Iridium Catalysis

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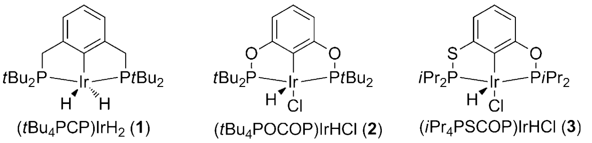
Selective Catalytic Transfer Dehydrogenation of Alkanes and Heterocycles by an Iridium Pincer Complex**

*Wubing Yao, Yuxuan Zhang, Xiangqing Jia, and Zheng Huang**

Abstract: *Catalytic alkane dehydrogenation is a reaction with tremendous potential for application. We describe a highly active PSCOP-pincer iridium catalyst for transfer dehydrogenation of cyclic and linear alkanes. The dehydrogenation of linear alkanes occurs under relatively mild conditions with high regioselectivity for α-olefin formation. In addition, the catalyst system is very effective in the dehydrogenation of heterocycles to form heteroarenes and olefinic products.*



(tBu$_4$PCP)IrH$_2$ (**1**) *Kaska/Jensen/Goldman*
(tBu$_4$POCOP)IrHCl (**2**) *Brookhart*
(iPr$_4$PSCOP)IrHCl (**3**) *This work*

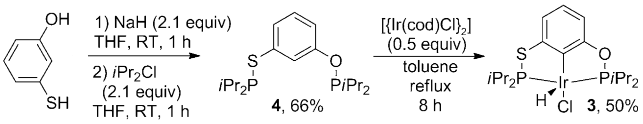
Figure 1. Structures of PCP, POCOP, and PSCOP iridium complexes.

The selective functionalization of abundant alkanes to form value-added products is an attractive, but highly challenging, task. Among the few reported transformations of alkanes, catalytic alkane dehydrogenation (AD) has received significant attention, because it converts low-value hydrocarbon feedstocks into olefins and arenes, which are important intermediates in organic synthesis and widely used as raw materials in many industrial processes. Heterogeneous AD is carried out on a large-scale in the petrochemical industry; however, such processes typically operate at very high temperatures (> 500 °C) and afford low product selectivities.[1]

Pioneered by Crabtree and Felkin,[2] numerous homogenous AD catalysts, mainly the group 9 metal complexes, have been developed in the past three decades.[3] A major breakthrough in homogenous AD was the report of bis(phosphine) (PCP)Ir pincer catalysts for dehydrogenation of cyclic and linear alkanes by Kaska, Jensen, and Goldman.[4] Following that, the Brookhart group reported the isostructural bis(phosphinite) (POCOP)Ir pincer complexes (Figure 1).[5] The subtle change of the linker from CH$_2$ group to an O atom leads to Ir catalysts that are somewhat more efficient than the PCP analogues in transfer dehydrogenation of cyclooctane. More recently, related (PCP)Ir complexes with metallocene backbones,[6] (PCP)Ir and (PCP)Ru complexes containing fluorinated phosphino substitutes,[7] and CCC pincer carbene–Ir complexes[8] have been developed for homogenous AD. In addition, Goldman and Brookhart have developed several Ir-pincer AD-based tandem reactions, such as alkane metathesis,[3a,9] alkane dehydroaromatization,[10] and the synthesis of *p*-xylene from ethylene.[11]

Despite tremendous progress in the field of homogenous AD, the reported catalytic systems suffer from harsh reaction conditions (150–250 °C) and the lack of regioselectivity in the dehydrogenation of acyclic alkanes.[3b] Furthermore, poor functional-group compatibility of these homogenous catalysts restricts the application of catalytic dehydrogenation in the synthesis of fine chemicals. Herein, we report the preparation of a PSCOP-type Ir pincer complex supported by a hybrid phosphinothious/phosphinite pincer ligand (Figure 1). The (iPr$_4$PSCOP)Ir complex exhibits very high catalytic activity for transfer dehydrogenation of cyclic alkanes.[12] It effects dehydrogenation of linear alkanes under mild conditions and affords excellent regioselectivity for α-olefin formation. This new system can be applied to the selective dehydrogenation of a variety of heterocycles to access heteroatom-containing aromatic or olefinic compounds.

The synthesis of (iPr$_4$PSCOP)IrHCl complex **3** is outlined in Scheme 1. Deprotonation of *meta*-mercaptophenol with NaH, followed by diphosphorylation with chlorodiisopropylphosphine afforded the PSCOP ligand **4** in 66 % yield. The iridium complex **3** was obtained in 50 % yield through cyclometalation of the ligand with [{Ir(cod)Cl}$_2$] (cod = 1,5-cyclooctadiene) in toluene under reflux. The ^{31}P{^{1}H} NMR spectrum of complex **3** exhibits an AB splitting pattern, which is consistent with two nonequivalent metal-bridged P nuclei. The characteristic hydridic (IrH) resonance appears at −37.06 ppm in the ^{1}H NMR spectra, which is close to that expected for a five-coordinate Ir^{III} hydrido chloride species with the hydride *trans* to a vacant coordination site.



Scheme 1. Synthesis of (iPr$_4$PSCOP)IrHCl **3**.

Complex **3** was first tested as a precatalyst for transfer dehydrogenation of cyclooctane (COA) with *tert*-butylethy-

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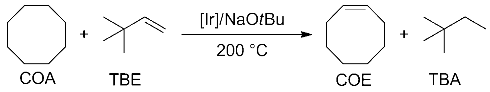
lene (TBE) as the hydrogen acceptor. The COA/TBE transfer dehydrogenation is a benchmark reaction. A system containing Ir precatalyst **3** (1.3 mM), NaO*t*Bu (1.95 mM), COA (3.9 M), and TBE (3.9 M, 3000 equiv relative to Ir), was heated at 200 °C under argon in a sealed vessel. The results are summarized in Table 1. Upon activation with NaO*t*Bu, **3** was highly active for the COA/TBE transfer dehydrogenation. Catalysis with **3** gave 2649 turnovers after 1 h, and 2905 turnovers after 4 h. The process converted > 99 % of TBE to TBA (2985 turnovers) after 8 h. Analysis of the dehydrogenation products by NMR spectroscopy revealed the formation of 1,3-cyclooctadiene (1,3-COD) besides the major product COE (COE/1,3-COD = 5.4:1).[13]

Table 1: TONs for transfer dehydrogenation of COA and TBE catalyzed by complexes **3** and **2** upon activation with NaO*t*Bu.[a]



Entry	*t* [min]	3[b]	2[b]	3[c]	3[d]
1	10	485	1186	937	–
2	30	1399	1423	999	–
3	60	2649	1514	–	1401
4	240	2905	1794	–	3805
5	480	2985	1876	–	5728
6	900	–	–	–	5901

[a] Average of three runs. TONs were calculated based on conversion of TBE determined by GC analysis. [b] Using a 3000:3000:1 ratio of COA/TBE/catalyst with 3.9 M TBE. [c] Using a 4840:1000:1 ratio of COA/TBE/**3** with 1.3 M TBE. [d] Using a 6000:6000:1 ratio of COA/TBE/**3**.

For comparison, we carried out catalysis in parallel with the Brookhart complex (tBu$_4$POCOP)IrHCl **2**, which has been reported for effective COA/TBE transfer dehydrogenation.[5b] Although the initial rate with **3** was lower than catalysis with **2** (485 turnovers with **3** in 10 min vs. 1186 turnovers with **2**), the productivity of the former is significantly higher than the latter (2985 turnovers with **3** in 8 h vs. 1876 turnovers with **2**). The initial lower turnover frequencies (TOFs) for the reaction with **3** compared to that with **2** is likely due to catalysis inhibition by TBE at high concentrations, as found for the PCP-Ir system.[4a] Indeed, we found that the concentration of the hydrogen acceptor affects the reaction rate. A run using TBE (1.3 M, 1000 equiv relative to **3**) gave 937 turnovers after 10 min, compared to 485 turnovers in the reaction with TBE (3.9 M; Table 1).

To further evaluate the catalytic efficiency of **3**, we decreased the loading of the catalyst in the COA/TBE transfer dehydrogenation. A ferrocene-based iridium pincer catalyst has been previously reported to be most active for the transfer dehydrogenation of COA; a TON of up to 3300 was obtained after 8 h at 180 °C with a COA/TBE/catalyst ratio of 21 420:21 420:1.[6,14] When a 6000:6000:1 molar ratio of COA/TBE/**3** was used, the reaction gave 5728 turnovers after 8 h and 5901 turnovers after 15 h at 200 °C (Table 1); more than 98 % of TBE was converted to TBA in 15 h.

Next, we investigated the catalytic activity of **3** in the transfer dehydrogenation of a linear alkane. A system containing **3** (1.0 mM), NaO*t*Bu (1.5 mM), TBE (0.5 M, 500 equiv relative to Ir) in an *n*-octane solution was heated at 200 °C under argon. The reaction gave 495 turnovers after 30 min at 200 °C, and TBE was fully converted into TBA within 60 min (500 turnovers) (Table 2, entry 1). As a comparison, performing the catalysis with (tBu$_4$PCP)IrH$_2$ **1** and (tBu$_4$POCOP)IrHCl **2** under identical reaction conditions gave only 135 and 143 turnovers after 60 min, respectively (entries 2 and 3). The initial rate of the *n*-octane/TBE transfer dehydrogenation using **3** is also greater than that obtained using complexes **1** and **2** (114 turnovers with **3** in 5 min vs. 69 with **1** and 19 turnovers with **2**). Additionally, the reaction conducted with a higher concentration of TBE (3.0 M, 3000 equiv relative to **3**) gave 930 after 1 h and 1211 turnovers after 4 h (entry 4). On the basis of comparison with precedents,[4j] we conclude that **3**/NaO*t*Bu is among the most active systems for transfer dehydrogenation of linear alkanes.

The selective formation of valuable α-olefins by alkane dehydrogenation is of fundamental interest. Goldman et al. have shown that the (tBu$_4$PCP)Ir complex **1** exhibits high kinetic regioselectivity for α-olefin formation, but the terminal olefin can be rapidly converted into internal olefins through olefin isomerization.[4e] As shown in Table 2, after 5 min of thermolysis at 200 °C, 1-octene constitutes 33 %, 51 %, and 26 % of the total octenes for the run with complexes **3**, **1**, and **2**, respectively (entries 1–3). At first glance, the regioselectivity for α-olefin formation with **3** appears to be significantly lower than that with **1**. However, a comparison of the product distributions after the same turnovers reveals a similar regioselectivity between complexes **3** and **1**. The reaction with **3** afforded 33 % of 1-octene after 114 turnovers in 5 min; and the run with **1** gave 31 % of 1-octene after 120 turnovers in 30 min.

Homogeneous catalysis under mild conditions is important for broad synthetic applications of alkane dehydrogenation. Given the high activity of **3** in transfer dehydrogenation of alkanes at 200 °C, we assessed its catalytic performance at lower temperatures. To our delight, complex **3** exhibits appreciable activity for the *n*-octane/TBE transfer dehydrogenation at 100 °C. Significantly, it shows exceptionally high regioselectivity for α-olefin formation under these conditions at low turnover numbers. As shown in Table 2, entry 5, 1-octene is the sole dehydrogenation product within the first hour at 100 °C (14 turnovers). After heating for 8 h (35 turnovers), 1-octene still accounts for 48 % of the total octenes, and the combined percentage of 1-octene and 2-octenes accounts for 100 % of the total. The data imply that the **3**-catalyzed isomerization of 2-octenes to 3- or 4-octenes is much slower relative to the isomerization of 1-octene to 2-octenes.

The high activity and mild reaction conditions in AD encouraged us to examine the viability of the new Ir complex **3** in the dehydrogenation of heterocycles. Compared to well-documented catalytic dehydrogenation reactions of alkanes,[3b,15] alcohols,[15] and amines,[15] examples of homogeneous catalytic dehydrogenation of heterocycles are rare. In 1997, Jensen and Kaska reported the complex **1**-catalyzed transfer dehydrogenation of tetrahydrofuan (THF) with TBE to give a mixture of dihydrofurans and furan at 200 or 150 °C.[4c] In

Table 2: Ir-catalyzed transfer dehydrogenation of *n*-octane and TBE at 200 or 100 °C.[a]

$$n\text{-octane} + \underset{(0.5\text{ or }3.0\text{ M})}{\text{TBE}} \xrightarrow[\text{200 or 100 °C}]{\substack{\text{[Ir] (1.0 mM)}\\ \text{NaO}t\text{Bu (1.5 mM)}}} \text{octenes} + \text{TBA}$$

Entry	Cat.	*t* [min]	TON	1-Octene [mM]	1-Octene fraction [%][b]	*trans*-2-Octene [mM]	*cis*-2-Octene [mM]
1[c,d]	**3**	5	114	38	33	44	20
		10	192	37	19	77	37
		30	495	13	3	137	65
		60	500	10	2	110	50
2[c,d]	**1**	5	69	35	51	20	10
		10	92	39	42	32	16
		30	120	37	31	48	23
		60	135	27	20	64	27
3[c,d]	**2**	5	19	5	26	9	4
		10	26	5	19	12	5
		30	84	6	7	31	14
		60	143	7	5	47	21
4[c,e]	**3**	10	154	43	28	64	25
		30	539	50	9	169	85
		60	930	47	5	211	109
		240	1211	39	3	220	107
5[f,d]	**3**	30	10	10	100	0	0
		60	14	14	100	0	0
		240	26	17	68	9	0
		480	35	17	48	11	7

[a] Average of three runs; TONs were calculated based on conversion of TBE, as determined by GC analysis. [b] The fraction of 1-octene relative to the total octenes. [c] At 200 °C. [d] Ir (1.0 mM), TBE (0.5 M). [e] Ir (1.0 mM), TBE (3.0 M). [f] At 100 °C.

2009, Fujita and Yamaguchi reported the first example of Ir-catalyzed dehydrogenation of tetrahydroquinolines.[16] Very recently, Xiao et al. demonstrated that a cyclometalated Ir^{III} imino complex is highly efficient for acceptorless dehydrogenation of N-heterocycles.[17] To date, however, the scope of heterocycles in dehydrogenation reactions is mainly limited to benzofused N-heterocycles bearing NH functional groups.[18] Catalytic dehydrogenation of O- and S-heterocycles, and N-heterocycles without benzofusion remains to be explored.

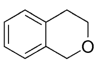
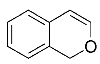
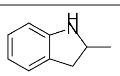
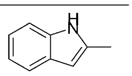
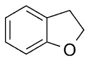
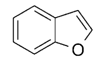
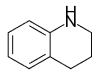
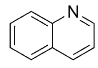
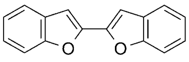
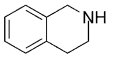
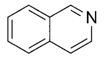
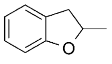
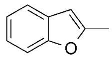
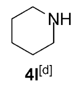
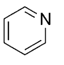
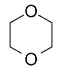
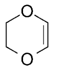
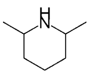
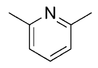
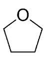
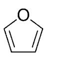
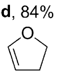
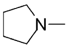
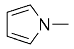
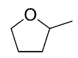
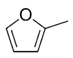
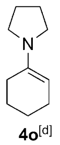
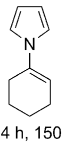
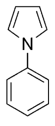
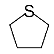
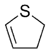
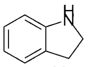
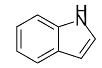
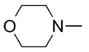
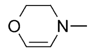
Our preliminary results show that the (iPr$_4$PSCOP)Ir complex is capable of catalyzing dehydrogenation of a variety of O- and N-containing heterocycles (Table 3). The reactions were carried out at 120 °C, unless otherwise noted.[19] In the presence of only 0.1 mol% of **3**, isochroman (**4a**) was readily dehydrogenated to form benzopyran (**5a**) in 91% yield. The dehydrogenation of 2,3-dihydrobenzofuran with TBE (1 equiv) gave benzofuran (**5b**) in 80% yield after 12 h. Notably, a minimal amount of 2,2′-bibenzofuran (**5b′**; 2%) was also detected in this reaction. This biaryl product was likely formed through dehydrogenative dimerization of **5b**. When TBE (2 equiv) and **3** (5 mol%) were used, the yield of **5b′** was increased to 37% and benzofuran **5b** was obtained as the minor product (11%). As expected, the introduction of a methyl substituent at the 2-position of 2,3-dihydrobenzofuran prevented dimerization. However, the dehydrogenation of 2,3-dihydro-2-methylbenzofuran **4c** is slower than the reaction with **4b**. Treatment of **4c** with TBE (2 equiv) using Ir (1 mol%) gave 2-methylbenzofuran **5c** in 67% yield after 24 h. Transfer dehydrogenation of 1,4-dioxane with **3** (1 mol%) selectively formed 1,4-dioxene **5d** in 84% yield after 12 h; no 1,4-dioxin from double dehydrogenation was observed, even in the presence of 2 equiv of TBE. Dehydrogenation of THF with TBE (2 equiv) using a higher catalyst loading (5 mol%) selectively formed furan **5e** in 72% yield after 24 h. Only a trace amount of 2,3-dihydrofuran (**5e′**; 2%) was observed under these conditions.[20] Similarly, the reaction of 2-methyltetrahydrofuan selectively yielded the fully dehydrogenated product 2-methylfuran (57%; **5f**) after 12 h at 150 °C. In contrast to the good conversion observed in reactions with O-heterocycles, transfer dehydrogenation of tetrahydrothiophene (**4g**) resulted in a low conversion. Because the neutral S donors are softer and more polarizable than the neutral O donors, we tentatively attribute the low reactivity of S-heterocycles to the high binding affinity of S atom to the Ir center, which inhibits the dehydrogenation process.

(iPr$_4$PSCOP)Ir-catalyzed transfer dehydrogenation of N-heterocycles occurred efficiently, although such substrates require a relatively high catalyst loading (1–5 mol%). Reactions of indolines, tetrahydroquinoline, and tetrahydroisoquinoline with TBE gave indoles **5h** (80%) and **5I** (96%), quinoline (**5j**; 76%), and isoquinoline (**5k**; 50%) in moderate to high yields. Dehydrogenations of N-heterocycles without benzofusion also occurred, albeit at relatively high temperatures (150–200 °C). The conversion of piperidines to pyridines **5l** (47%) and **5m** (63%) is remarkable, given the fact that the products are good ligands and the build-up of pyridines may result in catalyst inhibition. *N*-methylpyrrole (**5n**) was obtained in 83% yield from *N*-methylpyrrolidine.[18] The reaction of *N*-(1-cyclohexenyl)pyrrolidine with TBE (4 equiv) gave *N*-(1-cyclohexenyl)pyrrole **5o** (54%) and 1-phenylpyrrole **5o′** (16%) after 24 h at 150 °C. The results indicate Ir-catalyzed dehydrogenation of the pyrrolidine ring is more efficient than the dehydrogenation of the cyclohexenyl ring under these reaction conditions. Finally, the reaction of *N*-methylmorpholine with TBE (2 equiv) catalyzed by **3** (0.5 mol%) selectively formed 2,3-dehydro-*N*-methylmorpholine (**5p**) in 82% yield; the synthesis of **5p** is very challenging by other means.[21]

In conclusion, we have prepared a new phosphinothious/phosphinite (iPr$_4$PSCOP)Ir pincer complex. Upon activation with NaO*t*Bu, this complex exhibits exceptionally high activity for transfer dehydrogenation of alkanes with *tert-*

Table 3: Transfer dehydrogenation of heterocycles with TBE. The product yield was determined by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard, unless otherwise noted.

$$\underset{\textbf{4a–p}}{\text{heterocycles}} + \underset{(1\text{–}4\ \text{equiv})}{\text{TBE}} \xrightarrow[120\ ^\circ\text{C},\ p\text{-xylene}]{\substack{0.1\text{–}5\ \text{mol}\ \%\ \textbf{3}\\ 0.2\text{–}10\ \text{mol}\ \%\ \text{NaO}t\text{Bu}}} \underset{\textbf{5a–p}}{\text{dehydrogenated heterocycles}} + \text{TBA}$$

Substrate	Product	Substrate	Product
 **4a**[a]	 12 h: **5a**, 91%	 **4i**[c]	 12 h: **5i**, 96%
 **4b**[a]	 12 h: **5b**, 80%	 **4j**[d]	 12 h: **5j**, 76%[f]
4b[b]	 6 h: **5b'**, 37%	 **4k**[d]	 12 h: **5k**, 50%[f]
 **4c**[c]	 24 h: **5c**, 67%	 **4l**[d]	 24 h, 200 °C: **5l**, 47%[f]
 **4d**[c]	 12 h: **5d**, 84%	 **4m**[d]	 24 h, 200 °C: **5m**, 63%[f]
 **4e**[b]	  24 h: **5e**, 72%; **5e'**, 2%[f]	 **4n**[d]	 12 h, 150 °C: **5n**, 83%
 **4f**[b]	 12 h, 150 °C: **5f**, 57%	 **4o**[d]	  24 h, 150 °C: **5o**, 54%; **5o'**, 16%
 **4g**[b]	 24 h: **5g**, 5%		
 **4h**[c]	 12 h: **5h**, 80%	 **4p**[e]	 12 h: **5p**, 82%

[a] With **3** (0.1 mol%) and TBE (1 equiv). [b] With **3** (5 mol%) and TBE (2 equiv). [c] With **3** (1 mol%) and TBE (2 equiv). [d] With **3** (5 mol%) and TBE (4 equiv). [e] With **3** (0.5 mol%) and TBE (2 equiv). [f] The yield of product was determined by GC analysis with mesitylene as an internal standard.

butylethylene as the hydrogen acceptor. In addition, the (iPr$_4$PSCOP)Ir complex gives high kinetic selectivity for dehydrogenation of linear alkanes to α-olefins under relatively mild reactions conditions. The new catalytic system can be applied to the selective dehydrogenation of a wide variety of heterocycles to produce heteroarenes and olefinic products by transfer dehydrogenation.

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[13] Determined by ^{13}C NMR spectroscopy, the sum of COE and COD double bonds equals TON of TBE within 10% difference. Trance amount of ethylbenzene (<2%) and o-xylene (<2%) were detected by GC/MS.

[14] During the preparation of this manuscript, Yamamoto et al. reported Ir pincer complexes containing a "7-6-7" fused-ring backbone, which gave a maxium TON of 4100 after 24 h at

200 °C with a COA/TBE/catalyst ratio of 10000:6750:1; see: Y. Shi, T. Suguri, C. Dohi, H. Yamada, S. Kojima, Y. Yamamoto, *Chem. Eur. J.* **2013**, *19*, 10672.

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