution phase species observed by ^1H NMR likewise has a bound molecule of water. Arguing against that possibility, however, is the observation that addition of 1 equiv water to a C_6D_6 solution of $[(^{tBu4}PCP)IrH]^+$ results in the formation of $(^{tBu4}PCP)Ir(OH)H$[72] at room temperature; the fate of the lost proton (eq 6) is not clear. In a related manner, under the same conditions where alkane dehydrogenation was observed, i.e., in the presence of KO^{t}Bu, addition of water led to conversion to $(^{tBu4}PCP)Ir(OH)H$ and catalysis was completely inhibited.

Scheme 5. Proposed Pathway for the Formation of the Trans C−H Addition Product of Acetophenone via Loss of 2H from (^{tBu4}PCP)IrH$_2$ through Hydrogenation of Norbornene (ref 80) and through Oxidation and Deprotonation (Present Work)



$$[(^{tBu4}PCP)IrH]^+ + H_2O \rightarrow (^{tBu4}PCP)Ir(H)(OH) + H^+ \quad (6)$$

Weak binding of water to the Ir center is indicated by the long Ir−O bond distance, 2.207(2) Å, a value typical of cationic Ir aquo complexes,[73−78] which compares with 2.00(3) Å reported for (^{tBu4}PCP)Ir(OH)H.[72] By contrast, the Ir−P and Ir−C bond lengths, as well as the P−Ir−C angles, are identical for aquo and hydroxy[72] complexes within the standard error of the crystallographic determinations.[58]

Trapping the Ir(I) Intermediate. As noted above, deprotonation of the cationic oxidation species, (pincer)IrH$^+$, would afford the Ir(I) intermediates, (pincer)Ir, which are presumed to be the species that effect alkane dehydrogenation in the catalyses with olefinic acceptors.[53,79] This fragment, at least in the case of the ^{tBu4}PCP pincer ligand, has been reported to undergo an unusual and characteristic reaction with arenes with coordinating functional groups (acetophenone, nitrobenzene).[80] Specifically, it undergoes addition of the C−H bond ortho to the functional group to give a six-coordinate complex in which the added C and H are positioned mutually trans, while the coordinating functional group is trans to the ^{tBu4}PCP ipso carbon (**1-trans**; Scheme 5). It was therefore concluded that the coordinating group did not act as a "directing" group but rather acted to trap the initial C−H addition product. Importantly, the C−H-trans isomer **1-trans** was found to be the *kinetic* product of C−H addition and O-coordination, as evidenced by the fact that it slowly isomerized to the thermodynamically more stable C−H-cis isomer, **1-cis**, upon heating (Scheme 5).[80]

To help determine if C−H addition induced by oxidation/deprotonation proceeded through the same key intermediate resulting from hydrogenation of olefin, 2 equiv of Ag[BF$_4$] and KO^{t}Bu were added to a *p*-xylene-d_{10} solution of (^{tBu4}PCP)IrH$_2$ and acetophenone. The immediate formation of (^{tBu4}PCP)IrH$^+$ was observed by ^{1}H NMR spectroscopy. Heating at 100 °C afforded C−H adduct **1-trans**, i.e., the same product that was previously obtained from the reaction of (^{tBu4}PCP)IrH$_2$ with norbornene in the presence of acetophenone.[80] Further heating at 120 °C resulted in isomerization to the thermodynamically more stable **1-cis**, again as previously observed in the reaction with norbornene (Scheme 5).[80]

The formation of the trans-C−H adduct **1-trans** is inconsistent with C−H addition occurring while the carbonyl oxygen is coordinated to iridium, i.e., with the carbonyl acting as a "directing group."[80] It strongly implicates the transition state **TS-1**, the same transition state as is proposed for addition following loss of hydrogen to olefin. By extension, it implies the same prior intermediate, the three-coordinate (^{tBu4}PCP)Ir(I) fragment, obtained by deprotonation of (^{tBu4}PCP)IrH$^+$ in the case of the present reaction.

Use of Other Bases. We attempted the use of several bases as alternatives to KO^{t}Bu for catalytic COA dehydrogenation, in all cases with 10 mM (^{tBu4}PCP)IrH$_2$ in *p*-xylene-d_{10} with 400 mM COA, 8 equiv of Ag[BF$_4$] and 8 equiv of base (thus the theoretical yield is 4 equiv or 40 mM COE). After 16 h at 150 °C, 3.8 equiv of COE was obtained with the use of KO^{t}Bu under these conditions. When triethylamine or ^{i}Pr$_2$NH was used in its place, no COE was observed (Table 3, entries 2 and 3), which is presumably attributable to these being much weaker bases than KO^{t}Bu.[47] Potassium bis(trimethylsilyl)amide (KHMDS) and ^{t}BuPN(pyrr)$_3$ phosphazene[81] were also found to be ineffective (Table 3, entries 4 and 5), perhaps because they are sterically very hindered or perhaps because they are insufficiently basic. Lithium amide and lithium diisopropylamide appeared to successfully deprotonate (^{tBu4}PCP)IrH$^+$, although the resulting conjugate acids coordinated to iridium to give (^{tBu4}PCP)Ir(amine). Continued heating, however, did result in catalysis,

Table 3. Use of Various Bases to Promote PCET-Driven Dehydrogenation[a]

entry	base	pK_{aH} (MeCN)	pK_{aH} (H_2O)	TON COE
1	KO^{t}Bu	40[b]	20[c]	3.8
2	Et$_3$N	18.8[d]	10.7[d]	none
3	^{i}Pr$_2$NH	19[e]	11[e]	none
4	KN(SiMe$_3$)$_2$	34[b]		none
5	^{t}BuPN(pyrr)$_3$	28.4[d]	17.5[d]	none
6	LiNH$_2$	41[f] (DMSO)	38[f]	2.8
7	Li^{i}Pr$_2$N (LDA)	36[g] (THF)		3.2

[a]Conditions: (^{tBu4}PCP)IrH$_2$ (10 mM), [Ag][BF$_4$] (80 mM), base (80 mM), COA (400 mM), 150 °C, and 16 h in *p*-xylene-d_{10}. [b]Ref 47. [c]Ref82. [d]Ref 81. [e]Extrapolated from values in ref 81. [f]Ref 83. [g]Ref 84.

although yields were somewhat lower than obtained with KO^{t}Bu (Table 2, entries 6 and 7).

SUMMARY AND CONCLUSIONS

We report the first example of alkane dehydrogenation by proton-coupled electron transfer using molecular catalysts (pincer-ligated iridium complexes) and pairs of oxidants and bases. Previous approaches to alkane dehydrogenation with molecular catalysts have relied on sacrificial alkene acceptors or forcing conditions that facilitate the removal of H_2. The PCET approach introduced here operates at relatively mild conditions. Mechanistic studies suggest a sequence of oxidation and deprotonation steps. In the absence of added base, the reaction of 2 equivalents of Ag[BF_4] with (^{tBu4}PCP)IrH_2 was found to rapidly yield (^{tBu4}PCP)IrH^+, i.e., a hydride ligand was in effect removed by oxidation. Subsequent deprotonation leads to C−H bond activation; evidence points to the formation of the same three-coordinate d^8 species that is produced in the reaction of (^{tBu4}PCP)IrH_2 with olefin, i.e., (^{tBu4}PCP)Ir, which is known to be the key intermediate in alkane transfer dehydrogenation by (^{tBu4}PCP)IrH_2. The (^{tBu4}POCOP)Ir fragment shows comparable catalytic activity.

Remarkably, even extremely weak oxidants such as $Cp^*_2Co^+$ were found to be effective. The deprotonation of (pincer)IrH^+ is apparently the energetically most demanding step under the range of conditions we investigated; accordingly, the dehydrogenation cycle with these catalysts requires a very strong base.

These results suggest that catalytically active fragments that are much more easily deprotonated than (^{tBu4}PCP)Ir or (^{tBu4}POCOP)Ir might be of greater practical value. Note that even with the use of oxidants with relatively modest oxidation potentials, weak bases could provide sufficient thermodynamic driving force for alkane dehydrogenation. For example, coupled with an oxidant with $E^\circ = 0.05$ V vs Cp_2Fe^+, diethyl ether (pK_a $HOEt_2^+ = 0.2$ in acetonitrile[85]) is sufficiently basic to provide the thermodynamic driving force (eq 5) required for COA dehydrogenation. Note also that fragments much less basic than (^{tBu4}PCP)Ir or (^{tBu4}POCOP)Ir would not necessarily be less active toward C−H activation. Indeed, to use one extreme example, the cationic fragment with a pyridine-based backbone, (^{tBu4}PNP)Ir^+, which is isoelectronic to (^{tBu4}PCP)Ir and is presumably an extremely weak base, adds C−H bonds much *more* favorably[86,87] than (^{tBu4}PCP)Ir. Moreover, such electron-poor catalytically active fragments should also offer resistance to overoxidation. Research efforts in this direction, based on both electrochemistry and the use of chemical oxidants, are currently underway in our laboratories.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c05160.

Complete experimental details and synthetic procedures, NMR data, and crystallographic data for [(^{tBu4}PCP)Ir(H)(H_2O)][BF_4] (PDF)

Crystallographic data for [(^{tBu4}PCP)Ir(H)(H_2O)][BF_4], CCDC 2043161 (CIF)

AUTHOR INFORMATION

Corresponding Author

Alan S. Goldman − *Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, United States;* orcid.org/0000-0002-2774-710X; Email: alan.goldman@rutgers.edu

Authors

Arun Dixith Reddy Shada − *Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, United States*

Alexander J. M. Miller − *Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States;* orcid.org/0000-0001-9390-3951

Thomas J. Emge − *Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acscatal.0c05160

Notes

The authors declare no competing financial interest.

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