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Alkane Metathesis by Tandem Alkane-Dehydrogenation–Olefin-Metathesis Catalysis and Related Chemistry

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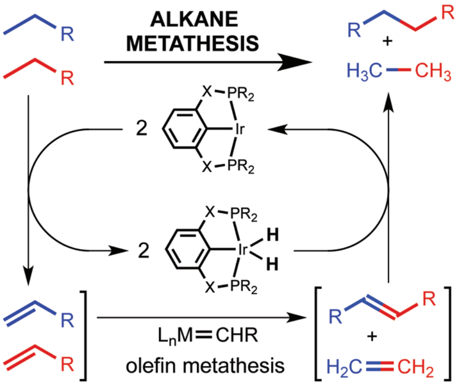
CONSPECTUS



Methods for the conversion of both renewable and non-petroleum fossil carbon sources to transportation fuels that are both efficient and economically viable could greatly enhance global security and prosperity. Currently, the major route to convert natural gas and coal to liquids is Fischer–Tropsch catalysis, which is potentially applicable to any source of synthesis gas including biomass and nonconventional fossil carbon sources. The major desired products of Fischer–Tropsch catalysis are *n*-alkanes that contain 9–19 carbons; they comprise a clean-burning and high combustion quality diesel, jet, and marine fuel. However, Fischer–Tropsch catalysis also results in significant yields of the much less valuable C_3 to C_8 *n*-alkanes; these are also present in large quantities in oil and gas reserves (natural gas liquids) and can be produced from the direct reduction of carbohydrates. Therefore, methods that could disproportionate medium-weight (C_3–C_8) *n*-alkanes into heavy and light *n*-alkanes offer great potential value as global demand for fuel increases and petroleum reserves decrease.

This Account describes systems that we have developed for alkane metathesis based on the tandem operation of catalysts for alkane dehydrogenation and olefin metathesis. As dehydrogenation catalysts, we used pincer-ligated iridium complexes, and we initially investigated Schrock-type Mo or W alkylidene complexes as olefin metathesis catalysts. The interoperability of the catalysts typically represents a major challenge in tandem catalysis. In our systems, the rate of alkane dehydrogenation generally limits the overall reaction rate, whereas the lifetime of the alkylidene complexes at the relatively high temperatures required to obtain practical dehydrogenation rates (ca. 125 –200 °C) limits the total turnover numbers. Accordingly, we have focused on the development and use of more active dehydrogenation catalysts and more stable olefin-metathesis catalysts. We have used thermally stable solid metal oxides as the olefin-metathesis catalysts. Both the pincer complexes and the alkylidene complexes have been supported on alumina via adsorption through basic *para*-substituents. This process does not significantly affect catalyst activity, and in some cases it increases both the catalyst lifetime and the compatibility of the co-catalysts.

These molecular catalysts are the first systems that effect alkane metathesis with molecular-weight selectivity, particularly for the conversion of C_n *n*-alkanes to C_{2n-2} *n*-alkanes plus ethane. This molecular-weight selectivity offers a critical advantage over the few previously reported alkane metathesis systems. We have studied the factors that determine molecular-weight selectivity in depth, including the isomerization of the olefinic intermediates and the regioselectivity of the pincer-iridium catalyst for dehydrogenation at the terminal position of the *n*-alkane.

Our continuing work centers on the development of co-catalysts with improved interoperability, particularly olefin-metathesis catalysts that are more robust at high temperature and dehydrogenation catalysts that are more active at low temperature. We are also designing dehydrogenation catalysts based on metals other than iridium. Our ongoing mechanistic studies are focused on the apparently complex combination of factors that determine molecular-weight selectivity.

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Introduction

The activation of inert C–H bonds by transition metal complexes has been one of the major areas of interest in organometallic chemistry for the past three decades. Such research is generally conducted with the ultimate goal of catalytic functionalization of the substrate; indeed, as the present issue of Accounts attests, significant advances continue to be made in terms of this important goal. Nevertheless, consideration of the world economy, now and for the foreseeable future, leads to the realization that the total value of *unfunctionalized* hydrocarbons far exceeds the value of their functionalized derivatives. This is of course largely due to the value of unfunctionalized hydrocarbons as high energy-density transportation fuels. The work described in this Account is based on the prospect of exploiting organometallic C–H activation to convert alkane substrates to alkane products, particularly products that are highly desirable as transportation fuel.

The developed world and the largest developing countries have relatively meager and dwindling petroleum reserves that will supply a continually decreasing fraction of demand. Even global reserves of readily recoverable oil will satisfy an increasingly small fraction of the demand for liquid hydrocarbons.[1,2] By contrast, the same developed and developing countries (particularly the United States, China, and India) have large reserves of non-petroleum fossil fuel, and the global supply of non-petroleum fossil fuel will long outlast that of petroleum.[1,2] Fischer–Tropsch catalysis[3] (oligomerization of CO and H_2, i.e., syngas) is the major route from such non-petroleum resources to liquid fuel. The syngas feedstock for Fischer–Tropsch plants is currently derived from natural gas and from coal, but oil shale, oil sands, and waste are potential sources as well.[4] Perhaps most attractively, biomass gasification presents the opportunity for a hydrocarbon fuel cycle that is in principle carbon-neutral, as does the reduction of CO_2 driven by a sustainable energy source such as solar or nuclear.

"Fischer–Tropsch diesel", which is largely *n*-alkanes of chain length 9–19 carbons, is the ideal liquid transportation fuel. Diesel engines are ca. 30% more efficient than gasoline engines[5] but unfortunately have a greater tendency to produce particulate matter.[6] *n*-Alkanes, however, are much less prone to particulate formation upon combustion than are typical alicyclic and aromatic components in diesel and jet fuel;[6–8] moreover, *n*-alkanes in the C_9–C_{19} range have excellent diesel combustion quality.[6–9]

Although Fischer–Tropsch technology has steadily improved since its discovery almost a century ago, the distribution of *n*-alkane products is still approximately stochastic.[3] Products greater than C_{19} are generally hydrocracked to lower weight to give a distribution of hydrocarbons from C_1 to C_{19}. Accordingly, a significant fraction of the total *n*-alkane produced is in the range ca. C_3–C_8 which is not desirable as transportation fuel. Lighter *n*-alkanes are also in great supply as the primary constituent of natural gas liquids, representing ca. 10% of current world oil production, a value estimated to rise to ca. 20% by 2030.[1] *n*-Alkanes lower than C_8 can also be obtained efficiently, and potentially in large quantities, from the direct reduction of carbohydrates.[10]

The ability to combine shorter chain *n*-alkanes to give Fischer–Tropsch-diesel-range products is thus a challenge of tremendous importance. One approach to this goal which, uniquely, involves no reagent other than alkane itself, nor does it produce any byproduct, is alkane metathesis (AM, eq 1), the recombination or rearrangement of *n*-alkanes to give *n*-alkanes of different chain lengths.

$$\begin{aligned} &R^1{-}CH_2{-}CH_2{-}R^2 + R^3{-}CH_2{-}CH_2{-}R^4 \\ &\quad \rightleftharpoons R^1{-}CH_2{-}CH_2{-}R^3 + R^2{-}CH_2{-}CH_2{-}R^4 \qquad (1) \end{aligned}$$

In 2003, the National Science Foundation announced a program to establish "Chemical Bonding Centers" (CBCs) which focused on collaborations designed to address high-risk high-impact challenges. In response, a group including the authors formed the Center for the Activation and Transformation of Strong Bonds (CATSB) led by Karen Goldberg at the University of Washington. Thanks to this impetus, and informed by an ongoing collaborative relationship with Dr. William Schinski at Chevron, we decided to pursue the goal of a molecular catalytic system for AM. As this project developed and expanded with NSF support through the CBC program, then the CCI program (Centers for Chemical Innovation), Susannah Scott (UC-Santa Barbara) and Richard Schrock (MIT) joined us on the collaborative AM project.

At the outset of the work described in this Account, heterogeneous catalytic AM systems had been reported by two groups. Basset and co-workers had reported[11,12] systems based on tantalum hydride supported on silica and tungsten hydride supported on alumina that effected AM with smaller alkanes, for example, the disproportionation of ethane to give methane and propane. A system that seemed more closely related to our own research in alkane dehydrogenation,[13–17] brought to our attention by Bill Schinski, had been reported by Burnett and Hughes at Chevron.[18] The Burnett–Hughes system effected AM using heterogeneous catalysts for alkane dehydrogenation and olefin metathesis (platinum-on-alumina and tungsten-oxide-on-silica, respectively). This system

SCHEME 1

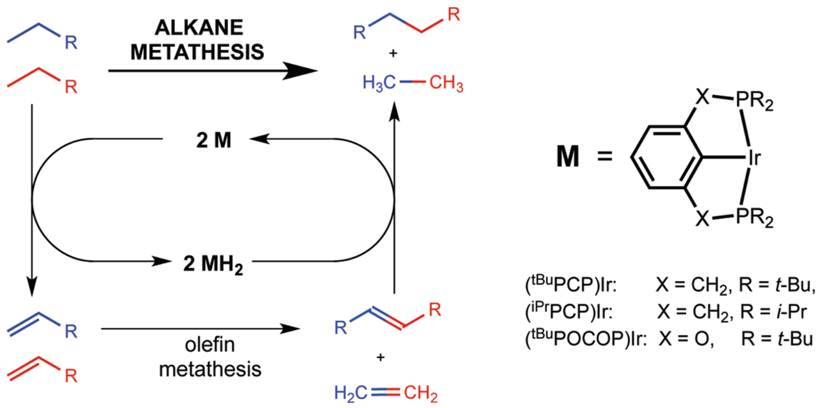


TABLE 1. Metathesis of *n*-Hexane (7.6 M) by (^{tBu}POCOP)Ir(C_2H_4) or (^{tBu}PCP)IrH_2 (10 mM) and Mo-F12 (16 mM): Distribution of C_2–C_{15} *n*-Alkane Products (mM) (from ref 25)[a]

Ir catalyst precursor	[TBE]/mM	temp/°C	time	C_2	C_3	C_4	C_5	C_7	C_8	C_9	C10	C_{11}	C_{12}	C_{13}	C_{14}	$C_{\geq 15}$	total (M)
(^{tBu}POCOP)Ir(C_2H_4)	0	125	6 h	123	123	105	183	131	73	70	47	10	4	2	1	0.3	0.75
			24 h	233	233	191	319	234	133	122	81	22	9	5	2	1	1.35
			2 d	261	261	215	362	265	147	138	89	25	11	6	3	**1**	1.52
			4 d	264	264	218	372	276	154	146	95	26	12	6	3	1	1.57
	added additional Mo-F12 (8 mM)																
			5 d	502	502	436	721	420	239	223	153	56	30	18	10	5	2.81
(^{tBu}PCP)IrH_2	20	125	23 h	(131)	176	127	306	155	37	49	232	18	4	4	10	2	1.25
	added additional Mo-F12 (6.4 mM)																
			46 h	(189)	255	193	399	208	61	81	343	31	9	9	22	7	1.81

[a] 6.4 mM Mo-F12 added initially. For experiments with (^{tBu}POCOP)Ir(C_2H_4), no separation of C_2 and C_3 peaks was obtained. See ref **25** for details.

operated at high temperatures (400–800 °C) and gave an essentially stochastic distribution of predominantly *n*-alkanes from a given *n*-alkane feedstock. We considered the possibility that homogeneous catalysts operating on the same principle might offer significant advantages such as lower operating temperatures and greater selectivity.

Discovery of a Molecular Tandem Catalytic Alkane Metathesis System

The pincer-ligated iridium-based alkane-dehydrogenation catalyst precursor (^{tBu}PCP)IrH_2 (^{R}PCP = κ^3-C_6H_3-2,6-(CH_2PR_2)$_2$) was introduced by Craig Jensen and William Kaska in 1996.[19] In collaboration with Jensen, we subsequently demonstrated that (^{tBu}PCP)Ir (the catalytically active species[20,21]) and the less bulky and more active analogue, (^{iPr}PCP)Ir, were selective for dehydrogenation at the terminal position of *n*-alkanes (although the α-olefin kinetic product subsequently underwent rapid double-bond isomerization).[15] Dehydrogenation of a C_n *n*-alkane at the terminal position followed by olefin metathesis and then hydrogenation of the metathesized olefin products would yield C_{2n-2} *n*-alkane plus ethane. The basic catalytic cycle for AM is illustrated in Scheme 1.

In our initial efforts to achieve the catalysis outlined in Scheme 1 we combined (^{tBu}PCP)IrH_2 and 2 equiv of a sacrificial acceptor (e.g., *t*-butylethylene, TBE) with the Grubbs catalyst $(PCy_3)_2Cl_2Ru{=}CHPh$[22] in *n*-alkane. No *n*-alkane metathesis was observed. Instead, the iridium complex had apparently undergone reaction with the olefin-metathesis catalyst to give the catalytically inactive species (^{tBu}PCP)IrHCl. This illustrates a common obstacle to the design of tandem catalytic systems, the requirement of catalyst compatibility.[23]

In further experiments, the dehydrogenation-catalyst precursor (^{tBu}POCOP)Ir(C_2H_4)[13,14] was combined with the Schrock catalyst "Mo-F12".[24] An *n*-hexane solution of (^{tBu}POCOP)Ir(C_2H_4) and Mo-F12 was heated at 125 °C under argon in a sealed glass vessel. After 24 h, 135 equiv of *n*-hexane was converted to a range of C_2 to C_{15} *n*-alkanes (1.35 M).[25] No branched or cyclic alkanes were detected. Further heating resulted in relatively little additional conversion. Results are summarized in Table 1.

^{31}P NMR spectroscopy revealed that although the reaction effectively stopped after ca. 24 h, the dehydrogenation catalyst was not decomposed, and was present as various olefin complexes of (^{tBu}POCOP)Ir. This suggested that the deactivation of the catalyst system originated with the olefin-metathesis catalyst. Indeed, AM resumed upon addition of fresh Mo-F12 to a solution that had lost its catalytic activity. (Decay of Mo-F12 is expected based on previous studies by Schrock.[26]) This serves to illustrate that the aforementioned issue of compatibility of co-catalysts in a tandem system extends beyond the possibility of a reaction between the co-catalysts; an equally important consideration is that both catalysts must be tolerant of the same reaction conditions.[23]

The use of either (^{tBu}POCOP)IrH_2 or (^{tBu}PCP)IrH_2 and 2 equiv of TBE, under the same conditions as the above experiment, gave turnover numbers (TONs) comparable to those obtained with (^{tBu}POCOP)$Ir(C_2H_4)$. Presumably, one equiv of TBE is hydrogenated by the initially added (pincer)-IrH_2, while the second undergoes transfer hydrogenation resulting in a steady state of 1 mol "(pincer)Ir" and 1 mol olefin throughout the course of the reaction.

The formation of linear products primarily C_{10} or lower is consistent with alkane metathesis proceeding via dehydrogenation followed by olefin metathesis and hydrogenation, rather than other possible mechanisms, including that of the Basset systems.[11,12]

Development of New Pincer-Iridium Dehydrogenation Catalysts

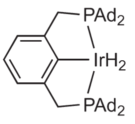
The pincer ligand motif is particularly amenable to catalyst tuning. The discovery of the tandem systems for catalytic alkane metathesis has stimulated continuing efforts toward the design and development of new pincer-based dehydrogenation catalysts,[27] including catalysts incorporating other metals and coordinating groups other than the P–C–P set (i.e., PCP and POCOP type pincers).

We have recently reported several new catalysts with the P–C–P set of coordinating groups. Prior to the AM work, we had shown that (^{iPr}PCP)Ir precursors were more active for both acceptorless- and transfer-dehydrogenation than the (^{tBu}PCP)Ir "parent" complexes.[15] Thus, decreased steric crowding apparently favored catalytic activity. The ^{iPr}PCP complexes did not seem as robust, however, and the isolation and crystallization of ^{iPr}PCP complexes has generally been much more difficult than the ^{tBu}PCP analogues. We reasoned that ligands with Me groups would obviously be less crowded, and could be more resistant to cyclometalation and dehydrogenation than *i*-Pr groups, and perhaps more easily isolated due to lesser conformational flexibility. Accordingly, we conducted a systematic experimental/computational investigation of steric effects in which *t*-Bu groups were replaced with Me groups.[28]

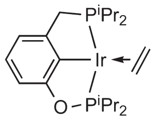
Density functional theory (DFT) calculations predicted that replacement of just one *t*-Bu group by a Me group would have a very significant effect on the kinetics of alkane dehydrogenation by the (pincer)Ir fragment. Relative to the 1-alkene-bound resting state, the advantage of (^{tBu3Me}PCP)Ir was smaller (due to stronger olefin binding to the less bulky pincer complex) but still significant. Additional substitutions of *t*-Bu groups by Me groups were calculated to have a smaller effect on the barrier to the reaction of (pincer)Ir with *n*-alkane, and even that was mostly canceled out by stronger binding to 1-alkene in the resting state. Accordingly, (^{tBu3Me}PCP)IrH_4 was synthesized and indeed found to be an excellent catalyst for dehydrogenation,[28] affording rates and yields even greater than those obtained using (^{iPr4}PCP)IrH_4. Consistent with its higher activity as a transfer-dehydrogenation catalyst, (^{tBu3Me}PCP)IrH_4 gave higher rates and yields in AM than the ^{tBu4}PCP and ^{iPr4}PCP analogues (^{R4}PCP = ^{R}PCP; this nomenclature is used for clarity in the context of ligands with mixed R groups).

A second Me-for-^{t}Bu substitution was also investigated.[28] (^{tBuMe}PCP^{tBuMe})IrH_4 afforded catalytic rates of transfer-dehydrogenation and alkane-metathesis that were greater than those obtained with (^{tBu4}PCP)IrH_4 but less than those with (^{tBu3Me}PCP)IrH_4. Thus, experimental work seemed to support the prediction of DFT calculations that further Me-for-^{t}Bu substitution would not afford much rate enhancement. Moreover, there were experimental indications that dimerization posed an additional problem upon further decreasing steric bulk.[28] Therefore, we did not pursue further such substitutions and, more generally, we learned to be cautious about the benefits of decreased steric bulk of (pincer)Ir catalysts.

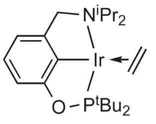
Numerous other pincer ligands have since been developed in our laboratories, and their iridium complexes have been found to be very effective for dehydrogenation, including precursors of (^{Ad}PCP)Ir (Ad = 1-adamantyl),[29] (^{iPr}POCOP)Ir,[30] (^{iPr}PCOP)Ir,[30] and (^{iPr2}NCOP^{tBu2})Ir.[31] Preliminary results in several of these cases indicate activity for AM comparable to that of (^{tBu3Me}PCP)IrH_4. Screening in our laboratories continues with a shift in emphasis toward new pincer motifs and metals other than iridium.



(^{Ad}PCP)IrH_2



(^{iPr}PCOP)$Ir(C_2H_4)$



(^{iPr2}NCOP^{tBu2})$Ir(C_2H_4)$

Development of New Mo- and W-Based Olefin-Metathesis Catalysts

As noted above catalytic activity of the pincer-Ir/Mo-F12 tandem system was limited by the stability of the molybdenum metathesis catalyst at 125 °C. Mo-F12 exhibits high activity and a long lifetime at significantly lower temperatures

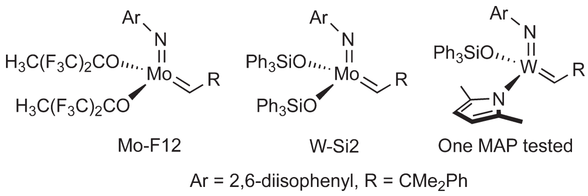


FIGURE 1. Selected olefin-metathesis catalysts.

(e.g., 500 TO min^{-1} at 25 °C for *cis*-2-pentene disproportionation),[24] whereas the pincer-Ir complexes operate most efficiently at temperatures above ca. 125 °C. In order to address this issue of catalyst interoperability, the Schrock group began a systematic investigation into the design of new olefin-metathesis catalysts that could be more effective as co-catalysts for AM.

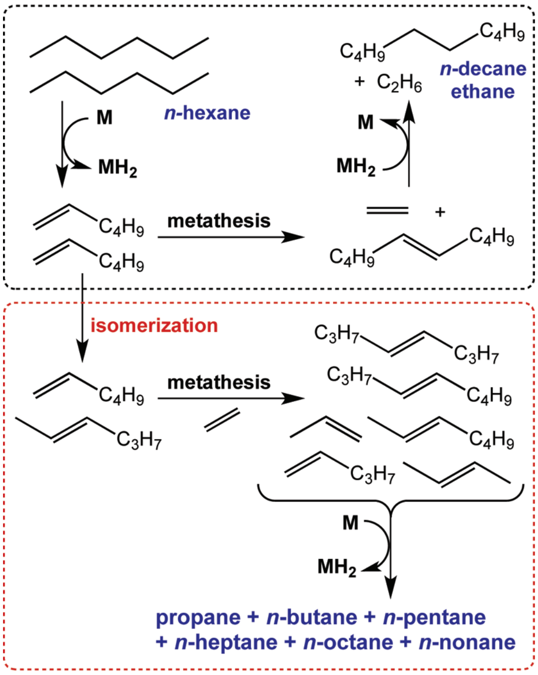
Over 40 bis(alkoxide) and mono(alkoxide)mono(pyrrolide) (MAP) complexes of Mo and W, varying the imido, alkoxide, and pyrrolide ligands, were prepared (Figure 1).[32] These catalysts were evaluated in the tandem-catalyzed metathesis of *n*-octane by (^{tBu}POCOP)Ir(C_2H_4) and the alkylidene at 125 °C. Overall, W-based catalysts outperformed the analogous Mo complexes. Notably, the W-analogue of Mo-F12 was an order of magnitude more effective than Mo-F12 itself (2.7 M vs 0.24 M total product). The most effective catalyst, W(NAr)-(CH_2CMe_2Ph)($OSiPh_3$)$_2$ (W-Si2), afforded 3.0 M product.

Metathesis of *n*-octane by (^{tBu}POCOP)Ir(C_2H_4) invariably yielded a roughly Gaussian distribution of *n*-alkanes centered at C_8, while (^{tBu}PCP)IrH_2 and (MeO-^{tBu}PCP)IrH_2 showed some selectivity for the formation of *n*-tetradecane. Interestingly, the degree of selectivity was quite dependent upon the nature of the olefin-metathesis catalyst, with the Mo catalysts generally yielding higher selectivity than the W catalysts. Unfortunately, of the catalysts screened for selectivity, none gave greater selectivity for C_{2n-2} product than the Mo-F12 catalyst originally used.

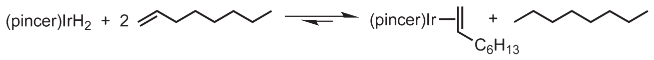
Distribution of Products from Alkane Metathesis

We were very pleased with the observation of AM under mild conditions, giving exclusively unbranched products with fairly high turnover numbers using well-defined molecular catalysts. Somewhat disappointing and puzzling, however, was the initially observed MW-selectivity, particularly that obtained with precursors of (^{tBu}POCOP)Ir. Based on the assumption of terminal regioselectivity for dehydrogenation, as indicated in Scheme 1, the expected AM products from C_n *n*-alkane were $C_{2n-2}H_{4n-2}$ and ethane, respectively (e.g., *n*-decane and ethane from *n*-hexane). However, of the four possible heavy (C_{7-10}) primary products from AM of *n*-hexane, *n*-decane was observed to be the *least* abundant when (^{tBu}POCOP)Ir precursors were used as dehydrogenation co-catalysts (ca. 15% of total C_7–C_{10} product; Table 1).

SCHEME 2



SCHEME 3. Interconversion of (pincer)IrH2 and (pincer)Ir(1-octene)



at equlibrium: [(pincer)IrH_2] = K_{eq}•[(pincer)Ir(1-octene)]•[n-octane] / [1-octene]^2

We presumed that the low selectivity for C_{2n-2} product was due to double-bond isomerization occurring prior to hydrogenation. This could easily account for the observed product distribution as indicated in Scheme 2.

Surprisingly, however, in contrast with the very low selectivity for the C_{2n-2} product resulting from AM co-catalyzed by (^{tBu}POCOP)Ir, under the same conditions, the use of (^{tBu}PCP)Ir as the dehydrogenation co-catalyst gives at least modest selectivity for *n*-decane from *n*-hexane (ca. 50% of total C_7–C_{10} product; Table 1). To our knowledge, this is the only report of such molecular-weight selectivity achieved by any AM system. We have found it quite intriguing that such an apparently minor structural variation results in a large and very important change in selectivity.

Olefin Isomerization. Our initial presumption was that the difference between the product distribution from the two pincer complexes resulted from (^{tBu}POCOP)Ir being a more active catalyst for olefin isomerization (as per Scheme 2)

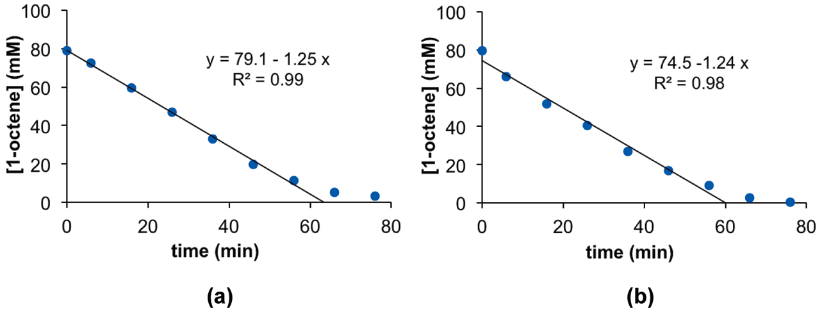
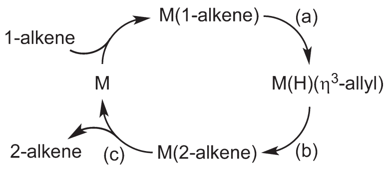


FIGURE 2. Catalytic isomerization of 1-octene to internal octenes by **1** (5 mM) at 125 °C: (a) *n*-octane solvent and (b) *p*-xylene solvent.

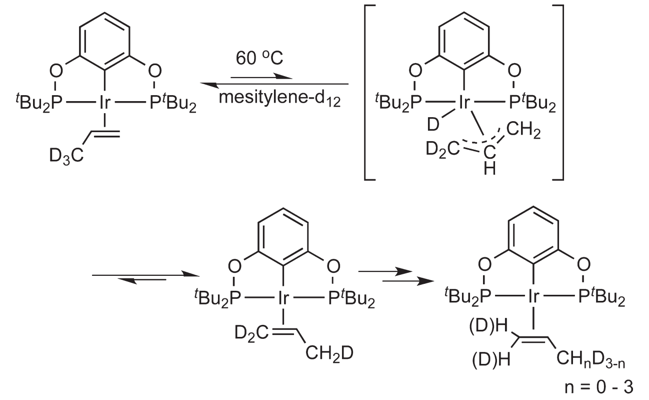
SCHEME 4. Schematic π-Allyl Pathway for 1-Alkene Isomerization



than (^{tBu}PCP)Ir. Control experiments however indicated that this was not the case. Addition of 1-octene (100 mM) to solutions of (^{tBu}PCP)IrH_2 or (^{tBu}POCOP)IrH_2 (5 mM) resulted in the rapid and complete conversion to (pincer)Ir(1-octene). Rates of isomerization were similar; although the kinetics in the (^{tBu}POCOP)Ir reaction were not straightforward, they were somewhat slower than the (^{tBu}PCP)Ir reaction particularly when the concentration of olefin is low as is the case during the AM reactions. Thus, a difference in isomerization rates between these two species apparently cannot account for the different selectivity observed in the AM reactions.[33]

Interestingly, the isomerization rates were independent of solvent. Although the major species in solution were olefin complexes, it might be expected that a minor concentration of hydride complex would be the active isomerization species. However, according to the equilibrium shown in Scheme 3, isomerization would then be favored by alkane versus arene solvent; as seen in Figure 2, the rates in *n*-octane and *p*-xylene are identical. The dependence on [1-octene] is seen to be zero-order in [1-octene] down to ca. 20 mM 1-octene (Figure 2); this also argues against isomerization by a hydride mechanism but is consistent with a π-allyl mechanism (Scheme 4). Such a mechanism is supported by DFT calculations, and by the observation of intramolecular H/D exchange observed with (^{tBu}POCOP)Ir($CH_2{=}CH_2CD_3$) (Scheme 5). Moreover, whereas a hydride mechanism would result in intermolecular exchange, when (^{tBu}POCOP)Ir(propene-d_6) was treated with free perprotio-propene in mesitylene-d_{12}, no crossover of H/D between the perdeuterio and perprotio species was observed.

SCHEME 5. Hydrogen/Deuterium Scrambling via an Ir(III) η^3-Allyl Hydride Intermediate



The key π-allyl hydride intermediate shown in Scheme 5 was independently generated and characterized by NMR spectroscopy by the reaction of (^{tBu}POCOP)IrH_2 with allene at −88 °C (Scheme 6). Upon warming to −58 °C, the π-allyl hydride converts to the propene complex, demonstrating the low kinetic barrier to this interconversion.

Regioselectivity in Alkane Dehydrogenation. As noted above, dehydrogenation catalysts based on either (^{tBu}PCP)Ir or the much less sterically hindered (^{iPr}PCP)Ir fragment are kinetically selective for dehydrogenation at the terminal position of *n*-alkanes. At the outset of this work, we therefore presumed that (pincer)Ir species as bulky or bulkier than (^{iPr}PCP)Ir, and perhaps even any (pincer)Ir complex, would also be terminal-selective. Thus, the low selectivity in AM from (^{tBu}POCOP)Ir was initially attributed to relatively rapid isomerization of an α-olefin kinetic product. In view of the isomerization experiments discussed above, however, we have reconsidered our assumptions about the regioselectivity of dehydrogenation by pincer-iridium catalysts and investigated in depth the difference between (^{tBu}POCOP)Ir and (^{tBu}PCP)Ir.[34]

Simple transfer-dehydrogenation of *n*-alkanes with (^{tBu}PCP)Ir or (^{iPr}PCP)Ir precursors clearly showed that the α-olefin was the kinetically favored product of dehydrogenation, while subsequent isomerization led to the formation of a mixture that was predominantly internal olefin. In the case of (^{tBu}POCOP)IrH$_2$, however, a product mixture of predominantly internal olefins was observed even at the earliest times at which dehydrogenation product was detectable.[34] Additional evidence for the different regioselectivity of (^{tBu}POCOP)Ir versus either (^{tBu}PCP)Ir or (^{iPr}PCP)Ir was obtained from intermolecular competition experiments between the dehydrogenation of *n*-alkane and cycloalkanes. Consistent with the apparent preference of (^{tBu}POCOP)Ir for dehydrogenation at the internal position of *n*-alkanes, dehydrogenation of *n*-alkane/cycloalkane mixtures by (^{tBu}POCOP)Ir showed a strong preference for cycloalkane (cyclooctane or cyclotetradecane) whereas (^{tBu}PCP)Ir showed a strong preference for dehydrogenation of *n*-alkane.[34]

Inspection of DFT-based models or crystal structures[13,29] of (^{tBu}POCOP)Ir and (^{tBu}PCP)Ir complexes reveals that the C_{aryl}–O and O–P bonds of POCOP are shorter than the corresponding C_{aryl}–CH_2 and CH_2–P bonds of PCP, while the C_{aryl}–O-P angle is greater than the C_{aryl}–CH_2–P angle (Figure 3). As a result, the P–Ir–P angle is smaller, and the gap between the opposing phosphino-*t*-butyl groups is substantially less in (^{tBu}PCP)Ir than in (^{tBu}POCOP)Ir (Figure 4).

DFT-based investigations of the origin of the respective regioselectivity of the different fragments are ongoing, but preliminary results suggest that terminal selectivity can arise from either of two distinct sets of conditions. In the case of the relatively *uncrowded* species (^{iPr}PCP)Ir (or truncated computational models with even less severe crowding), C–H addition is the rate-determining step in alkane-to-metal hydrogen transfer. C–H addition is in all cases more favorable at the terminal position; therefore, α-olefin formation is favored by these less-crowded species. In the case of the *moderately crowded* species (^{tBu}POCOP)Ir, β-hydrogen elimination is slower and is rate-determining; β-H elimination to give *internal* olefin is more favorable than β-H elimination to give terminal olefin in this case, for reasons based on electronic effects (including, perhaps, the same factors that stabilize the free internal olefin, but this remains to be determined). Finally in the case of the *very* bulky species (^{tBu}PCP)Ir, β-H elimination is still rate-determining but severe crowding leads to domination of steric effects and α-olefin formation is again favored.[34]

Heterogenized Alkane Metathesis Systems

For large-scale applications, the AM catalyst systems must be heterogeneous for ease of catalyst separation and recycling.

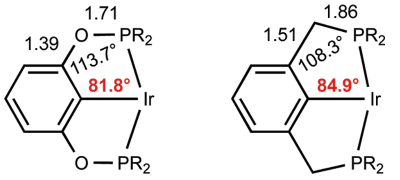


FIGURE 3. From ref 33.

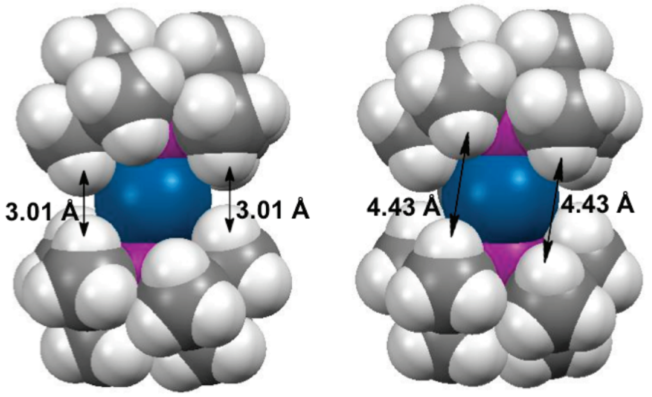
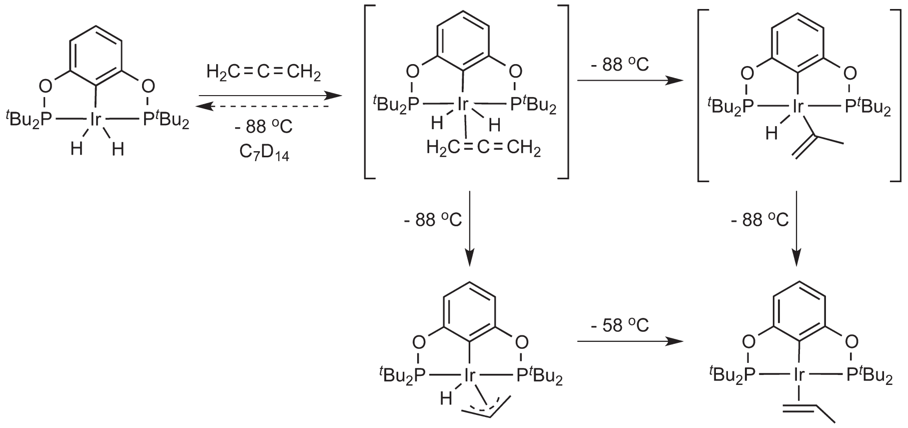
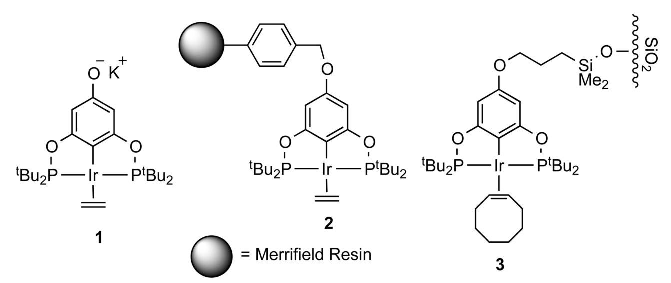


FIGURE 4. Space-filling models of structures of (^{tBu}PCP)Ir and (^{tBu}POCOP)Ir (calculated using DFT with PBE functional) with closest H–H distances indicated. From ref 33.

SCHEME 6. Formation of (POCOP)Ir(H)(η^3-allyl) and (POCOP)Ir(η^2-propene)



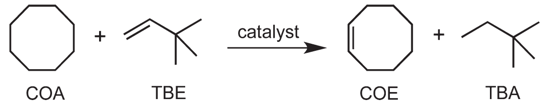
SCHEME 7



1 2 3

Furthermore, the soluble molybdenum and tungsten alkylidene homogeneous catalysts have limited stabilities at the temperatures required (125−200 °C) for dehydrogenation using iridium pincer catalysts. Our initial experiments involved employing classical heterogeneous olefin-metathesis catalysts, particularly rhenium oxide (Re_2O_7) on alumina, in combination with iridium pincer complexes. Significant improvements in catalyst system lifetimes and turnover numbers were achieved. A highly effective catalyst pairing proved to be (MeO-^{iPr}PCP)IrH_4 in combination with Re_2O_7/Al_2O_3. In a typical experiment, 2.5 mL of an *n*-decane (5.1 M) solution of (MeO-^{iPr}PCP)IrH_4 (9 mM) and TBE (35 mM) was heated with 535 mg of 3% Re_2O_7 on alumina. After 18 h, 3.2 M product (all alkanes except C_{10}) was formed; after 9 days, 4.4 M product was produced. Linear alkanes with carbon numbers C_2−C_{18} are observed as primary AM products along with some C_{19}−C_{30} alkanes as secondary products. Remarkably, after 9 days, the molar quantities of *n*-nonane and *n*-undecane are comparable to that of the starting alkane, *n*-decane (see Figure 5).

We also sought procedures to immobilize iridium pincer complexes on solid supports. Three approaches were taken: (1) covalent attachment of the pincer complex to a Merrifield resin, (2) covalent bonding of the catalyst to silica via a pendant alkoxysilane group, and (3) adsorption on γ-alumina through interaction with basic functional groups on the *para*-position of the pincer ligand.[35] Prior to employing these systems in AM, we screened their viability in transfer dehydrogenation catalysis using the benchmark system, the reaction of cyclooctane (COA) with *t*-butylethylene (TBE) to yield cyclooctene (COE) and *t*-butylethane (TBA) (eq 2).



(2)

The *p*-potassium oxide ^{tBu}POCOP derivative **1** (Scheme 7) was used to prepare both the Merrifield resin-derived catalyst, **2**, and the catalyst covalently attached to silica, **3**.[35] The Merrifield-based system showed both poor activity and poor recyclability while the silica-based systems showed better activity (750 turnovers) but poor recyclability.

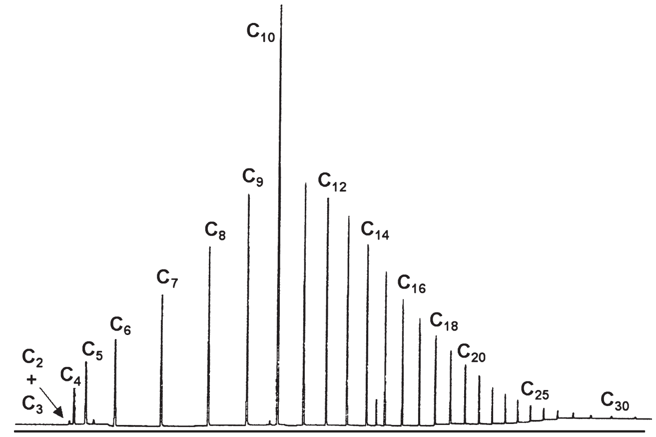
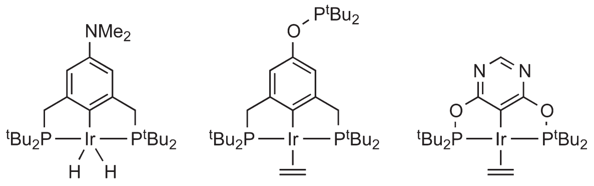


FIGURE 5. GC trace of product mixture resulting from the metathesis of *n*-decane by (MeO-^{iPr}PCP)IrH_4 and Re_2O_7/Al_2O_3 after 9 days at 175 °C. The signal for the hexamethylbenzene standard appears between C_{14} and C_{15}. Reproduced with permission from ref 25. Copyright 2006 American Association for the Advancement of Science.



4 5 6

FIGURE 6.

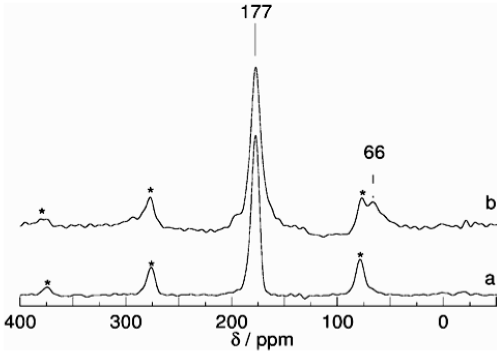


FIGURE 7. (a) Solid state ^{31}P MAS NMR of fresh 8/γ-Al_2O_3 and (b) solid state ^{31}P MAS NMR of 8/γ-Al_2O_3 after use for transfer dehydrogenation (1090 turnovers). 12 kHz MAS, 20 °C, referenced to 85% H_3PO_4. Starred signals represent spinning sidebands. Reproduced with permission from ref 35. Copyright 2009 Wiley-VCH Verlag GmbH.

Supporting pincer complexes by simple adsorption on γ-alumina proved by far the most convenient method for heterogenizing these systems, and provided robust, recyclable, and highly active catalysts. Several systems containing basic functionalities at the *para* position of the pincer ligand

TABLE 2. Total TONs and Concentration of Products from the Metathesis of *n*-Decane (2.5 mL, 5.12 M) by Re_2O_7/γ-Al_2O_3 (ca. 540 mg, 5 wt % Re_2O_7, 57 μmol), and Ir Catalysts **4**, **5**, or **6** without Additional Al_2O_3 at 175 °C

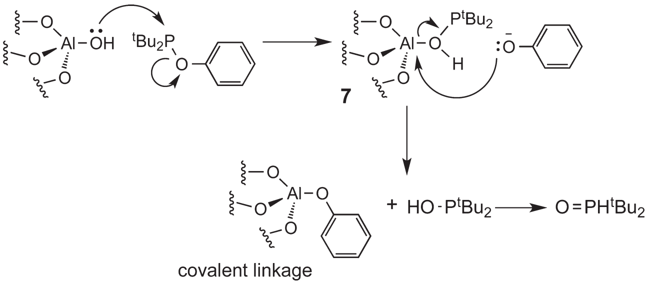
Ir catalyst	3 h: M (TONs)	1 day: M (TON)	7 days: M (TON)	14 days: M (TON)
4	0.489 (291)	1.20 (715)	2.38 (1420)	2.81 (1670)
5	0.366 (218)	2.32 (1380)	(3.65 (2180)	4.10 (2440)
6	0.687 (609)	3.22 (1910)	3.46 (2060)	

were investigated. Particularly effective systems included the (KO-^{tBu}POCOP)Ir catalyst, **1**, the (Me_2N-^{tBu}PCP)Ir complex, **4**, and the phosphinite-substituted system, **5**(Figure 6). Using **1** supported on γ-alumina that had been calcined with sodium oxide (to prevent TBE isomerization), and an 11 000:1 ratio of TBE/COA to iridium, 7000 turnovers were obtained in 40 h. ICP-MS analysis indicated less than 0.02% iridium was leached from the alumina in COA at 200 °C.

The supported catalyst was analyzed by ^{31}P MAS NMR spectroscopy in the laboratories of Susannah Scott. Figure 7 (lower spectrum) shows the spectrum of a fresh sample of **1** on γ-alumina. A single species is observed with a shift at 177 ppm. This ^{31}P shift compares favorably with the chemical shift of **1** in solution (170 ppm) and suggests that no significant changes in the coordination sphere around iridium occurred upon binding to alumina. This sample was used for transfer dehydrogenation in the COA/TBE system and after 1090 turnovers was reanalyzed by ^{31}P MAS NMR (see lower spectrum, Figure 7). The spectrum is largely unchanged except for a minor resonance at 66 ppm which arises from exposure of the sample to oxygen.

A particularly easily prepared catalyst is the *para*-phosphinite-substituted system, **5**, since inexpensive 1,3,5-trihydroxybenzene (phloroglucinol) can be readily converted to 1,3,5-(t-$Bu_2PO)_3C_6H_3$. Supporting **5** led to unanticipated but welcome results.[36] Analysis of the ^{31}P solid state NMR spectrum in the Scott lab showed a resonance at 176 ppm for the two coordinated phosphinite substituents, slightly upfield from the molecular complex in solution (181 ppm). Remarkably, the resonance for the "uncoordinated" *para*-phosphinite substituent moved from 151 in solution to 75 ppm in the supported system. Clearly, the interaction of the uncoordinated phosphinite group with alumina involves something more than a Lewis acid–base interaction. The model phosphinite, t-$Bu_2POC_6H_5$, showed a similar dramatic shift from 153 ppm in solution to 71 ppm when adsorbed on alumina. When the alumina is extracted with THF, the phosphine oxide, t-$Bu_2P(O)H$, is isolated while the C_6H_5O-group remains on the support. When authentic t-$Bu_2P(O)H$ is adsorbed on alumina, the ^{31}P shift observed is also at 71 ppm. We propose that the reaction shown in Scheme 8 occurs on the surface of the alumina. A surface-bound hydroxyl group (or oxide) attacks at phosphorus to generate species **7**. Displacement of the phosphinous acid, t-Bu_2POH, by phenoxide results in covalently linking the phenoxide to the alumina surface. The phosphinous acid rearranges rapidly to the much more stable phosphine oxide. Leaching experiments showed that **5** binds even more strongly to the alumina surface than **1**.

SCHEME 8. Proposed Mechanism for the Reaction of Phenyl Di(*tert*-butyl)phosphinite with a Basic Surface Hydroxyl Group on γ-Alumina[a]



[a] Adapted with permission from ref 36. Copyright 2011 Royal Society of Chemistry.

Having established that we can strongly bind *para*-substituted iridium pincer complexes to alumina and use them as robust hydrogen transfer catalysts, we moved on to employ these catalysts in alkane metathesis in combination with heterogeneous olefin-metathesis catalysts, normally Re_2O_7/Al_2O_3.[37] Numerous catalysts were screened. Strictly linear alkanes were produced but no molecular weight selectivity was observed. Turnover numbers were normally much higher than with homogeneous iridium catalysts.

Table 2 reports a typical set of experiments with three iridium catalysts, **4**, **5**, and catalyst **6** derived from 4,5-dihydroxypyrimidine, in combination with Re_2O_7/Al_2O_3. As seen in Table 2, complex **6** was most active at short times (609 TON at 3 h) but the phosphinite-based catalyst **5** was longest-lived and exhibited activity through 14 days (2440 TON, 4.1 M product). These turnover numbers are more than an order of magnitude greater than those observed in homogeneous solution employing the Schrock alkylidene Mo-F12 catalyst. In fact, under these improved conditions, decane becomes a minor component as the system approaches equilibrium. The "turnover number" computed in these cases is therefore far short of the number of actual catalytic events.

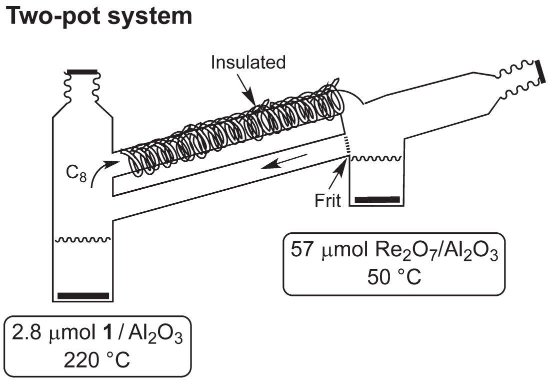


FIGURE 8. Two-pot device for alkane metathesis. Adapted with permission from ref 37. Copyright 2010 Wiley-VCH Verlag GmbH.

While high turnover numbers were achieved using iridium pincer catalysts adsorbed on alumina together with Re_2O_7 on alumina in the "same pot", a disadvantage of this protocol is that the iridium catalysts function best above 150 °C, while the rhenium olefin-metathesis catalysts function best in the 25–80 °C range and degrade moderately rapidly above 80 °C. To circumvent this problem, we constructed the device shown in Figure 8 which allows physical separation of the two heterogeneous systems and operation of these systems at temperatures optimal for each catalyst. The left-hand "pot" containing the iridium catalyst where transfer hydrogenations occur is heated to ca. 200–220 °C and lower molecular weight alkanes and olefins distill to the upper right-hand pot held at 50 °C where olefin-metathesis occurs in the presence of the rhenium catalyst. Metathesized product returns to the hot pot via the lower arm, and a frit prevents the rhenium catalyst from entering the lower pot.

Using this two-pot system, a TON of 1560 was noted after 18 h, while 3910 turnovers were obtained after 52 h. After removing the volatiles and recharging with alkane, the catalytic system remained active and it was possible to run additional cycles with only modest loss of reactivity.

Development of Supported Olefin-metathesis Catalysts. As noted above, a supported olefin-metathesis catalyst will presumably be required for large-scale implementation of the AM system. Based on our finding that pincer-Ir catalysts with basic *para*-substituents, for example, a dimethylamino group, could be effectively supported on γ-alumina through simple Lewis acid–base interactions, we aimed for a similar modification to the W catalyst framework, targeting the MAP catalysts featuring HIPTO ligands which were recently developed by Schrock and Hoveyda and shown to be *Z* selective in olefin homocoupling reactions.[38,39]

Our collaborators in the Schrock group synthesized the Me_2N-HIPTO-H ligand (Figure 9).[39] Tungsten MAP complexes bearing this ligand, such as **9**, were supported on Al_2O_3 in the same way as was $(Me_2N\text{-}^{tBu}PCP)IrH_2$. **9**/$Al_2O_3$ retained the activity of the free species in olefin homodimerization, and control experiments showed that the supporting process was nondestructive.

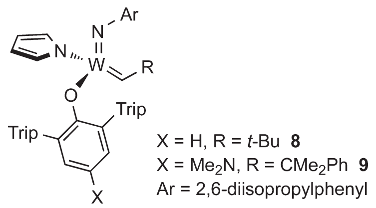
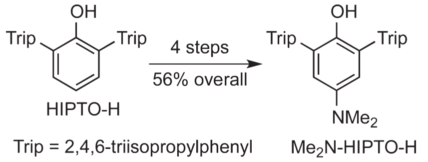


FIGURE 9. Olefin-metathesis catalysts with HIPTO ligands.

SCHEME 9. Me_2N-HIPTO-H: Designed for support on Al_2O_3



Conclusions and Outlook

Alkane metathesis has the potential to enable more efficient conversion of renewable and fossil feedstocks to alkanes of desired molecular weight ranges, and particularly to clean-burning high quality diesel and jet fuel. Using catalysts for alkane dehydrogenation and olefin metathesis operating in tandem, we have developed high-turnover systems for alkane metathesis using pincer-iridium complexes as dehydrogenation catalysts and various olefin-metathesis catalysts. The unique regioselectivity of the alkane-dehydrogenation catalysts has permitted, in some cases, selectivity for conversion of C_n *n*-alkanes to C_{2n-2} *n*-alkanes and ethane. Both the molecular alkane-dehydrogenation and olefin-metathesis catalysts have been successfully supported on alumina. Fully heterogeneous AM systems have been found to give particularly high turnover numbers.

Despite great progress, major challenges remain. Only moderate MW-selectivity has been achieved, and even that has been solely when using (^{tBu4}PCP)Ir-based dehydrogenation catalysts in tandem with Mo- and W-alkylidene based olefin-metathesis catalysts. The dehydrogenation catalysts give acceptable rates only at temperatures at which the alkylidene based olefin-metathesis catalysts tend to decompose. Thus, there is a pressing need to develop regioselective dehydrogenation catalysts that are more active at lower temperatures, along with olefin-metathesis catalysts that are more robust at higher temperatures. Efforts toward these goals are continuing; these include exploring new ligands and metals and investigating fundamental questions concerning the factors that govern catalyst regioselectivity, activity, stability, and MW selectivity.

Closely tied to the tandem nature of the catalytic systems described here is a tandem approach that has driven this work. The expertise at molecular and heterogeneous levels, in theory, synthesis, and mechanism, which has been brought to the effort by senior investigators and members of their research groups, continues to guide the improvement of the AM systems and the individual alkane-dehydrogenation and olefin-metathesis components.

We gratefully acknowledge our senior collaborators, Susannah Scott, Richard Schrock, and Karsten Krogh-Jespersen, as well as the dedicated and talented postdoctorals and graduate students who have coauthored the references cited here. We thank the National Science Foundation for funding through CENTC, the Center for Enabling New Technologies through Catalysis (CHE-0650456), which has not only funded this work but made possible interactions with many other CENTC members who have provided less direct yet valuable contributions to this work. M.C.H. thanks the NSF IGERT program (Renewable and Sustainable Fuel Solutions for the 21st Century) for a Graduate Training Fellowship.

BIOGRAPHICAL INFORMATION

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Sabuj Kundu was born in India and received his M.S. from the Indian Institute of Technology (IIT) Bombay in 2004. He then moved to Rutgers University and completed a Ph.D. under Alan Goldman's direction in 2009. After completing a postdoctoral appointment with William Jones at the University of Rochester in 2011, he joined Maurice Brookhart's lab at the University of North Carolina for a second postdoctoral appointment. Dr. Kundu's interests span synthetic, mechanistic, and catalytic chemistry of the late metals with emphasis on carbon–hydrogen bond activation and catalytic transformation of small molecules.

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 his Ph.D. degree in 1968, he spent 6 months as a postdoctoral fellow at UCLA followed by a year at Southampton University as a NATO fellow. Brookhart joined the University of North Carolina in 1969 and is currently a William R. Kenan, Jr. professor of chemistry. Brookhart's research interests span mechanistic, synthetic, and structural organometallic chemistry.

Alan S. Goldman received his B.A. degree from Columbia College in 1980. His doctoral work was 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, he joined the faculty at Rutgers, The State University of New Jersey. Goldman's research is focused on discovering and understanding catalytic and catalytically relevant reactions of organometallic complexes with small molecules, with an emphasis on the activation and functionalization of C–H bonds and understanding the formation and cleavage of C–C, C–O, and C–F bonds.

FOOTNOTES

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The authors declare no competing financial interest.

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