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Iridium PCP pincer complexes: highly active and robust catalysts for novel homogeneous aliphatic dehydrogenations

Craig M. Jensen

Department of Chemistry, University of Hawaii, Honolulu, HI 96822, USA. E-mail: jensen@gold.chem.hawaii.edu

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The PCP pincer complexes, $IrH_2\{C_6H_3(CH_2PR_2)_2\text{-}2,6\}$ (R = Bu^t, Pr^i) are extraordinarily active and robust catalysts for aliphatic dehydrogenation reactions. Their application to alkane dehydrogenation has resulted in the first efficient catalytic systems for homogeneous thermochemical alkane dehydrogenation without the use of a sacrificial hydrogen acceptor and for dehydrogenation of *n*-alkanes to α-olefins. The pincer catalysts also effect other aliphatic dehydrogenations which had not previously been accomplished *via* homogeneous catalysis including the conversion of cycloalkanes to arenes, ethylbenzene to styrene and tetrahydrofuran to furan. All of these catalytic reactions are inhibited by even traces of nitrogen. This is apparently due to the formation of the remarkably stable dinitrogen complexes: $[Ir\{C_6H_3(CH_2PR_2)_2\text{-}2,6\}]_2(\mu\text{-}N_2)$. Mechanistic studies have indicated that the high activity of the pincer catalysts may be in part due to 'agostic promotion' by phosphino aliphatic groups.

Introduction

The selective functionalization of aliphatic groups is one of the great unsolved problems of organic chemistry. The quest for methods to effect this type of transformation continues to entice chemical researchers through economic incentives and intellectual challenge. One of the most commercially tantalizing possibilities is the production of major organic feedstocks such as terminal alkenes (α-olefins) through regioselective aliphatic dehydrogenation reactions. Two decades ago, Crabtree *et al.* first reported the stoichiometric dehydrogenation of alkanes to alkenes by soluble transition metal complexes.[1] This was followed by the 1983 discovery by Baudry *et al.* of the first homogeneous catalyst for the transfer dehydrogenation of alkanes to alkenes.[2] A variety of other complexes were found during the next 12 years that operate in systems that are driven by the hydrogen transfer from alkanes to hydrogen acceptors (transfer-dehydrogenation),[3–9] photoirradiation,[5,10] and the thermal evolution of hydrogen.[11,12] The systems generally suffered from very slow reaction rates and rapid catalyst decomposition.[1–5,8,11,12] The first efficient thermochemical system for the transfer dehydrogenation of alkanes was achieved by Goldman and coworkers in 1991 using $Rh(CO)Cl(PMe_3)_2$ as catalyst under a hydrogen atmosphere.[6] Unfortunately, this system also catalyzes a 4–20 fold excess of direct (non-transfer) hydrogenation of the sacrificial alkene. It was subsequently found that closely related rhodium arsine[7] and phosphine enolate[9] complexes function as efficient catalysts under similar conditions. Notably the excess of acceptor which is consumed is significantly reduced when the reaction is catalyzed by arsine complexes.[7] While the state of the art of homogeneous alkane dehydrogenation catalysts had continuously advanced, it was apparent that the development of practical systems awaited the discovery of catalysts with greatly improved thermal stability and enhanced reactivity with alkane C–H bonds.

Hydrido complexes containing a tridentate monoanionic aryl bis(phosphino), 'PCP pincer' ligand were first prepared by Moulton and Shaw.[13] The complexes $IrClH\{C_6H_3(CH_2PBu^t_2)_2\text{-}2,6\}$ **1a** and $RhClH\{C_6H_3(CH_2PBu^t_2)_2\text{-}2,6\}$ **1b**, were found to possess unusually high thermal stabilities and sublime at 180–200 and 245–350 °C, respectively, without decomposition.[13] In 1979, it was observed that the intermediate resulting from the dehydrochlorination of **1b** with $NaN(SiMe_3)_2$, reacted readily with pentane, octane and cyclohexane to produce hydride complexes.[14,15] Thus it seemed that '$M\{C_6H_3(CH_2PBu^t_2)_2\text{-}2,6\}$' (M = Ir, Rh) might have the right combination of thermal stability and high reactivity with aliphatic C–H bonds to function as practical alkane dehydrogenation catalysts. Unfortunately, '$Rh\{C_6H_3(CH_2PBu^t_2)_2\text{-}2,6\}$' has proven to be too unstable to isolate. Attempts to utilize the complex for the catalytic transfer dehydrogenation of alkanes upon *in situ* generation from **1b** were also unsuccessful. Thus we considered alternative methods of generating a PCP pincer catalyst.

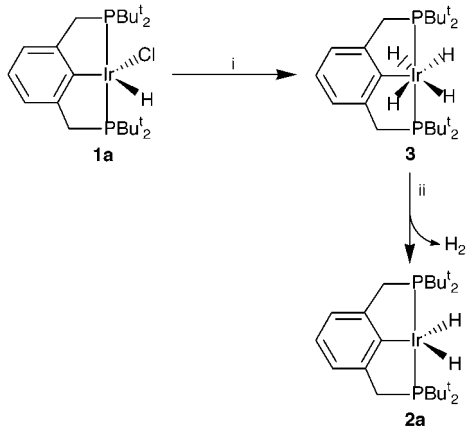
A number of dihydrido iridium bis(phosphine) complexes had been found to be catalysts for alkane dehydrogenation.[3–5,8,11] Therefore, we reasoned that the dihydrido PCP pincer complexes $MH_2\{C_6H_3(CH_2PBu^t_2)_2\text{-}2,6\}$, (M = Ir, **2a**; Rh, **2b**) were logical catalyst candidates. As we began our exploration of the pincer catalyst in the spring of 1996, we were unaware that the groups of Goldman[16] and Leitner[17] had independently identified rhodium complexes containing very similar chelating phosphine ligands as likely candidates for advanced alkane dehydrogenation catalysts and were embarking on similar studies.

Synthesis and characterization of dihydrido pincer complexes

The dihydrido complex **2a** had not previously been synthesized and isolated. A species previously generated *in situ* and identified as **2a**[18] is actually the tetrahydride complex, $IrH_4\{C_6H_3(CH_2PBu^t_2)_2\text{-}2,6\}$, **3a**. We have found methods whereby the dihydride complexes can be prepared and isolated in > 85% yield.[19] The iridium complex **2a** was synthesized by the two step procedure seen in Scheme 1. This reaction

Craig M. Jensen is a Professor of Chemistry at the University of Hawaii. He was born and raised in Wenatchee, Washington, USA. His undergraduate education began at the University of Washington and was completed, after a sabbatical in the Aleutian Islands, at the University of California at Santa Barbara. He obtained his PhD at the University of California at Los Angeles under the supervision of Professor H. D. Kaesz. Following a postdoctoral appointment at the University of California at San Diego, he joined the faculty at UH in 1986. In addition to pincer catalysts, his research group is developing advanced hydrogen storage materials.

sequence had previously been developed by Kaska and coworkers for the preparation of $IrH_2\{HC(C_2H_4PBu^t_2)_2\}$ from $IrClH\{HC(C_2H_4PBu^t_2)_2\}$.[20] In the first step of this procedure, the hydrido chloride complex **1a** is converted to the white tetrahydride complex **3a** through reaction with $LiBEt_3H$ under an atmosphere of H_2. Following isolation and recrystallization of **3a**, the brown dihydrido complex, **2a** is obtained quantitatively upon heating finely powdered **3** at 130 °C *in vacuo*.



Scheme 1 *Reagents and conditions*: i, $LiEt_3BH$ (1 M in THF) 1 equiv., 1 atm H_2, 25 °C, pentane; ii, 3×10^{-3} torr, 130 °C, 24 h.

An X-ray structure determination was carried out on a single crystal of **2a** in order to verify the structural composition.[19] A diagram of the determined molecular structure is presented in Fig. 1. This depiction underscores how the rigid coordination

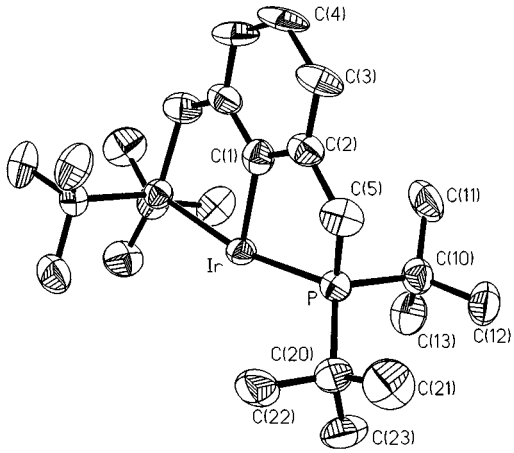


Fig. 1 Projection of $IrH_2\{C_6H_3(CH_2PBu^t_2)_2$-2,6} **2a** with the thermal ellipsoids at 50% probability. Selected bond distances (Å) and angles (°): Ir–C(1) 2.12(1), Ir–P 2.308(2), P–Ir–C(1) 82.41(6), P–Ir–P(a) 164.8(1).

framework of the PCP pincer ligand effectively restricts the access of the metal center to the P–C and C–C bonds of the ligand thus rendering the complex to be sufficiently robust to withstand high temperatures.

The synthesis of **2b** is not complicated by the formation of a tetrahydride. Thus the rhodium PCP dihydride can be prepared directly from the hydrido chloro complex. It was initially obtained among the products resulting from the treatment of **1b** with either $NaN(SiMe_3)_2$ or KH under an atmosphere of hydrogen.[15] A much cleaner reaction occurs with $LiBEt_3H$ under an atmosphere of H_2 and purified **2b** can be isolated upon recrystallization.[21]

Dehydrogenation of alkanes to alkenes

Cyclooctane

The enthalpy of dehydrogenation of cyclooctane is 23.3 kcal mol^{-1}, 5–7 kcal mol^{-1} lower than for most alkanes. This 'best case' substrate has been the conventional starting point for most studies of homogeneous catalysts for the dehydrogenation of alkanes. As mentioned above, a sacrificial hydrogen acceptor is generally required in thermochemical catalytic systems. Crabtree *et al.* found *tert*-butylethylene (tbe) to be a particularly effective acceptor in their early studies[1] and its use in these systems has become standard.

Our initial attempts to utilize the di- and tetra-hydrido pincer complexes as catalysts for the generic cyclooctane–tbe system were unsuccessful. No catalytic activity was observed when the complexes were used either directly upon generation *in situ* or in crude unpurified form. The key to the discovery of the extraordinary catalytic activity of both **2a**[19] and **3a**[21] was the recrystallization of the complexes from pentane to remove borate impurities introduced during its generation from $LiBEt_3H$. At 150 °C the dehydrogenation of cyclooctane by **2a** proceeds at a rate of 82 turnovers h^{-1} while a rate of 12 turnovers min^{-1} is observed at 200 °C. Appreciable activity (20.5 turnovers h^{-1}) is observed as low as 100 °C. Furthermore, no significant decomposition of the catalyst occurs within the time required for the complete consumption of the hydrogen acceptor. The long term maintenance of catalyst integrity contrasts with the short, *ca.* 12 h half lives which had typically been found for alkane dehydrogenation catalysts.

Prior to our studies of the pincer catalysts, only rhodium complexes had been found to exhibit high activity as alkane dehydrogenation catalysts.[6,7,9,10] Thus it is surprising that **2b** shows only very low catalytic activity. For example, a rate of only 0.8 turnovers h^{-1} was observed for the dehydrogenation of cyclooctane by **2b** at 200 °C.[21] *Ab initio* calculations have shown[22] that addition of H_2 to $Rh(PH_3)_2Ph$ is $\geqslant$ 20 kcal mol^{-1} less favorable than addition to $Ir(PH_3)_2Ph$, $Rh(PH_3)_2Cl$ or $Ir(PH_3)_2H$.[23] This suggests that addition of closely related C–H bonds to rhodium PCP pincer complexes may also be unfavorable thus accounting for the low observed catalytic activity. In support of this hypothesis, Milstein *et. al.* have recently found the alkyl rhodium pincer complexes $RhR\{C_6H_3(CH_2P^tBu_2)_2$-2,6}I (R = Pr^i, Pr^n, Et) to be exceptionally stable against intermolecular addition of the β-C–H bonds of the alkyl ligands.[24]

Nitrogen and alkene inhibition

The catalytic activity of the pincer complexes is suppressed by N_2. In order to achieve the maximum catalytic rates, reaction mixtures must be freeze–pump–thaw degassed prior to heating to remove any vestiges of N_2. This unusual N_2 inhibition of the catalytic activity is due to the formation of the surprisingly stable dinitrogen complex, $[Ir\{C_6H_3(CH_2PBu^t_2)_2$-2,6}$]_2(\mu$-$N_2)$ **4**.[25] The complex was isolated by treating a cyclohexane solution **2a** with a 15 fold excess of tbe under 1 atm of nitrogen at 80 °C. The dinitrogen complex is produced in nearly quantitative yield within 1 h. The formation of **4** is evidently initiated by the reaction of nitrogen with the intermediate resulting upon the dehydrogenation of **2a** by tbe as nearly one equivalent of *tert*-butylethane is produced in the reaction.

The molecular structure of **4** was elucidated through a single crystal X-ray structure determination[25] and is depicted in Fig. 2. The dihedral angle between the planes defined by Ir(1), P(11), P(12) and Ir(2), P(21), P(22) is 89.5°. This nearly perpendicular arrangement results in the encapsulation of the nitrogen ligand and is apparently responsible for the surprising stability of **4** and the pronounced inhibiting effect of nitrogen on the catalytic reactions.

The dehydrogenation activity of **2a** is inhibited by high concentrations of alkene. Thus the loading of hydrogen acceptor in the reaction mixture is restricted. For example, diminished rates of catalysis are found in solutions containing > 300 : 1 ratio of tbe to catalyst. In order to achieve high turnover numbers, a limited amount of tbe must be periodically added to reaction

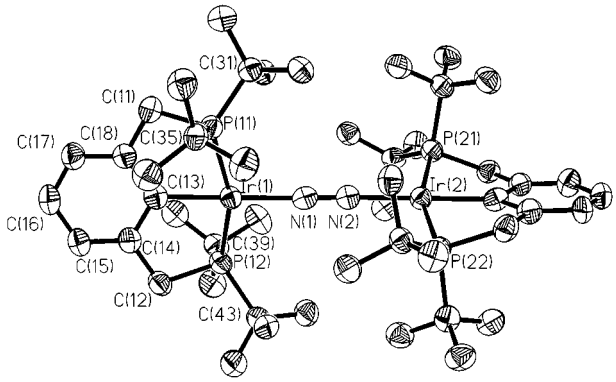


Fig. 2 Projection of [Ir{$C_6H_3(CH_2PBu^t_2)_2$-2,6}]$_2$(μ-N_2) **4** with the thermal ellipsoids at 25% probability. Selected bond distances (Å) and angles (°): Ir(1)–C(13), 2.053(12), Ir(1)–P(11) 2.312(3), Ir(1)–N(1) 2.007(11), N(1)–N(2) 1.176(13), C(13)–Ir(1)–P(11) 78.6(3), P(11)–Ir(1)–P(12) 160.22(10), Ir(1)–N(1)–N(2) 178.7(9).

mixtures. Following incremental additions of tbe, the dehydrogenation of cyclooctane is observed to again proceed at a rate of 12 turnovers min^{-1}.[21]

At higher concentrations, the cyclooctene product inhibits the catalyst and only *ca*. 10% of the cyclooctane can be dehydrogenated. Overcoming this problem of product inhibition is one of the major challenges to be met in the development of synthetically useful methods based on pincer complex catalyzed dehydrogenation reactions.

Linear alkanes

Terminal alkenes (α-olefins) are a major feedstock for the production of plastics, detergents and lubricants. Their production through the selective dehydrogenation of linear alkanes would be an attractive alternative to the present commercial processes based on hydrogen, ethylene and trialkylaluminium catalysts.[26] Several studies of alkane activation by rhodium and iridium complexes have shown that oxidative addition of primary C–H bonds is kinetically preferred despite their greater bond strength.[27] Thus it is plausible that a kinetically controlled, catalytic system based on rhodium or iridium complexes could be developed for the regioselective dehydrogenation of *n*-alkanes to terminal alkenes. An early study by Felkin *et al.* found that $IrH_5(PPr^i_3)_2$ catalyzes the transfer dehydrogenation of *n*-hexane to hex-1-ene with >90% selectivity.[3] However, only 0.3 catalytic turnovers were achieved owing to the low activity and stability of the catalyst. Other catalytic systems were found to have higher activity with *n*-alkanes but the observed product distributions were essentially thermodynamically controlled and contained little or no terminal alkene.[6,7,10] The hope of developing a system which capitalized on the kinetic preference of iridium and rhodium complexes for the activation of the terminal C–H bonds of alkanes was raised by the discovery that $RhCl(CO)(PMe_3)_2$ catalyzed a photochemical system for the efficient, regioselective carbonylation of the terminal position of *n*-alkanes.[28] In view of the high activity found for **2a** in our studies with cyclooctane, it seemed possible that its application to the dehydrogenation of *n*-alkanes might lead to the selective production of the kinetically preferred terminal alkenes.

Our initial studies of the dehydrogenation of *n*-octane with the pincer catalyst **2a** indicated that the reaction was highly selective for internal octenes over oct-1-ene.[29] However, a study of product distribution *vs*. time at 150 °C revealed a more complicated situation.[30] The data presented in Fig. 3 clearly illustrates the high kinetic selectivity of the reaction for oct-1-ene. To our knowledge this is the first catalytic system for the efficient and selective dehydrogenation of linear alkanes to terminal alkenes. It can also be seen that **2a** also functions less efficiently as an alkene isomerization catalyst. While the net

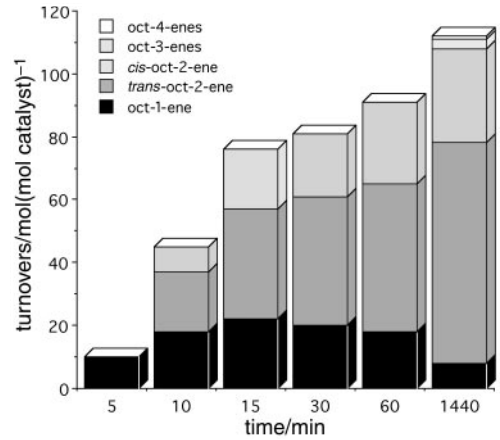


Fig. 3 Distributions of octenes produced at various times from the transfer dehydrogenation of *n*-octane catalyzed by **2a** at 150 °C.

production of octenes begins to level off within the first hour due to octene inhibition of the dehydrogenation reaction, the distribution of octenes continues to slowly shift towards the internal isomers. Although the practical utility of this system is limited by the secondary alkene isomerization reaction, modification of the system may permit production of high yields of terminal alkenes. For example, Goldman and coworkers have found that the rate of the isomerization reaction is sensitive to the steric bulk of hydrogen acceptor. Using the combination of dec-1-ene as hydrogen acceptor and **2a** as catalyst for the transfer dehydrogenation of *n*-octane, a 68% selectivity for oct-1-ene after 143 total turnovers is observed before its level begins to decline due to secondary isomerization.[30]

Acceptorless dehydrogenation of alkanes to alkenes

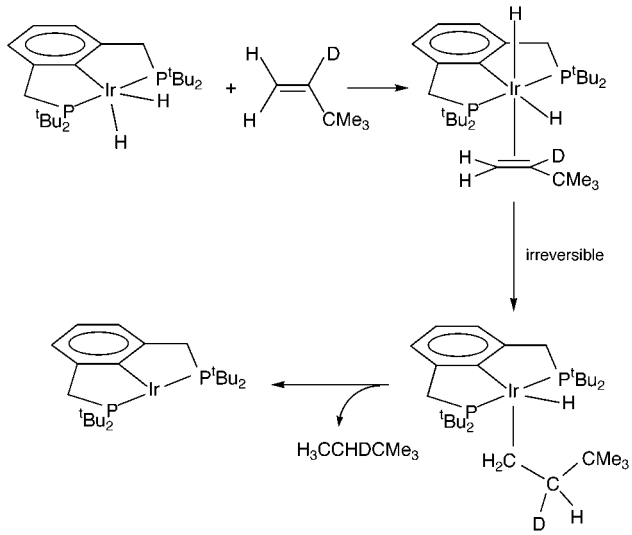
Both economical and environmental considerations preclude systems requiring a sacrificial hydrogen acceptor from consideration for the commercial production of alkenes. Thus there is great interest in the development of 'acceptorless' systems in which alkanes are transformed to alkenes upon the direct elimination of H_2. In 1990 Fujii and Saito reported the first thermochemical homogeneous catalytic systems for acceptorless dehydrogenation of alkanes.[11] In order to circumvent unfavorable equilibrium constraints, hydrogen was evolved from the refluxing systems *via* a continuous purge with an inert gas. Other systems for acceptorless alkane dehydrogenation were developed using this approach but suffered from the usual problems of very low catalytic activities (<2 turnovers h^{-1}) and catalyst instability.[11,12]

The iridium PCP pincer complexes have been found to be much more efficient catalysts for acceptorless dehydrogenation.[22,31] As a result of their high activity and long term stability at very high temperatures, the turnover numbers which can be achieved in continuously purged, open reflux systems are increased by two orders of magnitude. Recently, Liu and Goldman observed turnover numbers approaching 1000 for the acceptorless dehydrogenation of cyclodecane in experiments employing $IrH_2\{C_6H_3(CH_2PPr^i_2)_2$-2,6} **6**, the isopropyl analog of **2a,** as catalyst.[31]

Mechanistic studies

The overall mechanism of the transfer dehydrogenation of alkanes by **2a** is largely unexplored. However, the initial process in the catalytic sequence is undoubtedly the dehydrogenation of the dihydride by the hydrogen acceptor to produce the key intermediate '$Ir\{C_6H_3(CH_2PBu^t_2)_2$-2,6}'. This reaction occurs cleanly at 25 °C and has been studied in detail.[25] The dehydrogenation of **2a** in neat tbe at 25 °C gives a stoichiometric amount of *tert*-butylethane (tba) within 1 h. As seen in Scheme 2, experiments in neat $H_2C{=}CDCMe_3$ produce ex-

clusively β labeled tba. We also observed that no deuterium is scrambled into **2a** during the course of the dehydrogenation reaction. These findings lead to the conclusion that hydride migration to coordinated tbe is irreversible.



Scheme 2 Mechanism of the dehydrogenation of **2a** by $H_2C=CDCMe_3$.

Results of studies of dehydrogenation of **2a** contrast with those of our earlier study with the chloro complex $IrClH_2(P\text{-}Pr^i_3)_2$ **5**.[8] While coordination of tbe and subsequent hydride migration are also facile with **5**, the reductive elimination of tba from the resulting alkyl hydride complex requires the addition of an alkane and heating to 150 °C. The high barrier to elimination of tba in the case of **5** renders the hydride migration step reversible as demonstrated by the transfer of deuterium from $IrClD_2(PPr^i_3)_2$ (**5**-d_2) to the β position of tbe.

It is possible that an agostic interaction with a methyl C–H bond of a *tert*-butyl methyl group triggers tba elimination from the pincer complex. This hypothesis is supported by the observation of deuterium scrambling in the dideuterio complex, **2a**-d_2. The exchange between the deuteride and the methyl hydrogens of the *tert*-butyl methyl groups of the pincer ligand was apparent within 2 h of dissolving **2a**-d_2 in cyclohexane at 25 °C. In contrast, heating the dideuterio complex, **5**-d_2 in toluene solution at 150 °C for 24 h does not result in transfer of the deuterium label to isopropyl methyl groups of phosphine ligands.[32] The ability of the phosphine alkyl groups of **2a** to interact with the iridium center may eliminate the requirement of alkane association for tba elimination found for **5**.[8] Thus 'agostic promotion' by the pendent *tert*-butyl methyl groups may partially account for **2a** having much higher activity for the catalytic transfer dehydrogenation of alkanes than **5**.

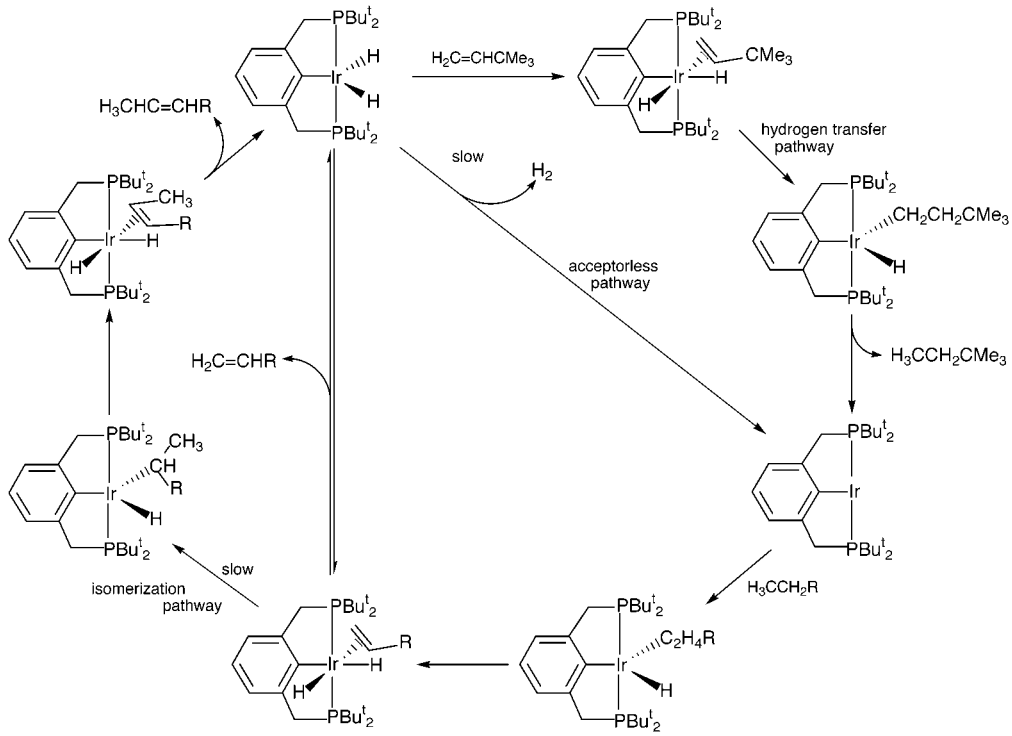
The complex which is produced upon the dehydrogenation of **2a** has been characterized by ^1H and ^{31}P NMR spectroscopy. These data confirm the presence of the pincer ligand and absence of hydride ligands. However, it remains questionable whether the product is the 14-electron species $Ir\{C_6H_3(CH_2P\text{-}Bu^t_2)_2\text{-}2,6\}$ as the spectroscopic data do not preclude the possibilities of highly fluxional agostic interactions with phosphine alkyl groups or the presence of tbe and/or solvent ligands which undergo rapid exchange with the bulk solution. As found for the rhodium analog, '$Ir\{C_6H_3(CH_2PBu^t_2)_2\text{-}2,6\}$' is highly reactive and all attempts to isolate it as a crystalline solid gave rise to a complicated mixture of unidentified products. Similar, highly reactive intermediates have recently been reported to result from the dehydrogenation of $IrFH_2(P\text{-}Bu^t_2Ph)_2$ by ethylene.[33] The '$Ir\{C_6H_3(CH_2PBu^t_2)_2\text{-}2,6\}$' intermediate reacts instantaneously at room temperature with N_2 to form the dinitrogen complex **4** and is trapped with ethylene by the formation of the stable complex $Ir(C_2H_4)\{C_6H_3(CH_2P\text{-}Bu^t_2)_2\text{-}2,6\}$.[30] Similar reactivity has been found for the analogous rhodium complexes $Rh\{C_6H_3(CH_2PBu^t_2)_2\text{-}2,6\}$[12] and $Rh\{CH(CH_2CH_2PBu_2)_2\text{-}2,6\}$.[34] Thus the nitrogen and alkene inhibition of the pincer catalytic dehydrogenation reactions apparently arise through this intermediate. The surprisingly low alkene affinity, which has been ascribed to crowding in the coordination sphere of the metal, accounts for the occurrence of catalytic inhibition only at high alkene concentrations.

The alkane dehydrogenation side of the catalytic cycle can be envisioned to proceed *via* a reversal of the mechanism for the hydrogenation of tbe: alkane substrate C–H oxidative addition, β-hydride elimination from the resulting alkyl group and dissociation of the product alkene to regenerate **2b**. This mechanism is complicated in the case of linear alkanes by the secondary catalytic alkene isomerization reaction. As seen in Scheme 3, the dissociation of terminal alkenes from the metal center is apparently much faster than hydride migration to the α-carbon of the coordinated alkene to produce a secondary alkyl group. This kinetic preference for the production of terminal alkenes can be ascribed to the pronounced steric constraints conferred by the pincer ligand. Goldman[30] has pointed out that the partitioning of the dehydrogenation/isomerization catalytic pathways can be viewed simply as a competition between the initial terminal alkene product and the sacrificial acceptor alkene for coordination to the dihydrido complex. This hypothesis accounts for the high concentrations of terminal alkenes which are obtained early in the dehydrogenation reaction when dec-1-ene is used as an acceptor in place of the sterically encumbered tbe.[30] The terminal alkenes do, however, eventually reassociate and follow the thermodynamically mandated isomerization pathway. The steric control of the kinetics of the isomerization process is further evidenced by the observation that the subsequent isomerization of alk-2-enes to further internalized alkenes occurs at much slower rates than the initial 1–2 isomerization.

The dehydrogenation of the dihydrido complexes in the absence of a hydrogen acceptor must occur by the direct reductive elimination of H_2 as seen in Scheme 3. Unlike the reaction with sacrificial alkenes which occurs at room temperature, the direct reductive elimination of H_2 occurs only at elevated temperatures. The sizable increase in the barrier to entering the dehydrogenation pathway results in the predominance of the isomerization pathway and thus precludes the possibility of production of significant concentrations of terminal alkenes. Even at very short reaction times, only traces of terminal alkenes are found when the catalytic dehydrogenation of linear alkanes are carried out in open reflux systems.

Dehydrogenation of cycloalkanes to arenes

The dehydrogenation of alkanes through catalytic reforming is the leading commercial method of producing arenes.[35] Platinum (often with a rhenium promoter) on alumina catalysts employed in this reaction require temperatures of 450 to 550 °C.[35] It is anticipated that homogeneous systems for the dehydrogenation of cycloalkanes to arenes would operate under milder conditions and give improved product selectivities. However, prior to our development of the pincer catalysts, only a few examples of such systems had been discovered.[36–41] Pioneering studies by Shilov and coworkers showed that K_2PtCl_4 catalyzes the reaction of H_2PtCl_6 with cycloalkanes to produce a mixture of arenes, alcohols and chlorinated species at 100–120 °C in aqueous trifluroacetic acid.[36] $Pd(OCOCF_3)_2$ has been reported to catalyze the dehydrogenation of cyclohexene to benzene[37] but reacts with cyclohexane only stoichiometrically in the presence of CF_3CO_2H to produce benzene.[38] $Ru(styrene)_2(PPh_3)_2$, $[Ir(cod)(PPh_3)_2]^+$, and $[Ir(cod)\{P(C_6H_4F\text{-}p)_3\}_2]^+$ catalyze the dehydrogenation of cyclohexene to benzene but are unreactive with cyclohexane[39] while $PdSO_4$ in the presence of



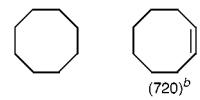
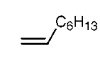
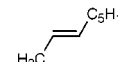
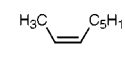
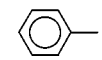
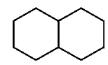
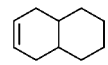
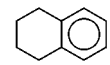
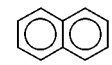
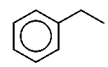
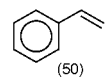
Scheme 3 Proposed mechanism for the catalytic dehydrogenation of linear alkanes by **2a**.

H_2SO_4 effects only the stoichiometric conversion of cyclohexane to benzene.[40] Crabtree *et al.* found an oxidative addition type system in which $IrH_2\{OC(O)CF_3\}(PPr^i_3)_2$ effects the dehydrogenation of alkanes to arenes at 150 °C in the presence of the hydrogen acceptor, tbe.[41] This system fails to turnover catalytically because hydrogenolysis of the phosphine P–C bonds occurs at the temperatures of 135 °C or above that are required for the release of the arenes from the intermediate complexes. Thus the development of a homogeneous system which was completely catalytic in precious metal awaited the development of catalysts such as the PCP pincer complexes that did not decompose at temperatures required to achieve arene elimination.

We have found **2a** will catalyze the transfer dehydrogenation of the six membered aliphatic ring of cyclohexane, methylcyclohexane, and decalin at temperatures as low as 150 °C.[19] The distribution of products arising after 1 h at 200 °C from solutions of the cycloalkanes containing equal loadings of the catalyst and tbe are given in Table 1. These data show that the initial dehydrogenation of cycloalkanes to cycloalkenes is much faster than the subsequent dehydrogenation of the cycloalkenes to arenes. It can also be seen that dehydrogenation reactions are sensitive to the stringent steric constraints at the iridium center. These conclusions are reinforced by the observation that the conversion of significant amounts of decalin to naphthalene occurs only after 72 h at 200 °C.

As mentioned previously, the dehydrogenation activity of **2b** is inhibited at tbe : catalyst ratios of $> 350:1$. Thus, high turnover numbers can be achieved only through periodic incremental additions of tbe. After about 10% of the saturated substrate has been consumed, product inhibition occurs and there is virtually no net increase in the amount of hydrogen that can be transferred to tbe. However, as is the case with linear alkanes, the complex also catalyzes secondary hydrogen transfer reactions. The dehydrogenation of methylcyclohexane at 200 °C provides an excellent example of this reactivity. As seen in Fig. 4, very little additional hydrogen elimination from the substrate occurs between 1 and 24 h of reaction. However, during this period the catalytic system remains active for the conversion of 2- and 3-methylcyclohexene to the thermodynamically preferred products, 1-methylcyclohexene and toluene. A similar time dependent shift in the product distribution toward the ternary alkene was observed in the dehydrogenation of methylcyclohexane to methylcyclohexenes by IrH_5-$(PPr^i_3)_2$.[4] However, the further dehydrogenation of methylcyclohexenes to toluene does not occur in this catalytic system.

Table 1 Product distributions [mol(mol **2a**)$^{-1}$] resulting after 1 h at 200 °C from the transfer dehydrogenation of various substrates using **2a** (5 μM) as catalyst and tbe as hydrogen acceptor

Substrate	Products (mol/mol catalyst)
	(720)[b]
	 (8)  (47)  (26)
	 (86)  (77)
	 (41)  (20)  (8)  (11)
	 (69)  (16)  (26)
	 (50)
	 (86) (6) (53)

[a] In all cases, the quantified amounts of dehydrogenated C–C bonds and *tert*-butylethane balance within 5%. [b] Accomplished through incremental addition of tbe.

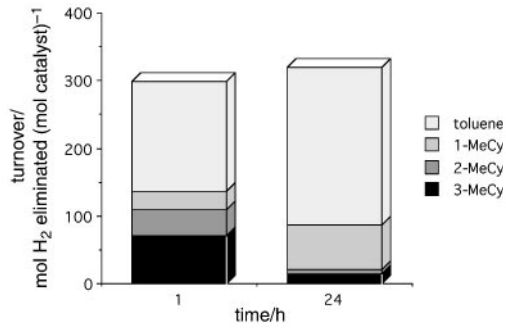


Fig. 4 Comparison of the product distributions obtained from transfer dehydrogenation of methylcyclohexane catalyzed by **2a** after 1 and 24 h of reaction at 200 °C.

Aliphatic dehydrogenation in the presence of functional groups

The catalytic dehydrogenation of aliphatic C–H bonds in the presence of functional groups is of major industrial importance. For example, the direct dehydrogenation of ethylbenzene accounts for 85% of the commercial production of styrene.[42] The reaction is carried out commercially at *ca.* 620 °C in the vapor phase over catalysts which primarily consist of iron oxide and potassium salt promoters.[42] Recently there has been considerable interest in the development of higher activity dehydrogenation catalysts which are also more selective for styrene over the degradation products, benzene and carbon.[42]

Our finding that **2a** remains catalytically active in the presence of relatively high concentrations of arenes suggested its application to the aliphatic dehydrogenation of alkyl benzenes. As seen in Table 1, **2a** will catalyze the transfer dehydrogenation of ethylbenzene to styrene.[43] However, the production of styrene ceases after only 50 turnovers. Thus it appears that the catalytic activity is inhibited by styrene at concentrations that are much lower than those observed for unfunctionalized alkenes. However, the observation of this catalytic activity was significant as it represented the first example of a homogeneous catalytic system for aliphatic dehydrogenation of a substrate containing an aromatic functionalization.

We have also investigated the reactivity of **1** with saturated ethers[43] and alcohols.[44] Surprisingly, the catalyst is not deactivated by either class of functionality. As seen in Table 1, the cyclic ether tetrahydrofuran (thf) is transfer dehydrogenated to a mixture of dihydrofurans and furan. However, pronounced product inhibition limits the reaction to < 200 turnovers. The dehydrogenation of alcohols is much more efficient and up to 80% conversion to products can be achieved. However, dehydrogenation of the aliphatic groups does not occur. Instead, much more pedestrian dehydrogenation of the alcohol functionality occurs to produce aldehydes from terminal alcohols and ketones from the internal alcohols.

Conclusions

Dihydrido iridium PCP pincer complexes have been found to be extraordinarily active and robust catalysts for aliphatic dehydrogenation reactions. This unique reactivity can be ascribed to the PCP pincer ligand which introduces a remarkable balance of electronic and steric effects such that the metal center is reactive with aliphatic C–H bonds but at the same time can not access the P–C and C–C bonds of the ligand. The resulting combination of high thermal stability and reactivity with aliphatic C–H bonds can be used to great advantage. The unusual high thermal stability of the pincer catalysts results in a two orders of magnitude improvement in the efficiency of homogeneous thermochemical systems for the dehydrogenation of alkanes without a sacrificial hydrogen acceptor. The unprecedented high reactivity of the pincer catalysts provides the basis for the first catalytic system of any kind for the selective dehydrogenation of linear alkanes to α-olefins. The combination of the pincer catalysts' high reactivity and stability has opened the door to other aliphatic dehydrogenations which had not previously been accomplished *via* homogeneous catalysis including the conversion of cycloalkanes to arenes, ethylbenzene to styrene and tetrahydrofuran to furan. These reactions represent major steps toward the development of viable methods for the selective functionalization of aliphatic groups. However, none are of practical value owing to the problems of product inhibition and/or requirement of sacrificial acceptors. Mechanistic studies have revealed the sources of these limitations and suggest possible designs for advanced catalysts. Modified PCP pincer complexes may well provide a means for the commercial production of commodity chemicals from alkanes and other abundant organic resources through catalytic aliphatic dehydrogenation reactions.

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