

Dehydrogenation and Related Reactions Catalyzed by Iridium Pincer Complexes

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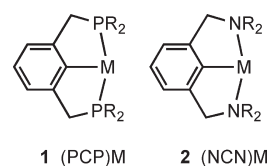
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1. INTRODUCTION

Since the seminal reports by Shaw and co-workers in the mid-1970s,^{1–7} the chemistry of pincer-ligated transition-metal complexes has experienced tremendous development and has been applied to a variety of fields ranging from stoichiometric and catalytic chemical transformations to sensors, switches, and supramolecular chemistry.^{8–10} The term “pincer ligand”, as used, for example, by Van Koten and Albrecht in their influential 2001 review on this topic,⁸ referred to species of the form $[2,6-(ECH_2)C_6H_3]^-$, where E is a neutral two-electron donor, particularly PR_2 or NR_2 as in the case of structures **1** and **2**. (The

prevailing nomenclature is based upon the coordinating atoms of the ligand; thus, **1** and **2** are complexes of “PCP” and “NCN” pincers, respectively.)



Usage of the term “pincer”, however, has broadened widely in recent years. It is clear that species with non-aryl,^{2–4,6,7,11} non-anionic,^{12,13} and non-carbon-coordinating^{14–19} central groups share many of the same properties as PCP- or NCN-type pincers. Likewise, the linkage between the central coordinating group and the terminal groups need not be restricted to CH_2 in the case of a central aryl group,^{20,21} nor must there be a total of two bridging atoms²² between central and terminal groups as in structures **1** and **2**. We can reasonably restrict the term “pincer” to ligands that generally (but not always) coordinate in a *mer* tridentate configuration. But, while it is probably useful to limit usage to species that bear some additional resemblance to the archetypal PCP and NCN species, ultimately we can perhaps do no better than former U.S. Supreme Court Justice Potter Stewart, who noted (in a different context) that “I could never succeed in intelligibly defining [the term in question] but I know it when I see it.”²³

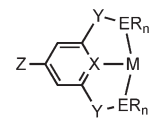
In general, the tridentate coordination mode of pincers results in strong binding to the metal center and engenders high stability of the pincer-metal unit. The rigidity of the framework probably tends to inhibit, though certainly not always prevent,^{24,25} cyclo-metalation at the terminal groups, such as dialkylphosphino. The high thermal stability of pincer complexes allows them to act as catalysts for highly endothermic reactions; this is certainly one of the key properties responsible for their success as dehydrogenation catalysts, the topic of this review.

The modular nature of pincer ligands allows for exquisite control over electronic and steric properties without significant perturbation of the coordination geometry. This enables

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	Group	Major Effect(s) of Variation
	ER _n	Steric control by varying substituents; control of electron density; lability.
	Y	Control over electron density; indirect control on steric properties.
	X	Electronic effects, particularly trans influence.
	Z	Remote control of electron density; solubility control.

Most common elements
 E: P, N, S, O, As
 X: C, N, B
 Y: CH₂, O, NH

Figure 1. Variable pincer ligand parameters for control over steric and electronic properties.

systematic investigation of electronic and steric effects and greatly facilitates optimization (e.g., catalyst tuning).^{10,26}

For example, in the case of the archetypal structures derived from aryl rings with substituents at the 2 and 6 positions, variations in the ER_n group (Figure 1) can dramatically influence steric crowding at the metal center with only a minimal electronic effect. Conversely, variations in Z can be used to exert well-controlled electronic effects independent of any complicating steric factors. Variations in X can exert profound electronic effects, particularly through the trans influence, while variations in Y can result in significant but complicated electronic and steric effects.

The references noted in the discussion above comprise a very small (and not fully representative) sample of the literature. As a testimony to the intense interest in pincer-ligated complexes, many reviews regarding these topics have been published.^{8–11,27–30} The focus of this review is on dehydrogenation and related reactions catalyzed by iridium pincer complexes, an area of particularly intense research activity since 1996, when Jensen and Kaska first used iridium pincer complexes for alkane transfer–dehydrogenation.³¹ This review is divided into three main parts: (1) alkane dehydrogenation and its applications, (2) dehydrogenation involving heteroatom–H bonds, and (3) reactions related to dehydrogenation mediated by iridium pincer complexes. More general information about the dehydrogenation of alkanes^{27,32–34} and amine–boranes^{35,36} can be found in recently published reviews.

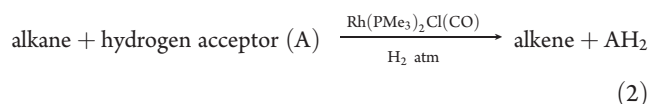
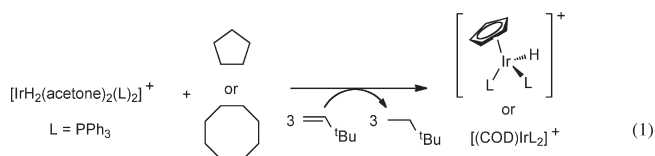
2. DEHYDROGENATION OF ALKANES

2.1. Background: Alkane Dehydrogenation Catalyzed by Non-Pincer-Ligated Transition-Metal Complexes

Olefins are perhaps the most important and versatile feedstocks in the chemical industry, but are far less naturally abundant than alkanes. Thus, the direct production of alkenes from alkanes via dehydrogenation has drawn great attention. Selective dehydrogenation is attractive for applications ranging in scale from fuels to fine chemicals. Many heterogeneous catalysts are known to effect dehydrogenation at high temperatures (ca. 500–900 °C), but applications are limited to simple molecules such as ethane or ethylbenzene due to the low selectivity of these catalyst systems.^{37–41} In the case of higher alkanes, lack of selectivity (including catalyst-deactivating coking) severely impacts the utility of dehydrogenation.^{41–45}

The first stoichiometric dehydrogenation of alkanes by a soluble homogeneous metal complex was reported by Crabtree in 1979.⁴⁶ The cationic complex [IrH₂(acetone)₂(PPh₃)₂][BF₄] was reported to dehydrogenate cyclopentane or cyclooctane (COA) in the presence of *tert*-butylethylene (TBE; 3,3-dimethyl-1-butene), which functions as a hydrogen acceptor, to produce the corresponding cyclopentadiene or

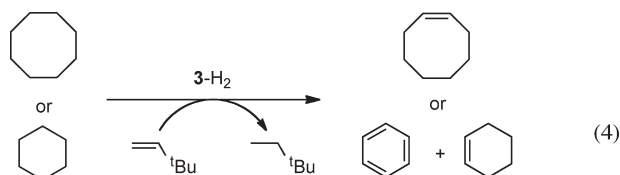
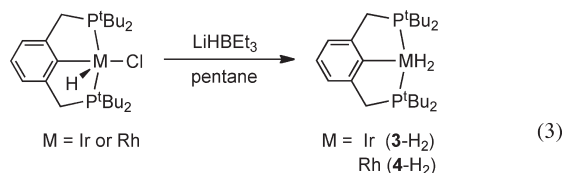
cyclooctadiene complexes (eq 1). Subsequently, Felkin and co-workers reported similar types of dehydrogenation of cycloalkanes with (PPh₃)₂ReH₇.^{47,48} Soon thereafter, the first examples of catalytic alkane transfer–dehydrogenation by homogeneous complexes were reported independently by Felkin^{49–51} and Crabtree,^{52–54} with both researchers having the greatest success with bis(trialkylphosphine) complexes of iridium. Crabtree also reported that IrH₂(O₂CR)(PCy₃)₂ effected acceptorless dehydrogenation of cyclooctane, to give up to 36 turnovers of cyclooctene in 48 h.⁵⁵ Turnover numbers were limited in these systems by catalyst decomposition due to the high temperatures required and the tendency of the metal centers, which are necessarily highly reactive, to attack their own ligands via either intra- or intermolecular paths. The rhodium complex Rh(PMe₃)₂(CO)Cl, by contrast, was found to be a very robust catalyst for photochemical alkane dehydrogenation⁵⁶ and subsequently for thermochemical transfer–dehydrogenation with a wide range of alkanes and hydrogen acceptors. Thermochemically, however, it was only operative (surprisingly) under a dihydrogen atmosphere (eq 2).^{57,58} The requirement of a H₂ atmosphere severely limited the utility of this system as more than 1 mol of acceptor was inevitably hydrogenated per mole of dehydrogenated product.



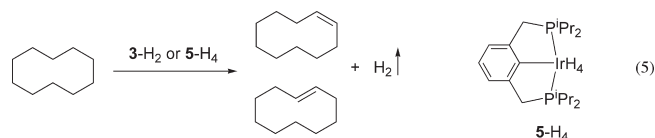
2.2. Dehydrogenation of Alkanes by Pincer Iridium Complexes

The application of pincer-ligated iridium complexes to alkane dehydrogenation was first reported by Jensen, Kaska, and co-workers in 1996.³¹ Given the high thermal stability of pincer complexes and the effectiveness of iridium and rhodium bis(trialkylphosphine) complexes in the catalytic dehydrogenation systems noted in the previous section, the pincer-ligated complexes (^tBu₄PCP)IrH₂ (3-H₂) and (^tBu₄PCP)RhH₂ (4-H₂) (R₄PCP = κ^3 -C₆H₃-2,6-[CH₂PR₂]₂) were prepared (eq 3) and tested for activity toward the transfer dehydrogenation of COA in the presence of the sacrificial hydrogen acceptor TBE (eq 4). The iridium complex 3-H₂ showed high activity for COA/TBE transfer dehydrogenation, affording 82 turnovers/h at 150 °C. In contrast, 4-H₂ and the less crowded (^{Me}PCP)Rh analogue⁵⁹ were found to be poor catalysts, yielding <1 turnover/h under the same conditions. Complex 3-H₂ displayed excellent thermal stability at elevated temperatures, yielding 12 turnovers/min and no observable decomposition over one week at 200 °C. High concentrations of TBE and trace amounts of N₂ were found to inhibit the reaction. Subsequently, Kaska and Jensen reported that other cycloalkanes such as cyclohexane, methylcyclohexane, and decalin were efficiently dehydrogenated by 3-H₂, in some cases to give aromatic products (eq 4).⁶⁰ It should be noted that the use of pincer iridium tetrahydrides as catalyst precursors has

never shown any significant difference from use of the corresponding dihydrides, other than requiring one additional mole of hydrogen acceptor in the case of transfer–dehydrogenation.



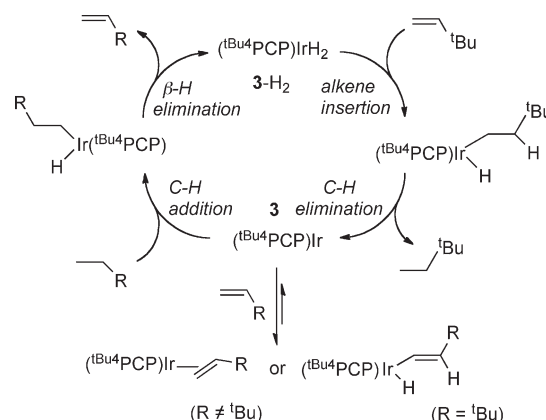
The high thermal stability of catalyst **3** enabled demonstration of the first example of efficient acceptorless dehydrogenation under reflux conditions (eq 5).⁶¹ The sterically less crowded isopropyl analogue (ⁱPr₄PCP)IrH₄ (**5-H₄**) afforded close to 1000 turnovers in the dehydrogenation of cyclodecane and the first reported example of acceptorless dehydrogenation of an acyclic alkane (*n*-undecane).⁶²



The mechanism of COA/TBE transfer dehydrogenation by (^tBu₄PCP)Ir was determined by a kinetic study of its constituent segments, TBE hydrogenation and COA dehydrogenation, in conjunction with detailed kinetic study of the full catalytic reaction.⁶³ Insertion of TBE into an Ir–H bond of (^tBu₄PCP)IrH₂ (**3-H₂**) followed by reductive elimination of *tert*-butylethane (TBA) generates the reactive 14-electron species (^tBu₄PCP)Ir (**3**). Within the catalytic cycle, complex **3** then undergoes oxidative addition of a C–H bond of the alkane substrate, and subsequent β -hydride elimination produces the olefin product and regenerates **3-H₂** (Scheme 1). Significantly, however, the 14-electron species **3** can also undergo out-of-cycle oxidative addition of the TBE vinylic C–H bond trans to the *tert*-butyl group as indicated in Scheme 1. The resulting vinyl hydride and **3** are in a rapid pre-equilibrium, the kinetics of which were independently quantified by dynamic NMR at low temperature.⁶⁴ Likewise, recent experimental results have shown that the resting state of the catalyst during the transfer–dehydrogenation of *n*-octane is (^tBu₄PCP)Ir(1-octene).^{65,66} Thus, in general, olefin can bind to (PCP)Ir, either by π -coordination or by C–H addition; in either binding mode, olefin, as either the sacrificial acceptor or dehydrogenated product, can thereby significantly inhibit activity. Indeed, the more facile dehydrogenation of cyclooctane vs *n*-alkane is not due to any selectivity for the former alkane ((^tBu₄PCP)Ir in fact shows 6:1 selectivity for *n*-octane vs cyclooctane) but rather due to weaker binding of the corresponding dehydrogenated product (cyclooctene) and therefore lesser inhibition.⁶⁷

The kinetic dependence on the sacrificial acceptor concentration is not simple. For example, although TBE can add to **3** and inhibit activity, in the limit of low [TBE], the catalyst resting state

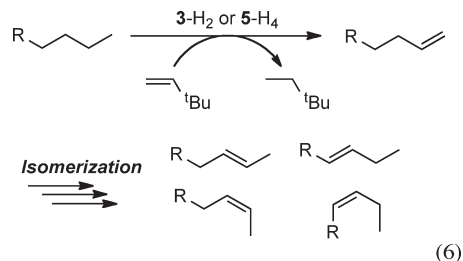
Scheme 1. Proposed Mechanism of *n*-Alkane/TBE Transfer Dehydrogenation by **3-H₂**



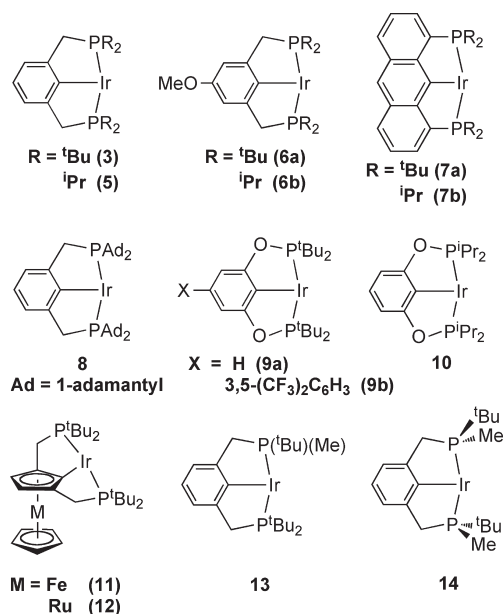
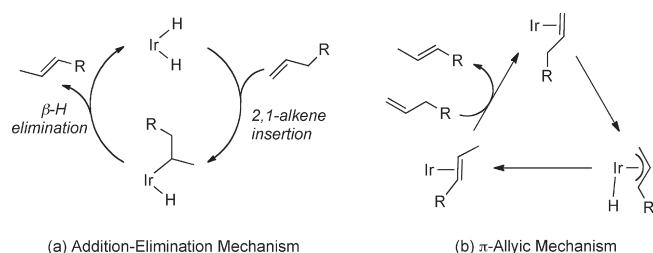
during COA/TBE transfer–dehydrogenation is **3-H₂**, not (PCP)Ir(CH=CH^tBu)(H). In that limit, the turnover-limiting step is hydrogenation of TBE and the catalytic reaction is first order in [TBE].⁶³ In the limit of high [TBE], the resting state is (PCP)Ir(CH=CH^tBu)(H). In that case, the turnover-limiting step is the reaction with COA, which follows a pre-equilibrium loss of TBE; the rate is therefore *inversely* dependent on [TBE].

In the case of acceptorless dehydrogenation, the active complex **3** is generated via thermolytic loss of H₂ from **3-H₂**; this is the turnover-limiting step of the cycle in the limit of effective removal of H₂ from the system.^{68–71} Catalytic activity is inhibited by the buildup of olefin product due to the formation of (^tBu₄PCP)Ir(olefin) and perhaps due to an increased rate of back-reaction (olefin hydrogenation).

Catalysts **3** and **5** show high kinetic selectivity for dehydrogenation of the terminal position of *n*-alkanes to give α -olefins. This regioselectivity holds great promise with respect to the formation of valuable α -olefins and products derived from them in tandem catalytic systems. Unfortunately, however, subsequent isomerization leads to the formation of the thermodynamically more stable internal olefins (eq 6).⁷² The mechanism of this observed olefin isomerization has therefore been the subject of careful study. It was initially assumed that olefin isomerization by **3-H₂** occurred via 2,1-insertion of the terminal olefin, followed by β -hydride elimination from carbon-3 (addition–elimination mechanism, Scheme 2a).⁷² However, recent studies indicate that isomerization proceeds predominantly through (^tBu₄PCP)Ir(1-alkene), which forms (^tBu₄PCP)Ir(η^3 -allyl)(H), which then rearranges to give (^tBu₄PCP)Ir(2-alkene). This π -allylic mechanism is shown Scheme 2b.⁶⁶



In part to develop improved catalysts for dehydrogenation of alkanes, a wide range of modified PCP pincer ligands with varying

Scheme 2. Possible Pathways for the Ir-Catalyzed Isomerization of Terminal to Internal Olefins**Figure 2.** Various iridium pincer complexes used for alkane dehydrogenation.

electronic and steric properties have been explored synthetically and computationally. DFT calculations indicated that electron-donating substituents such as methoxy groups in the *para* position of the ligand aryl ring favor oxidative addition of alkane C–H bonds to derivatives of the 14-electron complex **3**.²⁶ Experimentally, the *p*-methoxy-substituted complex (MeO-^tBu₄PCP)IrH₂ (**6a**-H₂; Figure 2) gave a 2–3-fold increase in turnovers for acceptorless dehydrogenation of cyclodecane as compared to **3**-H₂.⁷³ In particular, the sterically less bulky (MeO-ⁱPr₄PCP)IrH₄ (**6b**-H₄) was extremely effective in the acceptorless dehydrogenation of cyclodecane, with a total of 3050 turnovers obtained after 72 h under reflux conditions (201 °C). However, methoxy substitution did not greatly enhance catalytic activity in acceptorless dehydrogenation of *n*-alkanes or in the transfer dehydrogenation of COA or *n*-alkanes.⁷³

Although iridium pincer complexes have excellent thermal stability, they are still generally subject to decomposition at temperatures above ca. 200 °C for extended periods of time. This decomposition is of particular concern for acceptorless dehydrogenation, which requires much higher temperatures and longer reaction times to overcome the high enthalpic barrier of this reaction. Haenel, Kaska, Hall, and co-workers developed an anthraphos-supported iridium pincer complex (**7a**-H₂; Figure 2),

which was expected to be thermally very stable.⁷⁴ Indeed, the complex **7a**-H₂ tolerated reaction temperatures up to 250 °C, but was found to be significantly less reactive than **3**-H₂ under comparable conditions. The authors proposed that the inflexible anthraphos backbone forced the phosphino *tert*-butyl groups to block the metal center more so than in the case of pincers with the simple PCP *m*-xylyl backbone, thus inhibiting access of the alkane substrate to the metal center. It was proposed that the replacement of *tert*-butyl groups with isopropyl groups (complex **7b**) would enhance reactivity by reducing steric crowding. In another effort to prepare a more thermally stable complex without sacrificing catalytic activity, Punji et al. recently reported a thermally stable adamantyl-substituted iridium pincer complex, (^{Ad}₄PCP)Ir (**8**).⁷⁵ The adamantyl group was expected to be similar to a *tert*-butyl group with respect to both steric and electronic properties, but could offer more resistance to cyclo-metalation and/or P–C bond cleavage, which might be responsible for catalyst decomposition. Complex **8** indeed showed high thermal stability at 250 °C, which translated into improved catalytic activity for the acceptorless dehydrogenation of cyclodecane. Initial turnover frequencies obtained with **8**-H₂ were slightly less than those with **3**-H₂ and **5**-H₄, but overall turnover numbers from **8**-H₂ exceeded those from both **3**-H₂ and **5**-H₄.⁷⁵

One of the most notable modifications of the PCP ligand is represented by the bisphosphinite iridium pincer complexes (^R₄POCOP)Ir (^R₄POCOP = κ^3 -2,6-C₆H₃(OPR₂)₂) independently prepared by the Brookhart (**9**, R = ^tBu)²⁰ and Jensen (**10**, R = ⁱPr)²¹ groups. Both catalysts displayed higher catalytic activity in the benchmark COA/TBE transfer dehydrogenation reactions than **3**; (^tBu₄POCOP)Ir in particular showed activity an order of magnitude greater than that of **3** for this alkane/olefin couple. Conveniently, the catalytically active species is easily generated in situ from the reaction of air-stable (^tBu₄POCOP)Ir(H)(Cl) with NaOtBu. Variation of the substituents at the *para* position of the aryl ring of **9** was investigated, but no direct correlation between dehydrogenation activity and electron-donating ability was observed. Interestingly, in spite of its high activity for COA/TBE transfer–dehydrogenation, **9a** shows significantly lower reactivity than **3** for *n*-alkane/TBE transfer–dehydrogenation.^{65,76}

While the mechanism proposed for COA/TBE transfer–dehydrogenation by **9** (Scheme 3) is similar to that of (^tBu₄PCP)Ir (Scheme 1), there are subtle but significant mechanistic differences between the two catalysts.²⁰ While (^tBu₄PCP)Ir (**3**) reversibly reacts with TBE to give a vinylic C–H addition product, (^tBu₄POCOP)Ir forms a π -coordinated complex. More importantly, alkene hydrogenation by **9b**-H₂ is much more facile than by **3**-H₂. For example, TBE hydrogenations by **9b**-H₂ and **3**-H₂ proceed with comparable rates at –70 and 55 °C, respectively. Recent DFT calculations indicate that these differences are attributable to the fact that the metal center of (^tBu₄POCOP)Ir is much less sterically hindered than that of (^tBu₄PCP)Ir, as indicated in Figure 3.^{65,66,76} The lesser crowding in (^tBu₄POCOP)Ir is supported, for example, by Koridze's crystallographic characterization of (^tBu₄POCOP)Ir(CO), which can be compared with that of (^tBu₄PCP)Ir(CO) (P–Ir–P angles are 157.55(3)° and 164.510(8)°, respectively).⁷⁷ A more acute P–Ir–P angle results in a more open geometry in POCOP complexes; this is attributable to the shorter bonds to oxygen (P–O and C–O) and the wider bond angle (P–O–C) as compared with the analogous bond lengths and angles of the PCP methylene carbons.

Scheme 3. Proposed Mechanism of COA/TBE Transfer Dehydrogenation by 9

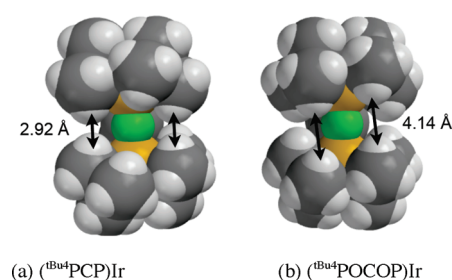
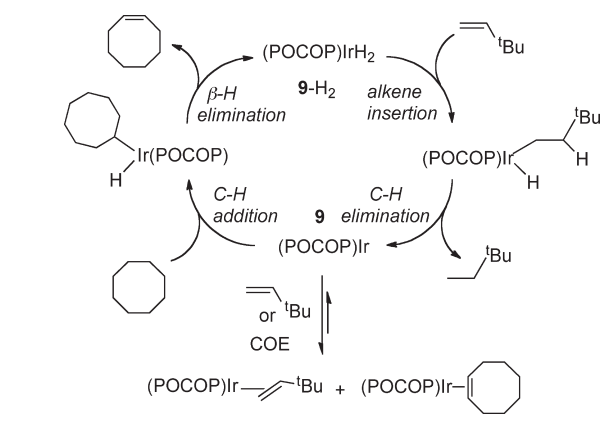


Figure 3. Geometric comparisons between $(^t\text{Bu}_4\text{PCP})\text{Ir}$ and $(^t\text{Bu}_4\text{POCOP})\text{Ir}$ (DFT-optimized structures).^{65,76}

While the difference in geometry between POCOP and PCP complexes is surprisingly large and well-defined, the electronic differences are, perhaps unexpectedly, fairly subtle and complex. Given the greater electronegativity of O vs C, one might expect reduced donating ability of the coordinating phosphorus atom and a commensurately less electron-rich metal center in POCOP complexes. However, DFT calculations show that the oxygen atoms donate substantial π -electron density to the aryl ring in the $(^t\text{Bu}_4\text{POCOP})\text{Ir}$ ligand. As a result, the iridium center in **9a** is calculated to be very slightly more electron-rich than that in **3**, at least in connection with the orbitals that are of π -symmetry with respect to the pincer aryl group.⁷³

The pronounced geometric difference between **9a** and **3** is probably the major factor responsible for the reactivity differences between them. For example, the ability of **9a** to coordinate TBE in a π -fashion would suggest, in accord with observation, that it could bind very strongly to α -olefins.^{65,76} Likewise, steric effects probably account for the observation that, as previously noted, complex **9a** shows faster rates of dehydrogenation of COA, but slower rates for linear alkanes in the presence of TBE acceptors. These differences between the two catalysts also play an important role in alkane metathesis, which will be discussed later.

Koridze et al. have reported that ferrocene and ruthenocene-based iridium pincer complexes **11-H₂** and **12-H₂** show excellent catalytic activity for COA/TBE transfer dehydrogenation, exceeding even that shown by **9a-H₂**. For example, turnover numbers of 3300, 2571, and 1843 were obtained for **11-H₂**, **12-H₂**, and **9a**, respectively, at 180 °C for 8 h.⁷⁷ The authors note that the five-membered cyclopentadienyl backbone rings result in a more acute P–Ir–P angle than in $(\text{PCP})\text{Ir}$ complexes. The

P–Ir–P angle in **11-CO** is in fact very comparable to that observed for $(^t\text{Bu}_4\text{POCOP})\text{Ir}(\text{CO})$; accordingly, the metal center in **11** is comparably less crowded than that in **3**. The authors also proposed that steric properties in metallocene-based complexes **11** and **12** are influenced by close contact between the non-metallated cyclopentadienyl ring and the *tert*-butyl group on the phosphine ligand. Given the favorable results obtained thus far, and the ability to exploit the bound CpM unit so as to tune the electronic properties of the pincer, these metallocene-based catalysts would seem to hold considerable promise.^{78,79}

The steric properties of the pincer ligand clearly have a major impact on the activity of pincer iridium dehydrogenation catalysts, as demonstrated, for example, by the much greater reactivity of $(^i\text{Pr}_4\text{PCP})\text{Ir}$ vs $(^t\text{Bu}_4\text{PCP})\text{Ir}$. A systematic investigation of the steric “tunability” was conducted by synthesizing analogues of **3** in which one or two of the phosphino-*tert*-butyl groups are replaced with methyl groups, while computationally all permutations of $(^{\text{Me},t\text{Bu}}_4\text{PCP})\text{Ir}$ were explored.⁸⁰ DFT calculations showed that the substitution of a single methyl group for a *tert*-butyl group had a large favorable energetic effect on the alkyl hydride β -hydrogen elimination step, the rate-determining step in the calculated dehydrogenation cycle. Indeed, $(^{\text{Bu}_3\text{Me}}\text{PCP})\text{Ir}$ (**13**) was found to dehydrogenate *n*-alkanes more efficiently than $(^t\text{Bu}_4\text{PCP})\text{Ir}$ (**3**), or even the less crowded $(^i\text{Pr}_4\text{PCP})\text{Ir}$ (**5**), both in the presence and in the absence of a hydrogen acceptor. For example, during the transfer–dehydrogenation of *n*-octane, catalyst **13** afforded 980 turnovers after 5 h at 150 °C, significantly greater than the 96 turnovers obtained with $(^t\text{Bu}_4\text{PCP})\text{Ir}$ and 208 turnovers observed with $(^i\text{Pr}_4\text{PCP})\text{Ir}$.

Further substitution of *t*Bu groups by Me groups was found to have little additional effect on the calculated barriers for the overall cycles. Decreased barriers to oxidative addition and β -hydrogen elimination were largely offset by increased energy of olefin binding to the less hindered metal centers. Experimental results obtained with *rac*-($^{\text{Bu}_2\text{Me}_2}\text{PCP})\text{Ir}$ (**14**) were slightly less favorable than those with **13**. This may be attributable to the stronger olefin-binding energy, in accord with the DFT calculations. However, attempts to crystallize *rac*-($^{\text{Bu}_2\text{Me}_2}\text{PCP})\text{Ir}$ precursors led to the isolation of dimeric species; this may suggest that the formation of inactive dimeric species under catalytic conditions may also play a role in the reduced reactivity of **14** as compared with the bulkier catalyst **13**.

It should be noted in general, as the above examples illustrate, that the relative effectiveness of different pincer iridium catalysts is very dependent on the specifics of the targeted reaction. The level of catalytic activity depends on the reactivity of the catalyst toward the specific alkane and acceptor and on the relative binding and deactivation by the acceptor and product. The nature of the rate-determining step is often dependent upon the olefin concentration, so that parameter too will influence the relative effectiveness of different catalysts. In addition, deactivation pathways other than simple olefin binding may depend on the nature of the olefins present as well as on other specific reaction conditions. Acceptorless dehydrogenation presents the additional concern that the rate of hydrogen extrusion from solution may be dependent on the reflux and stirring rates; thus, any quantitative comparisons between results with different catalysts by different workers should be interpreted cautiously.

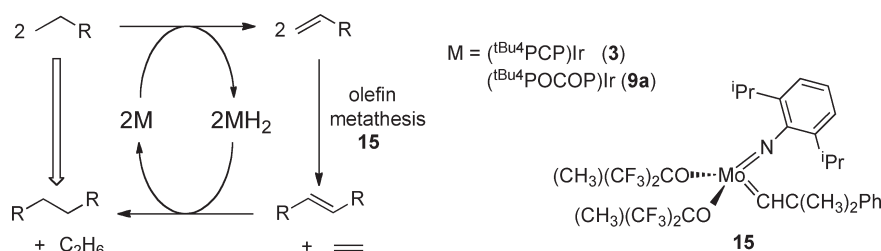
The immobilization of catalysts on solid supports offers significant advantages over homogeneous catalysts in terms of ease of separation and recycling. Scott, Brookhart, and Goldman⁸¹ recently prepared heterogeneous $(^t\text{Bu}_4\text{PCP})\text{Ir}$ and

Table 1. Metathesis of *n*-Hexane by 3 or 9a and 15: Distribution of *n*-Alkanes and Selectivity for Decane^a

Ir catalyst	time (h)	product concn (mM)				total product concn (M)	C ₁₀ /(C ₇ –C ₁₀) (%)
		C ₂ –C ₅	C ₇ –C ₉	C ₁₀	>C ₁₁		
(^t Bu ₄ PCP)IrH _n (3)	23	740	241	232	38	1.25	49.0
(^t Bu ₄ POCOP)IrH ₂ (9a)	24	1350	548	95	53	2.05	14.8

^a Reaction conditions: 3 or 9a (10 mM), 15 (16 mM), TBE (20 mM) in 7.6 M *n*-hexane at 125 °C.

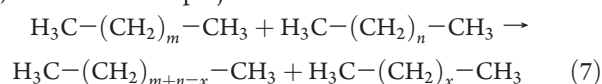
Scheme 4. Proposed Mechanism of Dual-Catalyst Alkane Metathesis



(^tBu₄POCOP)Ir catalysts via three different methods: (1) covalent attachment to a Merrifield resin, (2) covalent bonding to silica, and (3) adsorption on γ -alumina. The (^tBu₄POCOP)Ir catalysts on Merrifield resin and silica showed low to moderate activity for the transfer dehydrogenation of cyclooctane and were reported to decompose under the reaction conditions. However, (^tBu₄PCP)Ir and (^tBu₄POCOP)Ir derivatives possessing Lewis basic *para* substituents (e.g., NMe₂) bind strongly to γ -alumina and form thermally robust and recyclable catalysts. These γ -alumina-supported catalysts showed excellent activity toward COA/TBE transfer–dehydrogenation, with turnover numbers up to 7000 reported.

2.3. Alkane Metathesis

The ability to effect the metathesis of alkanes (which has also been referred to as disproportionation or molecular redistribution^{82,83}) has potential applications in fuel and bulk chemical production (eq 7). Oil refining and natural gas processing often yield a surplus of alkanes of certain carbon numbers; metathesis could potentially convert these to alkanes of more desirable molecular weights. A particularly promising application of alkane metathesis is in the context of Fischer–Tropsch (FT) catalysis. FT is likely to become increasingly important as both gas and coal become more plentiful relative to petroleum and perhaps as a route for the conversion of biomass to liquid fuel.^{84–86} Moreover, world demand for diesel fuel, the major FT fuel product, is increasing strongly relative to demand for gasoline, and this trend is projected to continue.⁸⁷

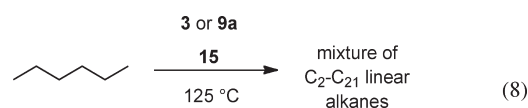


FT plants produce *n*-alkanes with carbon numbers ranging from 1 to >100. Waxes, C₂₀ or higher, are typically hydrocracked to lower MW. The resulting fraction from ca. C₉ to C₁₉ is particularly valuable as a clean-burning diesel component. This leaves a large fraction of *n*-alkane from C₃ to C₈, which is not in great demand as a transportation or heating fuel. Alkane metathesis potentially offers a route toward converting this

fraction into the diesel range, along with lesser amounts (by weight) of ethane.

The first example of alkane metathesis was achieved by Burnett and Hughes⁸² in 1973 using a mixture of two heterogeneous catalysts. At 400 °C, platinum/alumina acted as an alkane transfer–dehydrogenation catalyst, and tungsten oxide/silica catalyzed the metathesis of the resulting olefins. The reaction gave primarily *n*-alkanes, with a broad distribution of chain lengths. Later, Basset reported that silica-supported tantalum hydride complexes catalyzed alkane metathesis at lower temperatures (typically 150 °C).^{88,89} However, reports have been limited to low-MW reagents and products (mainly C_n < C₅), and yields and turnover numbers are relatively low. For example, silica-supported tantalum hydrides catalyzed the metathesis of propane to give 60 turnovers (6.1% conversion) after 120 h at 150 °C, producing mostly methane, ethane, and butanes.⁹⁰ Alumina-supported tungsten hydrides gave slightly greater turnover numbers for propane metathesis.⁹⁰

In 2006, Goldman, Brookhart, and co-workers reported alkane metathesis by tandem alkane dehydrogenation and olefin metathesis using combinations of an iridium pincer complex, 3 or 9a, and the Schrock catalyst 15.⁹¹ The pincer iridium complexes act as transfer–dehydrogenation catalysts, while the metathesized olefin products serve as hydrogen acceptors (Scheme 4). The systems exhibit high efficiency with overall product concentrations of 1.25 and 2.05 M obtained from 7.6 M *n*-hexane using 10 mM 3-H₂ and 9a-H₂, respectively, in combination with 15 (16 mM) after 1 day at 125 °C (eq 8 and Table 1).



The strategy underlying the tandem process is similar to that of the “hydrogen-borrowing methodology”^{92,93} commonly used in alcohol transformation, in which hydrogen is temporarily removed from substrates to enhance or change their chemical reactivity and is then returned to the products resulting from a chemical transformation.

Scheme 5. Product Formation Pathways for *n*-Hexane Metathesis: (a) Ideal Pathway To Produce *n*-Decane and Ethane Selectively, (b) Possible Pathway for Formation of *n*-Pentane and *n*-Heptane

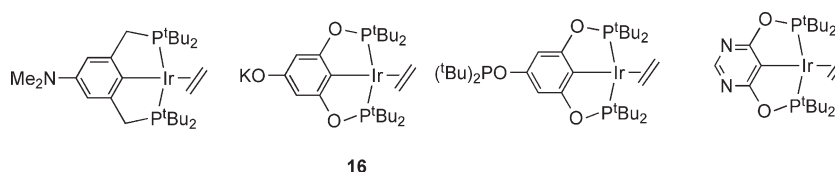
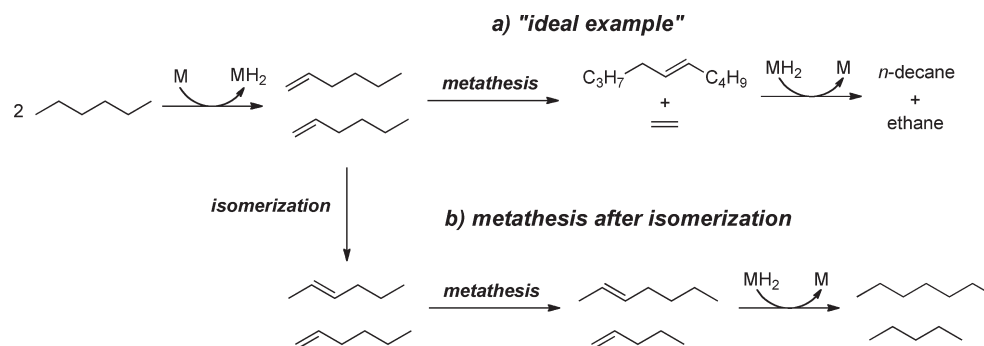


Figure 4. Iridium pincer complexes immobilized on alumina.

In what may be viewed as the ideal case, the pincer iridium catalyst effects dehydrogenation of C_n *n*-alkane at the terminal position to give α -olefin (as given in Scheme 4). Olefin metathesis then yields ethylene and the C_{2n-2} olefin, which are hydrogenated to the corresponding alkanes. When **9a** was used as the dehydrogenation catalyst, however, there was no selectivity for such products; instead the most abundant products were the C_{n+1} and C_{n-1} *n*-alkanes with decreasing amounts as the carbon number either increased or decreased from the carbon number of the substrate. In the case of **3**, the most abundant heavy product was in fact the C_{2n-2} *n*-alkane (specifically, *n*-decane from *n*-hexane) although selectivity was far from complete. The *n*-decane represented 49% of the total of "primary" heavy products (*n*-heptane, *n*-octane, *n*-nonane, and *n*-decane; higher MWs presumably result from the secondary metathesis of the primary alkane products).

It was initially proposed that primary products other than C_{2n-2} and ethane were predominantly formed via isomerization, prior to olefin metathesis, of the presumed α -olefin dehydrogenation product (Scheme 5b). Indeed, the known terminal regioselectivity⁷² of *n*-alkane dehydrogenation by **3** would seem to require isomerization to account for the relatively modest selectivity observed in the alkane metathesis. However, the complete lack of MW selectivity in alkane metathesis by **9a** may be more attributable to a lack of regioselectivity in the initial *n*-alkane dehydrogenation by this catalyst.^{65,76}

Differences in catalyst resting states were observed for alkane metathesis reactions catalyzed by **3**-H₂ and **9a**-H₂. For (^{*t*}Bu₄PCP)Ir, the corresponding dihydride complex was observed to be the catalyst resting state, implying that olefin hydrogenation is likely the turnover-limiting step. For (^{*t*}Bu₄POCOP)Ir, olefin-coordinated complexes were found to be the resting state, so loss of olefin from (^{*t*}Bu₄POCOP)Ir(olefin) followed by *n*-alkane dehydrogenation is likely to be the turnover-limiting sequence. This situation is related to that of the **3**-catalyzed COA/TBE transfer-dehydrogenation (Scheme 1) wherein, depending

upon the concentration of TBE, the turnover-limiting step could be either half of the overall cycle. (Note that under the alkane metathesis reaction conditions the steady-state concentration of olefin is very low and, accordingly, the hydrogenation part of the cycle is turnover-limiting in the case of alkane metathesis using **3**.)

Turnover numbers resulting from alkane metathesis by **3** and **15**, or by **9a** and **15**, are limited by the decomposition of the olefin metathesis catalyst **15**; this is not unexpected in view of the required high temperatures and long reaction times. This conclusion was confirmed by experiments in which addition of **15** to alkane metathesis reaction samples reinitiated catalytic activity after it had ceased. Therefore, a more thermally stable olefin metathesis catalyst, Re₂O₇/Al₂O₃, was investigated in lieu of **15**. This heterogeneous system was less reactive than the homogeneous Schrock complex **15**, requiring a higher temperature (175 °C) to achieve similar (although still slower) reaction rates. However, the reaction system indeed maintained catalytic activity for a longer period of time. The combination of **3**-H₂ (9 mM) and Re₂O₇/Al₂O₃ (16 mM effective Re₂O₇ concentration) yielded 3.62 M total *n*-alkane products (from C₂ to C₂₈) from 5.1 M *n*-decane after 11 days at 175 °C. The *p*-methoxy-substituted catalyst **6b**-H₄ gave even higher conversion, 4.37 M after 9 days.⁹¹

As noted above, Lewis basic substituents at the *para* position of the pincer ligands allow binding to γ -alumina without inhibiting catalytic dehydrogenation activity (Figure 4). Such systems, in combination with Re₂O₇/Al₂O₃, have been investigated for alkane metathesis and have afforded even greater turnover numbers.⁹⁴ Quite interestingly, the γ -alumina-supported dehydrogenation catalysts are compatible not only with Re₂O₇/Al₂O₃, but also with the Schrock catalyst **15**. Under these conditions, the Mo catalyst **15** is bound to alumina, a support which has not been previously reported for Schrock-type catalysts; the nature of this binding has not yet been determined.⁹⁴

Unfortunately, the heterogeneous alkane metathesis systems do not show high selectivity for C_{2n-2} product from C_n alkane. This may be due, in part at least, to a slower reaction of the heterogeneous olefin metathesis catalyst with α -olefin. Thus, the α -olefin has more time to undergo isomerization, catalyzed by the iridium complex, before it undergoes metathesis. In addition, γ -alumina and the olefin metathesis catalysts may also contribute to olefin isomerization.

A challenge in alkane metathesis is to avoid secondary metathesis, which decreases the overall selectivity. Thus, a two-pot system was designed as shown in Figure 5.⁹⁴ Using the apparatus shown, the dehydrogenation of n -alkanes and hydrogenation of olefins take place in the lower pot and the metathesis of olefins takes place in the higher pot. When dehydrogenation of a high-MW alkane product occurs, the resulting heavy olefin is unlikely to reach the higher pot and instead simply gets rehydrogenated, thus avoiding any net secondary reaction. For example, during n -octane metathesis using the two-pot apparatus, the only observed products of secondary metathesis were very small quantities of n - $C_{15}H_{32}$ and n - $C_{16}H_{34}$. Use of the two-pot system resulted in excellent turnover numbers (3910 after 52 h) and moderate recyclability of the catalysts.⁹⁴

A second advantage of the two-pot system follows from the fact that each catalyst typically functions most effectively under different reaction conditions.⁹⁵ As previously noted, the olefin metathesis catalyst **15** eventually decomposes under the reaction conditions of the alkane metathesis. Thus, keeping the two catalysts at different temperatures extends the catalyst lifetime as well as increases the selectivity of the system.

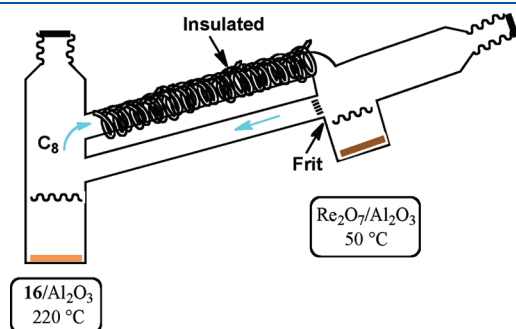


Figure 5. Two-pot system for alkane metathesis.

Since the instability of the olefin metathesis catalyst was found to limit the efficiency of the alkane metathesis systems, a range of olefin metathesis catalysts have been investigated in this context. Schrock and co-workers have tested more than 40 molybdenum and tungsten imido complexes in combination with pincer iridium complexes for alkane metathesis. In general, tungsten catalysts performed better than molybdenum analogues, presumably due to their greater stability.⁹⁶ The tungsten imido complex $W(NAr)(CHR)(OSiPh_3)_2$ ($Ar = 2,6$ -diisopropylphenyl, $R = CMe_2Ph$) gave the highest yields, about twice that obtained using the original molybdenum catalyst **15**.

Other pincer iridium catalysts were tested in combination with the Schrock catalyst **15** and gave improved reactivity.⁸⁰ Sterically less hindered $(^iPr_4PCP)Ir$ (**5**), $(^tBu_3MePCP)Ir$ (**13**), and $(^tBu_2Me_2PCP)Ir$ (**14**) complexes gave improved overall product yields, but lower selectivity for C_{2n-2} product (as shown in Table 2).⁸⁰ Catalyst **13** was the most effective of those tested, yielding 0.94 M total product after 8 h at 125 °C (ca. 2.5 times more than obtained with 3- H_n). In the case of $(^tBu_2Me_2PCP)Ir$ (**14**), the initial rates were comparable to those from $(^tBu_3MePCP)Ir$, but the productivity decreased rapidly, presumably due to catalyst decomposition.⁸⁰

Alkane metathesis has not been limited to linear alkanes. The metathesis of cyclooctane (Scheme 6) and cyclodecane has been reported.⁹⁷ $(^tBu_4POCOP)Ir$ and particularly $(^tBu_3MePCP)Ir$ (**13**) precursors were effective in this respect, giving cyclo-oligomers in decreasing amount with increasing carbon number (e.g., from COA, 14%, 9.4%, 4.6%, and 2.2% yield of cycloalkanes $C_{16}H_{32}$, $C_{24}H_{48}$, $C_{32}H_{64}$, and $C_{40}H_{80}$, respectively, after 12 h at 125 °C). $(^tBu_4PCP)IrH_2$ was much less effective at producing cyclo-oligomers (5.2% total yield of the C_{16} – C_{40} oligomers after 72 h under the same conditions) but, interestingly, gave significant amounts of polymer (29% yield after 72 h), which is apparently polyethylene resulting from ring-opening metathesis polymerization (ROMP) of cyclooctene and subsequent transfer–hydrogenation. Perhaps most surprisingly, $(^tBu_4PCP)IrH_2$ gave appreciable quantities (4% yield after 72 h) of the ring-contraction product cycloheptane; the ring contraction was proposed to occur via double bond isomerization of the C_9 alkylidene, leading to cycloheptene (Scheme 7), which underwent transfer–hydrogenation.

2.4. Dehydroaromatization of n -Alkanes

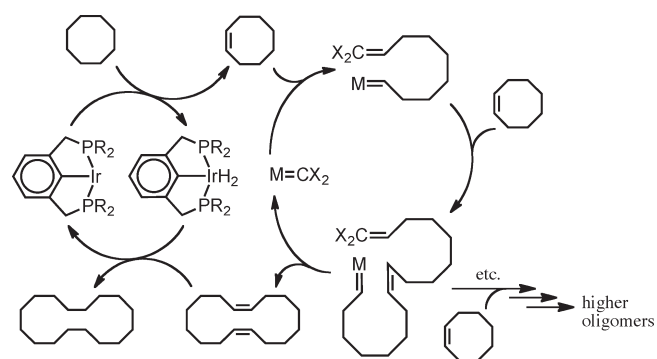
Aromatic compounds are critical building blocks in the chemical industry.⁹⁸ Alkylation of arenes currently ranks among

Table 2. Product Distribution for Metathesis of n -Hexane with Various Ir Catalysts^a

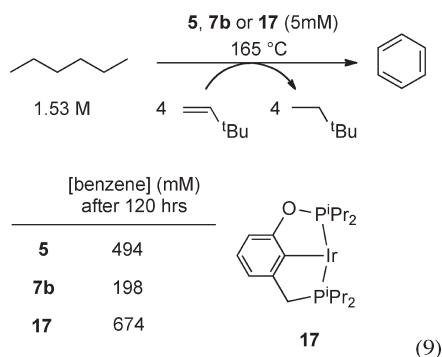
Ir catalyst	time (h)	product concn (mM)				total product concn (mM)	$C_{10}/(C_7-C_{10})$ (%)
		C_2-C_5	C_7-C_9	C_{10}	$C_{11}-C_{14}$		
$(^tBu_4PCP)IrH_n$ (3- H_n)	2	91	23	29	1	144	55.8
	8	203	67	114	8	391	63.0
$(^iPr_4PCP)IrH_4$ (5- H_4)	21	464	229	75	17	785	24.7
$(^tBu_3MePCP)IrH_4$ (13- H_4)	1	120	91	13	1	208	12.5
	3	305	240	38	7	574	13.7
	8	545	329	62	15	936	15.9
$(^tBu_2Me_2PCP)IrH_4$ (14- H_4)	1	145	81	15	3	244	15.6
	2	156	91	18	4	269	16.5
	7	264	157	34	12	467	17.8

^a Reaction conditions: 10 mM Ir, 6.4 mM Mo, 20 mM TBE in n -hexane (7.6 M) at 125 °C.

Scheme 6. Dimerization/Oligomerization of Cyclooctane via Dehydrogenation and Olefin Metathesis

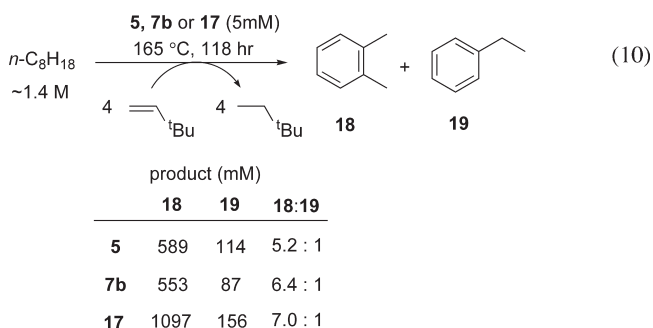
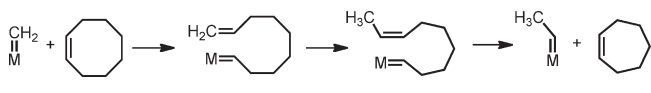


the largest scale chemical processes.^{99–102} The ability to selectively produce alkyl aromatics from alkanes, rather than from arenes and olefins, would have tremendous economic advantages. Heterogeneously catalyzed dehydroaromatization of *n*-alkanes is known to occur at very high temperatures (>500 °C), but such processes do not show any product selectivity, generally yielding a mixture of benzene and methyl-substituted arenes (toluene and xylenes) regardless of the feedstock.^{103–108} During an investigation of *n*-alkane dehydrogenation, the formation of benzene from *n*-hexane in low yield (2.3%) was observed using (MeO-^{*i*}Pr)₂PCP)Ir (**6b**) as a catalyst and norbornene (NBE) as a hydrogen acceptor.⁷³ More recently, an in-depth investigation of the dehydroaromatization of *n*-alkanes has been conducted, including the screening of various pincer iridium complexes, particularly **5**, **7b**, and **17** (eq 9).¹⁰⁹ The catalyst that emerged as most effective for this purpose was a hybrid phosphine/phosphinite pincer iridium complex (**17**) which gave 0.67 M benzene (44% yield) from 1.53 M *n*-hexane after 120 h at 165 °C in the presence of the TBE acceptor.

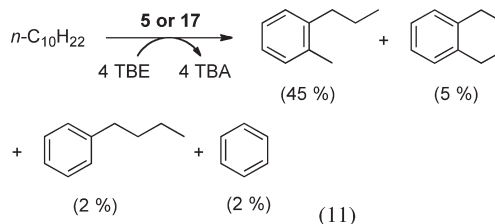


The dehydroaromatization of *n*-octane was catalyzed with even greater efficiency. Catalyst **17** converted *n*-octane to a mixture of *o*-xylene (**18**) and ethylbenzene (**19**) (eq 10) with a combined yield of 86% after 118 h at 165 °C. The formation of *o*-xylene was favored over that of ethylbenzene, and no *m*- or *p*-xylene was observed. The proposed mechanism for the dehydroaromatizations is shown in Scheme 8 for *n*-octane. Extensive dehydrogenation of *n*-alkane and isomerization generates a conjugated linear triene (**20** or **21**) which undergoes electrocyclic ring closure to yield the cyclic diene **22** or **23**. Dehydrogenation of **22** and **23** completes the aromatization.

Scheme 7. Cyclooctene Ring Contraction (the Key Segment of the Pathway for Cyclooctane Ring Contraction) via Isomerization of an Alkylidene Intermediate



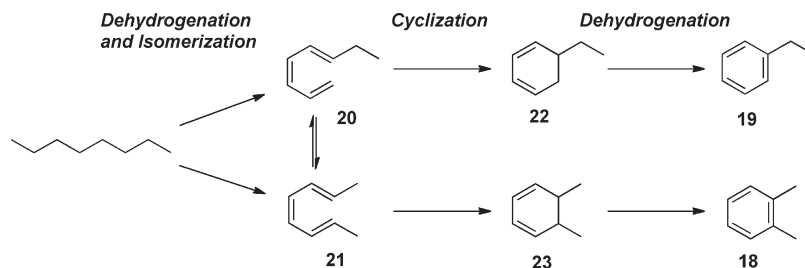
In industry, higher alkylarenes are currently synthesized from olefins and arenes.^{99–102} With olefins higher than ethylene, the products are always branched (although the products from linear olefins, particularly from α -olefins, are often referred to as linear alkylbenzenes). In contrast, when the dehydroaromatization of *n*-decane was catalyzed by **5** or **17**, no products with branched alkyl groups were observed; *o*-propyltoluene was the major product along with *n*-butylbenzene and 1,2-diethylbenzene as minor products (eq 11). Somewhat surprisingly, benzene formation was also observed.



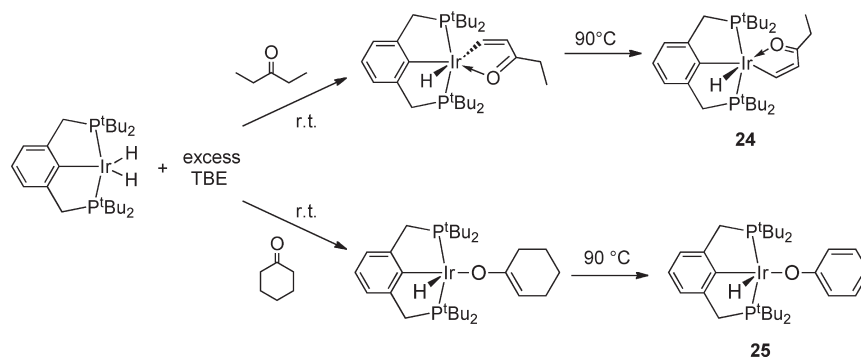
Dehydroaromatization of *n*-dodecane gave *o*-pentyltoluene as the predominant product with smaller quantities of 1-ethyl-2-propylbenzene, 1,2-dipropylbenzene, and *n*-hexylbenzene. In this case, however, surprisingly high quantities of benzene were formed (17% yield). The mechanism for benzene formation was not elucidated, but the kinetic profile indicates that it does not occur subsequent to electrocyclic ring closure. Accordingly, under similar reaction conditions, the use of either *n*-hexylbenzene or *n*-hexylcyclohexane as the dehydrogenation substrate does not yield appreciable amounts of benzene.¹⁰⁹

2.5. Dehydrogenation of Alkyl Groups of Functionalized Substrates

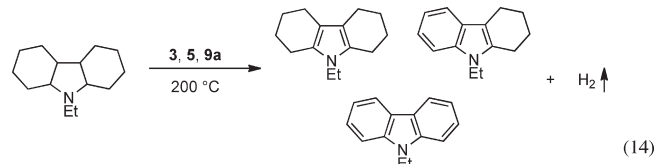
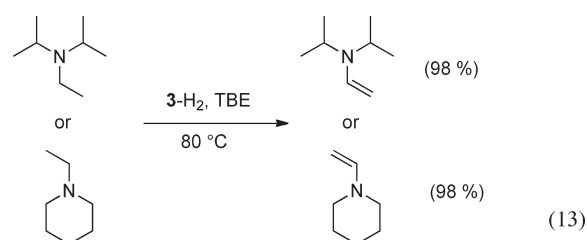
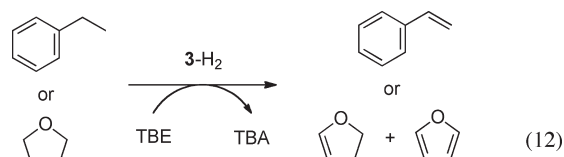
In addition to alkanes, the dehydrogenation of a number of functionalized substrates by pincer iridium catalysts has been reported. Immediately after the first report on dehydrogenation of alkanes by (^{*t*}Bu)₂PCP)IrH₂ (**3-H₂**), Kaska and Jensen reported the dehydrogenation of ethylbenzene and tetrahydrofuran (eq 12).¹¹⁰ The catalytic activity, however, was significantly lower than that reported for the dehydrogenation of cycloalkanes. The authors proposed that interaction between the catalyst and arene or oxygen groups inhibited the catalysis. Subsequent

Scheme 8. Proposed Mechanism for Dehydroaromatization of *n*-Octane

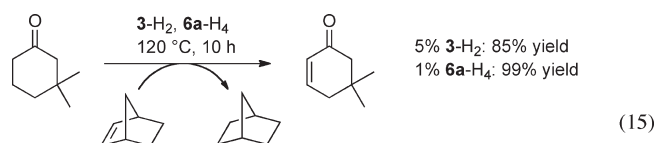
Scheme 9. Dehydrogenation of 3-Pentanone and Cyclohexanone



Work by Goldman and co-workers confirmed that **3** underwent addition of aryl and vinyl C–H bonds, which in fact inhibited the dehydrogenation of alkanes.^{63,64} The dehydrogenation of tertiary amines to form enamines in the presence of **3-H**₂ and TBE has been reported to occur in high yield and with good selectivity under relatively mild conditions (eq 13).¹¹¹ Several simple but previously unreported enamines such as *N,N*-divinylethylamine and *N,N*-di(isopropyl)vinylamine were prepared via amine dehydrogenation. In the context of hydrogen storage, acceptorless dehydrogenation of *N*-ethylperhydrocarbazole by pincer iridium complexes has been reported by Jensen (eq 14).¹¹²

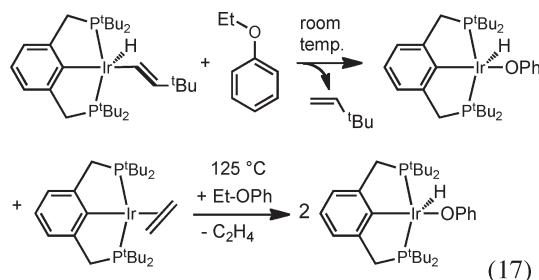
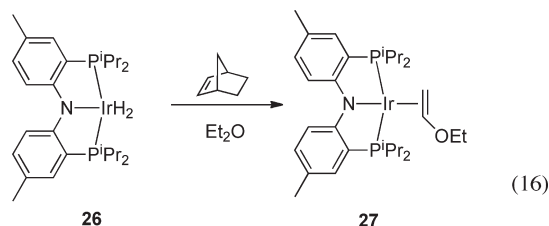


The direct synthesis of α,β -unsaturated ketones via the dehydrogenation of ketones has also been investigated. In most cases only stoichiometric reactions were observed, as catalysis was inhibited by the formation of catalytically inactive species resulting from reaction with the dehydrogenated product (Scheme 9).¹¹³ An exception to this was the catalytic dehydrogenation of 3,3-dimethylcyclohexanone to give α,β -unsaturated 3,3-dimethyl-6-cyclohexenone in high yield (eq 15).¹¹³

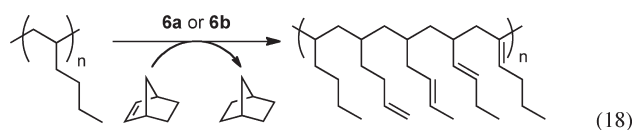


While the catalytic dehydrogenation of acyclic ethers by pincer iridium complexes has not yet been achieved, a stoichiometric dehydrogenation of diethyl ether has been reported by Grubbs. The reaction of Ozerov's (PNP)Ir complex **26** with diethyl ether was found to give the vinyl ethyl ether complex **27** (eq 16).¹¹⁴ Choi et al. have also investigated the reactions of acyclic ethers with **3**. The reaction of **3-H**₂ with diethyl ether in the presence of NBE gave a vinyl ethyl ether adduct apparently similar to compound **27**, but this product underwent decomposition even at room temperature. In contrast, the reaction of aryl ethyl ethers with **3**

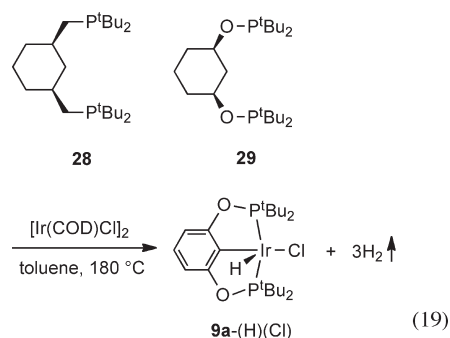
resulted not in dehydrogenation, but rather in the elimination of HOAr; apparently C–H addition is followed by β -aryloxide elimination, rather than β -hydride elimination (eq 17).¹¹⁵



The dehydrogenation of saturated polyolefins is an attractive route to their functionalization and may have the potential for the postpolymerization modification of physical and chemical properties of these materials. Coates and co-workers reported the dehydrogenation of poly-1-hexene by (MeO-^tBu₄PCP)Ir (**6b**) with yields up to 18% based on C₆ units (eq 18).^{116,117} Dehydrogenation was found only at the branches of the polymer and not in the backbone. Presumably, dehydrogenation was initiated at the terminal positions, and double bond isomerization subsequently occurred but was contained within the branches.



Recently, Wendt prepared cyclohexyl-based ^tBu₄PCP (**28**) and ^tBu₄POCOP (**29**) ligands in an attempt to synthesize sp³-hybridized carbon-supported pincer iridium complexes.¹¹⁸ Interestingly, during the metalation of **29** with [Ir(COD)Cl]₂, dehydrogenation of the cyclohexyl ring occurred to form the known complex **9a**-(H)(Cl) (eq 19).

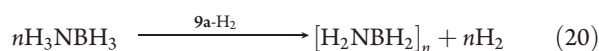


3. DEHYDROGENATION INVOLVING HETEROATOM–HYDROGEN BONDS

3.1. Dehydrogenation of Amine–Boranes

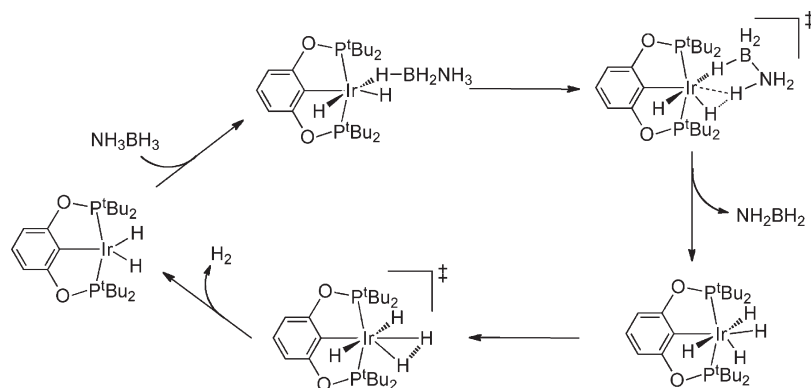
The use of dihydrogen as a fuel has emerged as a potential alternative to current petroleum-based transportation. There are, however, considerable challenges associated with the use of dihydrogen in transportation vehicles, including the question of its storage.^{35,119–124} Molecular hydrides represent one promising approach toward the development of efficient storage systems, and ammonia–borane (H₃N–BH₃) is of particular interest due to its high hydrogen content (19.6 wt %) and its stability in the solid state at ambient temperature. Transition-metal complexes, including those of Ru and Rh, have been investigated for the catalytic generation of dihydrogen from ammonia–borane and other amine–boranes (RNH₂–BH₃).^{35,125} Until recently,^{126–132} these reactions had generally been reported to be catalyzed not by homogeneous complexes, but by heterogeneous colloids or metal clusters.^{125,133,134}

In 2006, ammonia–borane dehydrogenation by a well-defined molecular complex was reported by Goldberg and Heinekey.¹³⁵ On the basis of the isoelectronic relationship between ammonia–borane and ethane, they considered that alkane dehydrogenation catalysts might also effect the dehydrogenation of ammonia–borane. Indeed, 0.5 mol % (^tBu₄POCOP)IrH₂ efficiently dehydrogenated ammonia–borane to produce 1 equiv of H₂ in 15 min at room temperature (eq 20). This remarkably high reaction rate was unchanged by the presence of elemental mercury, suggesting that the active catalyst was a soluble molecular species.



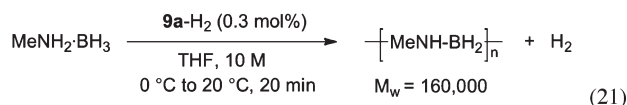
Although iridium pincer complexes catalyze the dehydrogenation of both alkanes and ammonia–borane, DFT calculations by Paul and Musgrave indicated that the ammonia–borane dehydrogenation occurs through a very different mechanism.¹³⁶ In contrast with alkane dehydrogenation, wherein the active species is the 14-electron pincer iridium center, (POCOP)IrH₂ was calculated to react directly with ammonia–borane (Scheme 10). A boron-bound hydride was calculated to coordinate to the 16-electron (POCOP)IrH₂, which is followed by concerted transfer of that hydride to Ir and a N-bound proton to one of the iridium-bound hydrides to give (POCOP)IrH₄. This pathway avoids the very endothermic loss of H₂ required in acceptorless dehydrogenation of alkanes and is thus consistent with the fact that the Goldberg–Heinekey system effects such rapid ammonia–borane dehydrogenation at room temperature. While ammonia–borane and ethane are formally isoelectronic, this pathway is enabled by both the very polar nature of the bonds to hydrogen in ammonia–borane (protic and hydridic, respectively) and the much lower endothermicity of ammonia–borane dehydrogenation.

While the dehydrogenation of ammonia–borane catalyzed by **9a**-H₂ rapidly generates dihydrogen, there are significant problems associated with this system in the context of hydrogen storage. First, only 1 equiv of dihydrogen was produced per molecule of substrate. Second, as the reaction proceeds, the catalyst becomes dormant due to the formation of (^tBu₄POCOP)IrH₂(BH₃) (**30**).¹³⁷ Finally, the product of the reaction is an insoluble oligoaminoborane, proposed to be a pentamer. The solubility issue was resolved by using *N*-methylamine–

Scheme 10. Proposed Mechanism of Ammonia–Borane Dehydrogenation by 9a-H₂

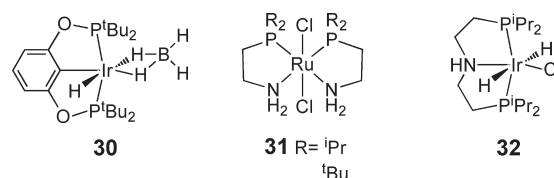
borane (MeAB), which underwent dehydrogenation by 9a-H₂ at a rate similar to that of ammonia–borane but giving a product soluble in THF.¹³⁸

Inspired by Goldberg and Heinekey's 2006 report,¹³⁷ Manners et al. demonstrated that dehydrogenation of amine–boranes catalyzed by 9a-H₂ offers an efficient route to high molecular weight poly(aminoborane)s,^{127,132} which are formally analogues of polyolefins. Treatment of a THF solution of MeAB (10 M) with 9a-H₂ generates well-characterized and soluble poly(aminoborane)s and 1 equiv of H₂ (eq 21). Gel permeation chromatography (GPC) analysis indicates a material with $M_w = 160\,000$ with a polydispersity index of 2.9; this characterization received further support from dynamic light scattering (DLS) studies. Use of ammonia–borane as the only monomer gives an insoluble polymeric product, but solutions of ammonia–borane and MeAB yield soluble random copolymers.^{127,132} The proposed mechanism of eq 21 involves the initial dehydrogenation of MeAB to generate unsaturated monomeric MeHN=BH₂, followed by metal-assisted polymerization.¹³² The poly(aminoborane)s represent a new class of inorganic polymers with promise in applications such as the synthesis of boron–nitride ceramics.^{36,127,132,139,140}



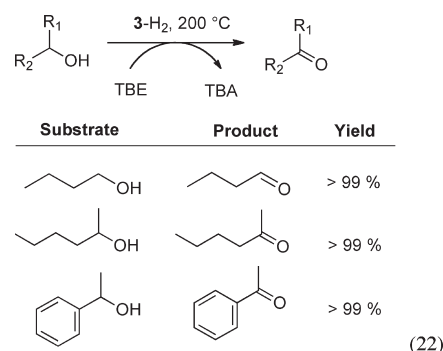
An interesting comparison can be made between the Musgrave mechanism for ammonia–borane dehydrogenation and the mechanism of alcohol dehydrogenation (the reverse of ketone hydrogenation) by Noyori-type catalysts;¹⁴¹ in both cases the metal center acts as a Lewis acid, accepting a hydride, while a proton is transferred to a ligand atom (H in the case of ammonia–borane dehydrogenation, N in the case of alcohol dehydrogenation). Other iridium pincer complexes have been investigated for the dehydrogenation of ammonia–borane or MeAB, at least in part with this consideration in mind. Fagnou and co-workers evaluated several efficient alcohol oxidation/reduction catalysts for ammonia–borane dehydrogenation.¹²⁸ Ru complex 31 in the presence of KO^tBu displayed excellent catalytic activity in the dehydrogenation of ammonia–borane and MeAB so that 2 equiv of H₂ was rapidly released from MeAB at room temperature. The authors also reported that

PNP iridium complex 32 in the presence of KO^tBu showed dehydrogenation activity, but much less than 31. Recent work by Manners has revealed that indeed a wide range of complexes, including Ru, Rh, and Pd species, are able to catalyze amine–borane dehydrogenation and polymerization.^{36,132,139,140}



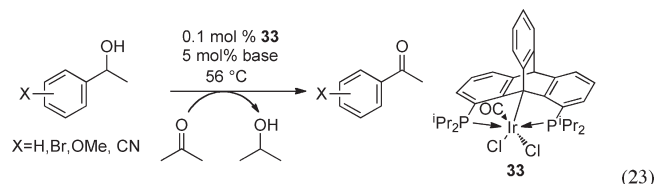
3.2. Dehydrogenation of C–N and C–O Linkages and Related Reactions

Jensen, Morales-Morales, and co-workers have reported that iridium pincer complex 3-H₂ catalyzes the transfer dehydrogenation of primary and secondary alcohols to give aldehydes and ketones, respectively (eq 22).¹⁴² The authors proposed that O–H bond activation of alcohols by (^tBu₄PCP)Ir (3) gave (^tBu₄PCP)Ir–(H)(alkoxide); β-hydride elimination from this species produced aldehyde or ketone and (^tBu₄PCP)IrH₂ (3-H₂), which hydrogenated TBE to regenerate 3. In the case of methanol, (^tBu₄PCP)Ir(CO) was obtained from decarbonylation of the resulting formaldehyde.

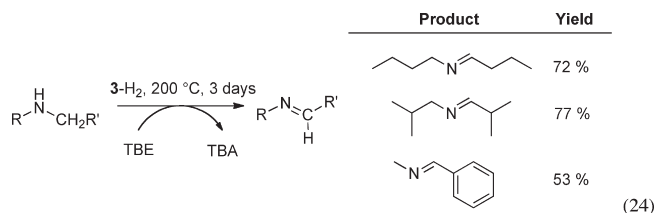


A different approach to alcohol dehydrogenation has been reported by Gelman with high-oxidation-state iridium pincer complexes and ketones as hydrogen acceptors. 1,8-Bis-(diisopropylphosphino)tritycene-supported pincer iridium

complex **33** was synthesized and displayed efficient catalytic activity for transfer dehydrogenation of alcohols in the presence of a base (eq 23).¹⁴³ Advantages associated with this system include high functional group tolerance and the ability to perform the reaction in air.



Primary and secondary amines are also subject to dehydrogenation by pincer iridium complexes. Jensen and Morales-Morales reported that **3-H₂** catalyzed the dehydrogenation of secondary amines to form imines (eq 24).¹⁴⁴ Two possible pathways for dehydrogenation of secondary amines were proposed: (1) initial N–H addition followed by β -H(alkyl) elimination or (2) initial C–H addition followed by β -H(amino) elimination. The authors favored the N–H bond activation pathway, which may receive some support from Hartwig and Goldman's reports of facile N–H bond activation by pincer iridium complexes.^{145,146} Unlike the dehydrogenation of tertiary amines,¹¹¹ the dehydrogenation of secondary amines was conducted at very high temperature (200 °C).



The reaction of **3** with *N*-ethyl-substituted secondary amines at ambient temperature has been reported by Zhang et al. to effect the stoichiometric dehydrogenation and cleavage of the aminoethyl C–C bond, giving two isomers of (PCP)Ir(H)(Me)(CNR), **34a** and **34b**.¹⁴⁷ The proposed mechanism is shown in Scheme 11. The initial step involves the dehydrogenation of a secondary amine to generate an imine, as reported in the work by Jensen and Morales-Morales. Oxidative addition of the resulting sp^2 C–H bond gives an iminoacyl

hydride. In analogy to metal acyl decarbonylation (CO deinsertion), migration of the imino methyl group to iridium gives isomeric isonitrile complexes **34a** and **34b**. Formation of these species, which are stable and presumably catalytically inactive at ambient temperature, can explain the need for elevated temperatures observed by Jensen and Morales-Morales and the less than quantitative yields of simple dehydrogenated product.¹⁴⁴

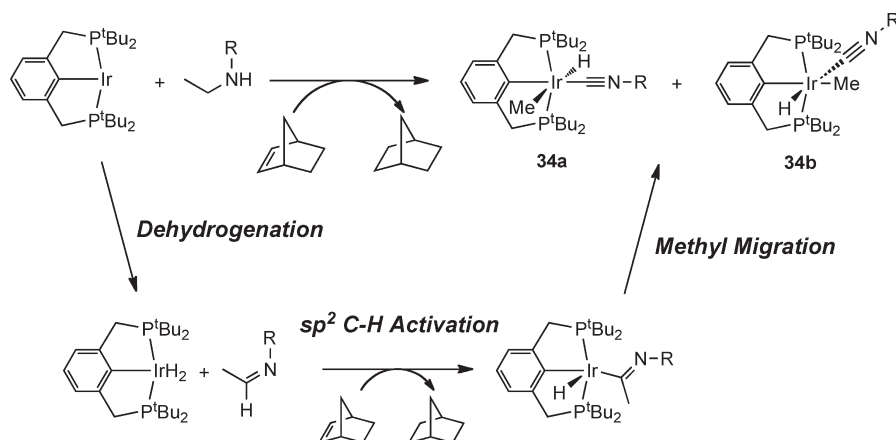
The transfer–dehydrogenation of primary amines by (^{*i*}Bu₄POCOP)Ir (**9a**) has been reported to yield nitriles (Scheme 12).¹⁴⁸ The mechanism of this reaction was extensively investigated in a series of kinetic and isotopic labeling experiments. Oxidative addition of an amine N–H bond, followed by turnover-limiting β -hydride elimination, produced intermediate **37**, which was readily converted to nitrile complex **38** via dehydrogenation. An equilibrium study and kinetic isotope effect measurements indicated that pre-equilibria (among **38**, **35**, and **36**) before the turnover-limiting β -hydride elimination significantly affected the overall reaction rate. Surprisingly, the conversion of imines to nitriles (**37** to **38**) was apparently a rapid step.

4. RELATED REACTIONS

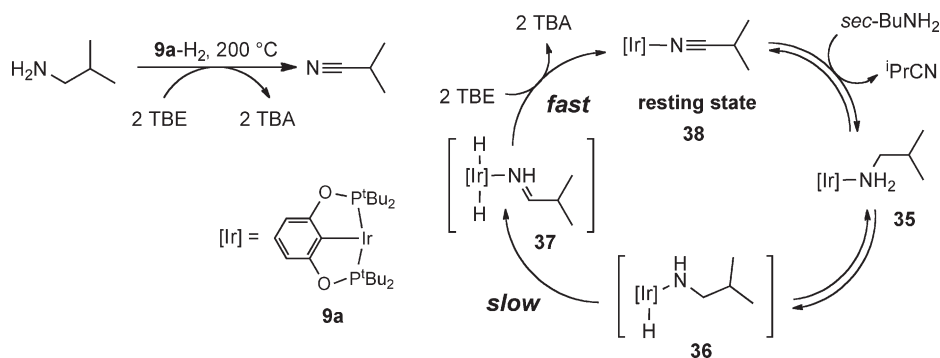
4.1. Hydrogenation of C=O Bonds

Pincer iridium complexes have been found to be effective for the catalytic hydrogenation of ketones and aldehydes under mild conditions. Abdur-Rashid, Gusev, and co-workers reported that air-stable [(^{*i*}Pr₂PC₂H₄)₂NH]IrH₂Cl (**32**) catalyzed the transfer–hydrogenation of various ketones with 2-propanol in the presence of KO^{*t*}Bu.¹⁴⁹ The amidodihydride complex [(^{*i*}Pr₂PC₂H₄)₂N]IrH₂ (**39**) and trihydride complex [(^{*i*}Pr₂PC₂H₄)₂NH]IrH₃ (**40**), synthesized independently, were also catalytically active, without requiring the use of base. These complexes were also able to catalyze ketone hydrogenation under a dihydrogen atmosphere.¹⁵⁰ An ionic hydrogenation mechanism was proposed (Scheme 13), related to the mechanism of ketone dehydrogenation by Noyori- or Shvo-type catalysts,^{141,151} in which an iridium hydride and a ligand-bound proton are donated in a concerted fashion. As noted above in the context of alcohol dehydrogenation, Gelman reported that air-stable complex **33** and derivatives thereof catalyze alcohol/ketone transfer–hydrogenation (eq 23); this has been applied to the transfer–hydrogenation of various acetophenones.^{152,153}

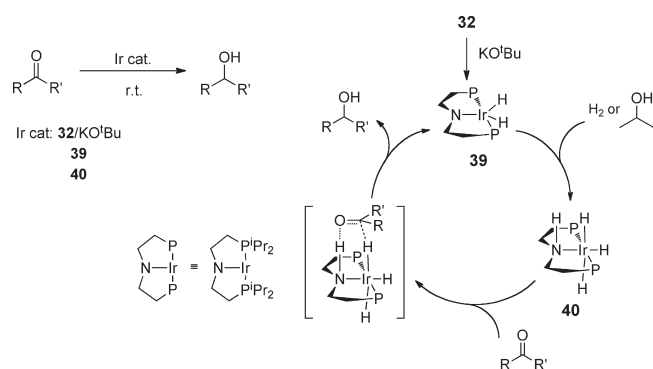
Scheme 11. C–C Bond Cleavage in Aminoethyl Groups in Secondary Amines



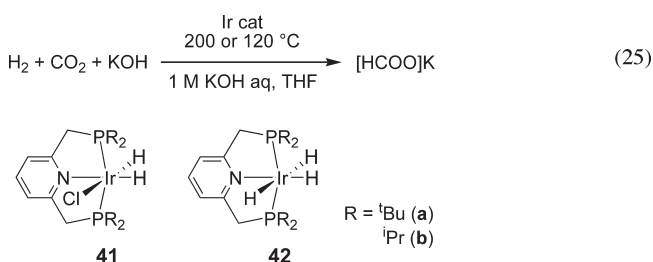
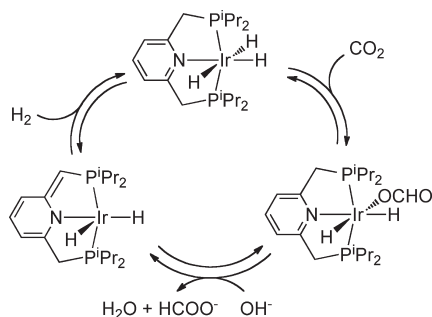
Scheme 12. Proposed Mechanism for the Dehydrogenation of Primary Amines to Nitriles by 9a



Scheme 13. Hydrogenation of Ketones by 32



addition of H₂ or benzene C–H bonds.¹⁵⁵ The mechanism of the reaction catalyzed by 3-H₂ was not proposed, but presumably does not involve ligand dearomatization.

Scheme 14. Proposed Mechanism for CO₂ Hydrogenation by 42b

Nozaki has recently reported the catalytic hydrogenation of carbon dioxide by pincer iridium complexes.¹⁵⁴ PNP (pyridine-based) complexes **41** and **42**, as well as the ^tBu₄PCP complex **3**, effected the hydrogenation of CO₂ in the presence of base to yield formic acid salts (eq 25). The most effective catalyst among those investigated was **42b**, giving turnover frequencies up to 150 000 per hour at 200 °C. 3-H₂ was also effective, giving 30 000 turnovers/h under identical conditions. The proposed mechanism (Scheme 14) involves dearomatization of the PNP ligand via deprotonation by potassium hydroxide, a reaction that has been well characterized by Milstein and co-workers during the

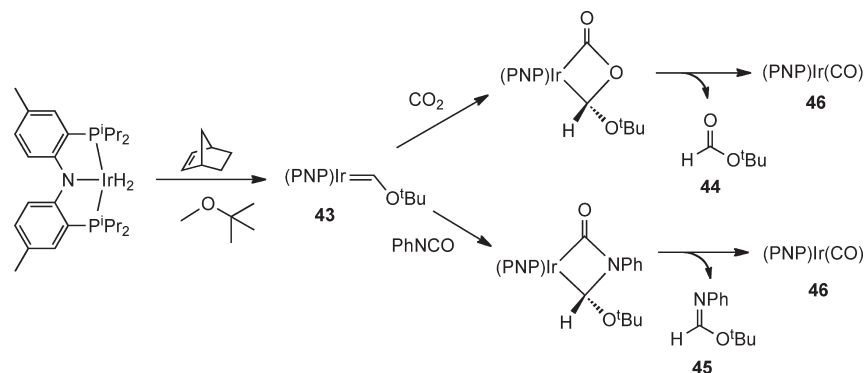
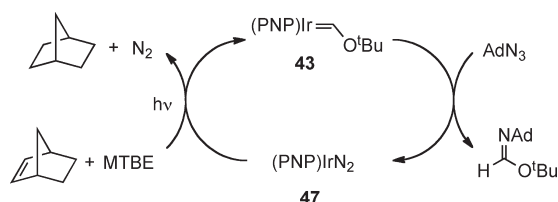
4.2. Formation of Carbene Complexes via α,α -Dehydrogenation and Reactions with Heterocumulenes

In 2008, Whited and Grubbs discovered that Ozerov's (PNP)Ir complex (PNP = [κ^3 -N(2-PⁱPr₂-4-Me-C₆H₃)₂])¹⁵⁶ undergoes α,α -dehydrogenation of methyl *tert*-butyl ether (MTBE) to form the iridium(I) carbene complex **43** (Scheme 15).^{157–159} Complex **43** possesses a nucleophilic iridium metal center^{160,161} and does not react with nucleophiles such as amines or alkoxides. It does react with heterocumulene electrophiles such as CO₂ or PhNCO to produce *tert*-butyl formate (**44**) or *tert*-butyl *N*-phenylformimidate (**45**) along with (PNP)Ir(CO) (**46**). The resulting CO ligand is strongly bound, precluding the completion of a catalytic cycle. The reactivity of **43** toward azides was thus investigated, and this analogously gave formimidate and (PNP)Ir(N₂) (**47**), but even N₂ bound too strongly to permit catalysis. It proved possible, however, to photolytically regenerate the 14-electron (PNP)Ir complex, thus achieving catalytic formation of *tert*-butyl *N*-adamantylformimidate (Scheme 16).¹⁶²

5. CONCLUSIONS AND OUTLOOK

Pincer ligands offer high thermal stability and great control of the steric and electronic properties of metal centers. These attributes are of obvious value in catalysis generally, as well as in other applications. With respect to iridium (and other platinum-group metals), the isolated pincer metal fragment generally has a d⁸ configuration and therefore a 14-valence-electron count. Such three-coordinate d⁸ fragments, iridium-based in particular, are notably effective for the oxidative addition of C–H bonds, leading to products that still have an available

Scheme 15. Generation of an Iridium Carbene Complex and Its Reaction with Heterocumulene

Scheme 16. Catalytic Conversion of MTBE to *tert*-Butyl *N*-Alkylformimidate

vacant coordination site, which allows β -hydrogen elimination. In the most basic pincer structure, with two ER_2 groups linked to a central coordinating group, the site *trans* to the central group is relatively open, while the *cis* sites are more obstructed by the R groups. This crowding tends to keep the *cis* sites available for the small hydride ligands derived from dehydrogenation. Indeed, the pincer iridium fragment seems almost custom-designed for the catalytic dehydrogenation of alkyl and related linkages. Given all these traits, it is not surprising that pincer iridium complexes have found utility in numerous applications (including, but not limited to, several catalytic reactions discussed in this review), but it is in the dehydrogenation of alkyl groups where they have dominated the field.

However, while PCP-type iridium dehydrogenation catalysts have been explored in depth, many other possible pincer motifs remain relatively or completely undeveloped. It seems unlikely that the (PCP)Ir class of fragments is uniquely suitable for dehydrogenation. Investigation of other pincers, and other metals, seems likely to yield dehydrogenation catalysts that are more robust, more active, and more selective. Such catalysts will likely emerge from purely exploratory work as well as from studies elucidating a deeper understanding of the properties that have led to the success of the (PCP)Ir class of catalysts.

Olefins are of little value as end products, but they are perhaps the single most important and diverse class of intermediates in organic chemistry. Alkane dehydrogenation catalysts would therefore seem to hold great potential in tandem catalysis, potential which workers in the field have just begun to realize. Pincer ligands, which frequently engender a high degree of crowding, may be particularly amenable to tandem-catalyst systems since such crowding may inhibit reactions with cocatalysts or coreagents.

The development of solid-supported pincer systems^{81,94,163–169} is a relatively new area, but one which is rapidly yielding successful results. Given the strong binding of pincers to a metal center, metal leaching in such heterogeneous systems is not likely to be a problem. This bodes well for the progression of pincer catalysts from research laboratories to industrial applications. Heterogenization may prove particularly valuable in the development of tandem systems by inhibiting potential reactions of pincer catalysts with cocatalysts (especially heterogeneous ones) and coreagents.

Finally, the factors that make iridium pincer complexes so effective for alkane dehydrogenation may also be applicable to seemingly unrelated reactions. For example, the ability to oxidatively add a C–H (or other) bond to yield a coordinatively unsaturated addition product could clearly lead to many different reactions. The ability of such adducts to undergo β -hydrogen elimination is critical for dehydrogenation, but the ability to undergo β -elimination of groups other than hydrogen,¹¹⁵ or α -elimination of hydrogen^{114,157–162} or of other groups,¹¹⁵ is perhaps beginning to open new avenues of catalyst development that exploit the same properties that make pincer iridium catalysts so effective for dehydrogenation.

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BIOGRAPHIES



Jongwook Choi received a B.E. and M.E. in chemical engineering at Hanyang University in Korea, working with Prof. Sang-man Koo. In 2007, he received a Ph.D. in chemistry under the direction of Prof. Jack R. Norton at Columbia University, where he studied transition metal hydrides and their applications. He then joined the lab of Prof. Alan Goldman at Rutgers University as a postdoctoral associate. His current research interests are in the activation of strong bonds such as C–H, C–O, and C–F, and in the mechanistic study of such reactions.



Amy H. Roy MacArthur received her B.A. from Wellesley College in 1998 and her Ph.D. from Yale University in 2003. Under the supervision of Professor John Hartwig, her graduate work focused on the scope and mechanism of Pd-mediated reactions of aryl halides and tosylates. She then participated in the development of a dual catalyst system for alkane metathesis during her postdoctoral work with Professor Maurice Brookhart at the University of North Carolina at Chapel Hill. In 2006 she joined the faculty at the United States Naval Academy as an Assistant Professor of Chemistry. Her research is currently focused on transition metal-catalyzed reactions of substrates with low reactivity, such as aryl chlorides, via tandem catalysis.



Maurice Brookhart grew up in the mountains of western Maryland and attended Johns Hopkins University in Baltimore, where he received an A.B. degree in chemistry in 1964. He carried out his doctoral work in physical organic chemistry at UCLA under the direction of Saul Winstein. After finishing the Ph.D. degree in 1968, he spent six months as a National Science Foundation postdoctoral fellow at UCLA followed by a year of

study at Southampton University as a NATO postdoctoral fellow. Brookhart joined the University of North Carolina faculty in 1969 and is currently a William R. Kenan, Jr., professor of chemistry. Brookhart's research interests span mechanistic, synthetic, and structural organometallic chemistry. Most recently, his efforts have focused on the development and mechanistic understanding of late transition metal complexes for olefin polymerizations and employing carbon–hydrogen bond activation processes in catalytic transformations of small molecules.



Alan Goldman grew up in the streets of eastern Queens in New York and attended Columbia College, where he received his B.A. degree in 1980. He carried out his doctoral work in organometallic photochemistry under the direction of Prof. David Tyler at Columbia University, where he received his Ph.D. degree in 1985. He then worked as a postdoctoral fellow in the laboratory of Prof. Jack Halpern at the University of Chicago. In 1987 Goldman joined the faculty at Rutgers, The State University of New Jersey, where he is currently Professor of Chemistry. Among his previous honors are the Dreyfus Distinguished New Faculty Award, a Sloan Foundation Fellowship, the Dreyfus Foundation Teacher-Scholar Award, and the Union Carbide Innovation Recognition Award. His research group is focused on discovering and understanding catalytic and catalytically relevant reactions of transition metal complexes with small molecules. Emphasis has been on the organometallic activation and functionalization of C–H bonds, and recent activity in the lab has also been directed at understanding the formation and cleavage of C–C, C–O, and C–F bonds.

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