

## Dehydrogenation of *n*-Alkanes Catalyzed by Iridium “Pincer” Complexes: Regioselective Formation of $\alpha$ -Olefins

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The development of methods for the functionalization of alkanes is of cardinal importance in catalytic chemistry. A specific functionalization of particularly great potential value is the conversion of *n*-alkanes to the corresponding 1-alkenes ( $\alpha$ -olefins) since these serve as precursors for a wide range of commodity-scale chemicals ( $>2 \times 10^9$  kg/yr).<sup>1,2</sup> Such a conversion is also an intriguing challenge as viewed from a fundamental perspective. *n*-Alkanes are the simplest organic molecules with the potential to undergo regioselective transformations;  $\alpha$ -olefins are the thermodynamically least stable of the corresponding double-bond isomers and any mechanism for their formation must presumably involve activation of the strongest bond (primary C–H) in the molecule. Herein we report the first system to efficiently catalyze the dehydrogenation of *n*-alkanes to give  $\alpha$ -olefins. Indeed, to our knowledge this is the first system reported to thermochemically catalyze any functionalization of the terminal position of *n*-alkanes with high efficiency and regioselectivity.<sup>3,4</sup>

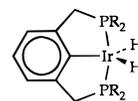
In the early 1980s examples were discovered of oxidative addition of C–H bonds to late-metal systems.<sup>5</sup> Perhaps the most remarkable and potentially valuable aspect of this chemistry was the regioselectivity, which favored reaction of the stronger C–H bonds (possibly due largely to steric effects):  $\text{CH}_4 > 1 > 2 \gg 3$ .<sup>6,7</sup> Within the same time frame, soluble late-transition-metal

based complexes were discovered that could catalyze the transfer of hydrogen from alkanes to sacrificial olefinic hydrogen-acceptors (eq 1).<sup>8,9</sup> Unfortunately, yields were severely limited



by ligand degradation. Nonetheless, unusual and potentially very valuable kinetic regioselectivity was observed including, in some cases, dehydrogenation with preference for the less substituted sites of the alkane, consistent with the selectivity of the C–H oxidative additions noted above.<sup>8,9</sup> In one case dehydrogenation of an *n*-alkane (*n*-hexane) was reported to give selectivity for the corresponding 1-alkene; however, after reaching only a minute level (78% of 0.48 mM total olefin), the concentration of 1-hexene decreased due to isomerization.<sup>8</sup>

Recently, an efficient catalyst for cycloalkane transfer-dehydrogenation was reported: the “pincer” complex (<sup>*t*</sup>-BuPCP)IrH<sub>2</sub> (**1**) (<sup>*t*</sup>-BuPCP = 2,6-bis[di(*t*-butyl)phosphinomethyl]phenyl).<sup>10</sup>



(<sup>*t*</sup>-BuPCP)IrH<sub>2</sub>

Initial results with *n*-alkanes suggested that transfer-dehydrogenation catalyzed by **1** did not give significant yields of the corresponding  $\alpha$ -olefins.<sup>11</sup> However, we report herein that when the analogous (<sup>*i*</sup>-PrPCP)IrH<sub>2</sub> (**2**) (<sup>*i*</sup>-PrPCP = 2,6-bis[di(*i*-propyl)phosphinomethyl]phenyl) complex was used,<sup>12,13</sup> it was apparent that the major kinetic product is the  $\alpha$ -olefin. Yields of  $\alpha$ -olefin much greater than those from any previously reported system can be obtained, although subsequent isomerization leads ultimately to the formation of internal olefins. Reexamination of catalysis using **1** reveals qualitatively similar results although  $\alpha$ -olefin yields are more severely limited by isomerization under typical conditions.

Table 1 shows representative results of the transfer-dehydrogenation of *n*-octane catalyzed by **1** and **2** (150 °C; 1.0 mM catalyst in *n*-octane solution in all cases) using various sacrificial acceptors.<sup>14</sup> It can be seen that in several cases 1-octene initially constitutes  $\geq 90\%$  of the octene product though the fractions decrease with time due to olefin isomerization. The combined fractions of 1- and 2-octenes remains at  $>95\%$  of total long after 1-octene is no longer the major product; subsequent isomerization to 3- or 4-octenes is much more rapid than subsequent isomerization to 2- or 4-octenes.

In comparing results obtained using catalyst **2** under varying conditions it appears that the overall reaction rate is fairly insensitive to the nature of the olefinic hydrogen-acceptor.

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(12) The protonated <sup>*i*</sup>-PrPCP ligand was synthesized according to Milstein<sup>13</sup> and reacted with [Ir(cyclooctene)<sub>2</sub>Cl] in refluxing toluene for 3 days. The resulting (<sup>*i*</sup>-PrPCP)IrHCl was isolated and converted to (<sup>*i*</sup>-PrPCP)IrH<sub>2</sub>, using the procedure previously reported for (<sup>*t*</sup>-BuPCP)IrH<sub>2</sub>.<sup>10</sup>

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(14) Concentrations were determined by GC (see ref 10). In all cases the measured concentration of hydrogenated sacrificial acceptor was within 20% of ([octenes] + 2 × [dienes]).

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<sup>‡</sup> University of Hawaii.

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(3) Despite the much greater bond strengths of primary vs secondary C–H bonds of *n*-alkanes, catalysts have been reported capable of oxidation of the former. However, to our knowledge, selectivity for primary oxidation is at best only approximately 1:1 on a per bond basis, in contrast with that of the present work ( $> 20:1$ ). For some lead references see: (a) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550–557. (b) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879–2932. (c) *Metalloporphyrins in Catalytic Oxidations*; Sheldon, R. A., Ed.; Marcel Dekker: New York, 1994.

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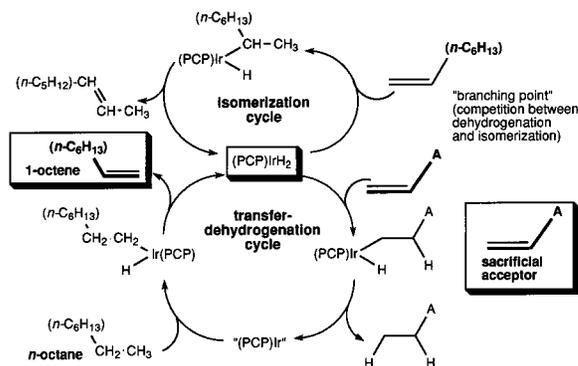
**Table 1.** Octene Distributions (Concentrations in mM) from Transfer-Dehydrogenation of *n*-Octane Catalyzed by **1** or **2** Using Various Hydrogen Acceptors. All Runs Conducted at 150 °C with 1.0 mM Catalyst in *n*-Octane Solution

cat <sup>a</sup>	accep	min	1-oct	<i>trans</i> -2	<i>cis</i> -2	other	total	%
<b>2</b>	nbe <sup>b</sup> 0.2 M	5	11	0.5	0.6	0	12	91
		10	23	4	3	0	30	76
		30	40	45	43	3	132	30
<b>2</b>	nbe 0.5 M	60	6	82	40	63	208	3
		5	8	0	0	0	8	>90
		10	19	2	1	0	22	87
<b>2</b>	tbe <sup>c</sup> 0.5 M	30	59	56	40	0	154	38
		60	59	105	71	3	238	25
		5	21	3	3	0	27	78
<b>2</b>	1-dec 0.5 M	10	27	6	6	0	40	68
		30	44	65	45	1	155	28
		60	41	103	78	19	250	16
<b>2</b>	1-dec 0.5 M	10	10	0	0	0	10	>90
		30	43	31	21	0	95	45
		60	10	64	40	13	134	8
<b>1</b>	tbe 0.2 M	6	10	0	0	0	10	>90
		15	18	19	8	0	45	40
		30	20	41	20	0	81	25
<b>1</b>	nbe 0.5 M	60	18	47	26	0	91	20
		15	23	4	2	0	29	79
		30	27	7	3	0	37	73
<b>1</b>	1-dec <sup>d</sup> 0.5 M	60	30	15	5	0	50	60
		15	13	0	0	0	13	>95
		30	34	1	0.6	0	36	95
<b>1</b>	1-dec <sup>d</sup> 0.5 M	60	74	7	4	0	86	87
		90	94	9	9	0	111	84
		120	97	32	14	0	143	68

<sup>a</sup> cat = catalyst; accep = acceptor; 1-oct = 1-octene; other = (other octenes + 2 × [dienes]); % = 100 × [1-octene]/total. <sup>b</sup> Norbornene. <sup>c</sup> *t*-Butylethene. <sup>d</sup> 1-Decene.

Furthermore, runs conducted with 0.5 and 0.2 M norbornene (nbe), respectively, gave virtually identical rates of transfer-dehydrogenation. Thus, neither the nature nor the concentration of the hydrogen-acceptor greatly affects the reaction rate. Surprisingly, however, both of these factors clearly and reproducibly affect the *observed distribution* of double-bond isomers produced (i.e., the observed regioselectivity) and in particular the percentage of  $\alpha$ -olefin product. For example, when 0.5 M nbe is the acceptor, after 30 min thermolysis, the concentration of 1-octene is 59 mM which constitutes 38% of the total octene. When 0.2 M nbe is used, under identical conditions and after the same time the concentration of 1-octene is 40 mM, representing 30% of the total octenes. After 60 min the difference is even more pronounced: 1-octene is present as 25 and 3% of the product in the reactions using 0.5 and 0.2 M nbe, respectively. When *t*-butylethene (tbe, 0.5 M) is used as the acceptor, the observed selectivity for 1-octene is significantly lower than that found with an equal concentration of nbe.

It would appear that in all cases the kinetic regioselectivity for  $\alpha$ -olefin formation is high and the observed isomer distribution is determined by the relative rates of isomerization and dehydrogenation. Figure 1 shows a possible mechanism (in accord with previously proposed mechanisms<sup>9</sup>) for the catalysis of both transfer-dehydrogenation and isomerization. The mechanism involves essentially only two steps and their microscopic reverse: (i) oxidative addition of an alkane C–H bond (with high selectivity for the terminal H), and (ii)  $\beta$ -hydrogen elimination. Despite its simplicity, the mechanism may be used to account for a number of observations, including the dependence of isomer distribution on nature and concentration of acceptor. We propose that the observed isomer distribution is largely determined by the competition between acceptor and 1-octene for insertion into the Ir–H bond of (PCP)IrH<sub>2</sub>. Thus, the fraction of 1-octene product will correlate with both the concentration and the intrinsic reactivity of the acceptor. For example, the better regioselectivity



**Figure 1.** Proposed mechanism of both transfer-dehydrogenation of *n*-octane and octene-isomerization catalyzed by the (PCP)Ir catalysts.

obtained with nbe versus tbe may be due to a greater ability of nbe to “trap” (PCP)IrH<sub>2</sub>. This might seem to be in contradiction with the observation that the reaction with tbe (0.5 M) is no slower than the reaction with nbe (0.5 M, Table 1). However, the rate-determining step of the catalysis is presumably not the reaction of olefin with dihydride (cf. the approximately zero-order kinetics in [nbe]); therefore, no such contradiction exists. Accordingly, when a 1:1 mixture of nbe:tbe is used as acceptor, the rate of nbe hydrogenation is approximately double that of the hydrogenation; i.e., nbe is apparently the more effective trap for (PCP)IrH<sub>2</sub>.

The *t*-BuPCP complex **1** gives lower reaction rates than the *i*-PrPCP analogue **2** and lower fractions of 1-octene when nbe or tbe is used as the acceptor. The poorer apparent regioselectivity is surprising as the bulkier *t*-butyl groups would be expected to enhance regioselectivity for the terminal position. However, the results are consistent with Figure 1 and the proposal that the 1-octene percentage reflects a competition between transfer-dehydrogenation and isomerization, i.e., a competition between acceptor and 1-octene for reaction with dihydride. The bulkier *t*-BuPCP complex should be more selective for 1-octene versus either tbe or nbe, ultimately resulting in lower fractions of 1-octene even if the kinetic regioselectivity of dehydrogenation is equal to or greater than that of the *i*-PrPCP complex. In accord with this reasoning, when the acceptor used is 1-decene (0.5 M) (which would react with (PCP)IrH<sub>2</sub> as efficiently as 1-octene), we find that the *t*-BuPCP complex gives *greater* selectivity than the *i*-PrPCP complex (Table 1); indeed it gives the best regioselectivity and 1-octene yield (97 turnovers) of any catalyst/acceptor system we have thus far investigated.<sup>15</sup>

In summary, we report the first catalytic system for the efficient and selective dehydrogenation of linear alkanes to give  $\alpha$ -olefins. Secondary isomerization limits the yield of  $\alpha$ -olefin obtained under our reaction conditions; however, our results suggest that modification of the catalyst/acceptor combination or efficient separation of  $\alpha$ -olefin to prevent isomerization may permit high yields. The oxidative addition of carbon–hydrogen bonds was first reported 16 years ago and has since held the attention of organometallic and organic chemists. This system may represent the closest example to date of a practical catalysis which exploits that intriguing mode of activation for the functionalization of alkanes.

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**Supporting Information Available:** Detailed table of octene distributions for experiments outlined in Table 1, including additional times and concentrations of dienes and *trans*-3-octene (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(15) The attempted use of ethene as acceptor resulted in complete inhibition of catalytic activity by either **1** or **2**, apparently due to the formation of a stable complex (<sup>η</sup>PCP)Ir(C<sub>2</sub>H<sub>4</sub>).