

Iridium Catalysis

# 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  $\alpha$ -olefin formation. In addition, the catalyst system is very effective in the dehydrogenation of heterocycles to form heteroarenes and olefinic products.

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.<sup>[1]</sup>

Pioneered by Crabtree and Felkin,<sup>[2]</sup> numerous homogeneous AD catalysts, mainly the group 9 metal complexes, have been developed in the past three decades.<sup>[3]</sup> 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.<sup>[4]</sup> Following that, the Brookhart group reported the isostructural bis(phosphinite) (POCOP)Ir pincer complexes (Figure 1).<sup>[5]</sup> The subtle change of the linker from CH<sub>2</sub> 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,<sup>[6]</sup> (PCP)Ir and (PCP)Ru complexes containing fluorinated phosphino substitutes,<sup>[7]</sup> and CCC pincer carbene–Ir complexes<sup>[8]</sup> have been developed for homogenous AD. In addition, Goldman and Brookhart have developed several Ir-pincer AD-based tandem reactions, such as alkane

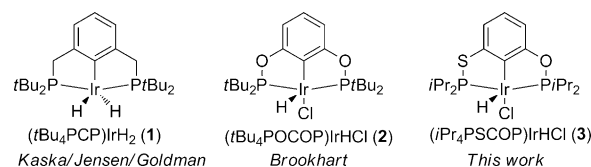
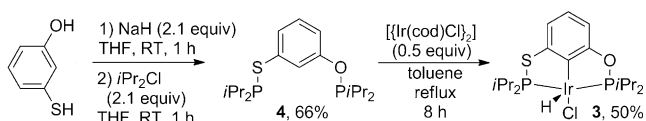


Figure 1. Structures of PCP, POCOP, and PSCOP iridium complexes.

metathesis,<sup>[3a,9]</sup> alkane dehydroaromatization,<sup>[10]</sup> and the synthesis of *p*-xylene from ethylene.<sup>[11]</sup>

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.<sup>[3b]</sup> 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 phosphinothioic/phosphinite pincer ligand (Figure 1). The (*i*Pr<sub>4</sub>PSCOP)Ir complex exhibits very high catalytic activity for transfer dehydrogenation of cyclic alkanes.<sup>[12]</sup> It effects dehydrogenation of linear alkanes under mild conditions and affords excellent regioselectivity for  $\alpha$ -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 (*i*Pr<sub>4</sub>PSCOP)IrHCl complex **3** is outlined in Scheme 1. Deprotonation of *meta*-mercaptophenol with NaH, followed by diphosphorylation with chlorodiisopropyl-



Scheme 1. Synthesis of (*i*Pr<sub>4</sub>PSCOP)IrHCl **3**.

phosphine 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)<sub>2</sub>] (cod = 1,5-cyclooctadiene) in toluene under reflux. The <sup>31</sup>P{<sup>1</sup>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 <sup>1</sup>H NMR spectra, which is close to that expected for a five-coordinate Ir<sup>III</sup> hydrido chloride species with the hydride *trans* to a vacant coordination site.

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

[\*] W. Yao, Y. Zhang, X. Jia, Prof. Dr. Z. Huang  
State Key Laboratory of Organometallic Chemistry, Shanghai  
Institute of Organic Chemistry, 345 Lingling Road  
Shanghai 200032 (China)  
E-mail: huangzh@sioc.ac.cn

[\*\*] We are very grateful to Prof. M. Brookhart for helpful suggestions and comments. Financial support from the National Natural Sciences Foundation of China (21272255, 21121062), the “1000 Youth Talents Plan”, and the Shanghai Rising Star Program (13A404200) is gratefully acknowledged.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201306559>.

lene (TBE) as the hydrogen acceptor. The COA/TBE transfer dehydrogenation is a benchmark reaction. A system containing Ir precatalyst **3** (1.3 mM), NaOrBu (1.95 mM), COA (3.9M), and TBE (3.9M, 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 NaOrBu, **3**

**Table 1:** TONs for transfer dehydrogenation of COA and TBE catalyzed by complexes **3** and **2** upon activation with NaOrBu.<sup>[a]</sup>

Entry	t [min]	<b>3</b> <sup>[b]</sup>	<b>2</b> <sup>[b]</sup>	<b>3</b> <sup>[c]</sup>	<b>3</b> <sup>[d]</sup>
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**.

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).<sup>[13]</sup>

For comparison, we carried out catalysis in parallel with the Brookhart complex (*t*Bu<sub>4</sub>POCOP)IrHCl **2**, which has been reported for effective COA/TBE transfer dehydrogenation.<sup>[5b]</sup> 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.<sup>[4a]</sup> 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.<sup>[6,14]</sup> 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), NaOrBu (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 (*t*Bu<sub>4</sub>PCP)IrH<sub>2</sub> **1** and (*t*Bu<sub>4</sub>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,<sup>[4i]</sup> we conclude that **3**/NaOrBu is among the most active systems for transfer dehydrogenation of linear alkanes.

The selective formation of valuable  $\alpha$ -olefins by alkane dehydrogenation is of fundamental interest. Goldman et al. have shown that the (*t*Bu<sub>4</sub>PCP)Ir complex **1** exhibits high kinetic regioselectivity for  $\alpha$ -olefin formation, but the terminal olefin can be rapidly converted into internal olefins through olefin isomerization.<sup>[4e]</sup> 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  $\alpha$ -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  $\alpha$ -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,<sup>[3b,15]</sup> alcohols,<sup>[15]</sup> and amines,<sup>[15]</sup> examples of homogeneous catalytic dehydrogenation of heterocycles are rare. In 1997, Jensen and Kaska reported the complex **1**-catalyzed transfer dehydrogenation of tetrahydrofuran (THF) with TBE to give a mixture of dihydrofurans and furan at 200 or 150 °C.<sup>[4c]</sup> In

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

		$n$ -octane + TBE (0.5 or 3.0 M)		$\xrightarrow[\text{200 or 100 } ^\circ\text{C}]{\text{[Ir] (1.0 mM), NaOtBu (1.5 mM)}}$		octenes + TBA	
Entry	Cat.	<i>t</i> [min]	TON	1-Octene [mM]	1-Octene fraction [%] <sup>[b]</sup>	<i>trans</i> -2-Octene [mM]	<i>cis</i> -2-Octene [mM]
1 <sup>[c,d]</sup>	<b>3</b>	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 <sup>[c,d]</sup>	<b>1</b>	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 <sup>[c,d]</sup>	<b>2</b>	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 <sup>[c,e]</sup>	<b>3</b>	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 <sup>[f,d]</sup>	<b>3</b>	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.<sup>[16]</sup> Very recently, Xiao et al. demonstrated that a cyclometalated Ir<sup>III</sup> imino complex is highly efficient for acceptorless dehydrogenation of N-heterocycles.<sup>[17]</sup> To date, however, the scope of heterocycles in dehydrogenation reactions is mainly limited to benzofused N-heterocycles bearing NH functional groups.<sup>[18]</sup> Catalytic dehydrogenation of O- and S-heterocycles, and N-heterocycles without benzofusion remains to be explored.





































Our preliminary results show that the (*i*Pr<sub>4</sub>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.<sup>[19]</sup> 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.<sup>[20]</sup> Similarly, the reaction of 2-methyltetrahydrofuran 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.

(*i*Pr<sub>4</sub>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.<sup>[18]</sup> 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.<sup>[21]</sup>

In conclusion, we have prepared a new phosphinothios/phosphinite (*i*Pr<sub>4</sub>PSCOP)Ir pincer complex. Upon activation with NaOtBu, 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  $^1\text{H}$  NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard, unless otherwise noted.

heterocycles + TBE		dehydrogenated heterocycles + TBA	
4a-p	(1–4 equiv)	5a-p	
Substrate	Product	Substrate	Product
	 12 h: <b>5a</b> , 91%		 12 h: <b>5i</b> , 96%
	 12 h: <b>5b</b> , 80%		 12 h: <b>5j</b> , 76% <sup>[f]</sup>
	 6 h: <b>5b'</b> , 37%		 12 h: <b>5k</b> , 50% <sup>[f]</sup>
	 24 h: <b>5c</b> , 67%		 24 h, 200 °C: <b>5l</b> , 47% <sup>[f]</sup>
	 12 h: <b>5d</b> , 84%		 24 h, 200 °C: <b>5m</b> , 63% <sup>[f]</sup>
	 24 h: <b>5e</b> , 72%; <b>5e'</b> , 2% <sup>[f]</sup>		 12 h, 150 °C: <b>5n</b> , 83%
	 12 h, 150 °C: <b>5f</b> , 57%		 24 h, 150 °C: <b>5o</b> , 54%; <b>5o'</b> , 16%
	 24 h: <b>5g</b> , 5%		 12 h: <b>5p</b> , 82%
	 12 h: <b>5h</b> , 80%		 12 h: <b>5p</b> , 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 (*i*Pr<sub>4</sub>PSCOP)Ir complex gives high kinetic selectivity for dehydrogenation of linear alkanes to  $\alpha$ -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.

Received: July 27, 2013  
Revised: October 7, 2013  
Published online: January 2, 2014

**Keywords:** alkanes · dehydrogenation · heterocycles · homogeneous catalysis · iridium

- [1] K. Weissmehl, H.-J. Arpel, *Industrial Organic Chemistry*, Wiley-VCH, Weinheim, **2003**, pp. 59–89.  
[2] a) M. J. Burk, R. H. Crabtree, *J. Am. Chem. Soc.* **1987**, *109*, 8025–8032; b) M. J. Burk, R. H. Crabtree, C. P. Parnell, R. J. Uriarte, *Organometallics* **1984**, *3*, 816; c) H. Felkin, T. Fillebeen-

khan, R. Holmes-Smith, L. Yingrui, *Tetrahedron Lett.* **1985**, *26*, 1999.

- [3] For reviews, see a) M. C. Haibach, S. Kundu, M. Brookhart, A. S. Goldman, *Acc. Chem. Res.* **2012**, *45*, 947; b) J. Choi, A. H. R. MacArthur, M. Brookhart, A. S. Goldman, *Chem. Rev.* **2011**, *111*, 1761; c) J. Choi, A. Goldman in *Iridium Catalysis, Vol. 34* (Ed.: P. G. Andersson), Springer, Berlin, **2011**, pp. 139–167; d) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.* **2003**, *345*, 1077; e) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507; f) “Activation and Functionalization of C–H Bonds”: *ACS Symp. Ser. Vol. 885* (Ed.: K. I. Goldberg, A. S. Goldman), American Chemical Society, Washington, DC, **2004**; g) R. G. Bergman, *Nature* **2007**, *446*, 391; h) R. H. Crabtree, *J. Chem. Soc. Dalton Trans.* **2001**, 2437; i) C. M. Jensen, *Chem. Commun.* **1999**, 2443.  
[4] a) M. Gupta, C. Hagen, R. J. Flesher, W. C. Kaska, C. M. Jensen, *Chem. Commun.* **1996**, 2083; b) W.-w. Xu, G. P. Rosini, K. Krogh-Jespersen, A. S. Goldman, M. Gupta, C. M. Jensen, W. C. Kaska, *Chem. Commun.* **1997**, 2273; c) M. Gupta, W. C. Kaska, C. M. Jensen, *Chem. Commun.* **1997**, 461; d) D. W. Lee, W. C. Kaska, C. M. Jensen, *Organometallics* **1998**, *17*, 1; e) F. Liu, E. B. Pak, B. Singh, C. M. Jensen, A. S. Goldman, *J. Am. Chem. Soc.* **1999**, *121*, 4086; f) M. W. Haenel, S. Oevers, K. Angermund, W. C. Kaska, H.-J. Fan, M. B. Hall, *Angew. Chem.* **2001**, *113*, 3708; *Angew. Chem. Int. Ed.* **2001**, *40*, 3596; g) K. Krogh-Jespersen, M. Czerw, K. Zhu, B. Singh, M. Kanzelberger, N. Darji, P. D. Achord, K. B. Renkema, A. S. Goldman, *J. Am. Chem. Soc.* **2002**, *124*, 10797; h) K. Zhu, P. D. Achord, X. Zhang, K. Krogh-Jespersen, A. S. Goldman, *J. Am. Chem. Soc.* **2004**, *126*, 13044–13053; i) A. Ray, K. Zhu, Y. V. Kissin, A. E. Cherian, G. W. Coates, A. S. Goldman, *Chem. Commun.* **2005**, 3388; j) S. Kundu, Y. Choliy, G. Zhuo, R. Ahuja, T. J. Emge, R. Warmuth, M. Brookhart, K. Krogh-Jespersen, A. S. Goldman, *Organometallics* **2009**, *28*, 5432–5444; k) B. Punji, T. J. Emge, A. S. Goldman, *Organometallics* **2010**, *29*, 2702.  
[5] a) I. Göttker-Schnetmann, P. White, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 1804; b) I. Göttker-Schnetmann, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 9330; c) I. Göttker-Schnetmann, P. S. White, M. Brookhart, *Organometallics* **2004**, *23*, 1766.  
[6] S. A. Kuklin, A. M. Sheloumov, F. M. Dolgushin, M. G. Ezernitskaya, A. S. Peregudov, P. V. Petrovskii, A. A. Koridze, *Organometallics* **2006**, *25*, 5466.  
[7] a) J. J. Adams, N. Arulsamy, D. M. Roddick, *Organometallics* **2012**, *31*, 1439; b) B. C. Gruver, J. J. Adams, S. J. Warner, N. Arulsamy, D. M. Roddick, *Organometallics* **2011**, *30*, 5133.  
[8] a) A. R. Chianese, A. Mo, N. L. Lampland, R. L. Swartz, P. T. Bremer, *Organometallics* **2010**, *29*, 3019; b) W. Zuo, P. Braunstein, *Organometallics* **2012**, *31*, 2606.  
[9] a) A. S. Goldman, A. H. Roy, Z. Huang, R. Ahuja, W. Schinski, M. Brookhart, *Science* **2006**, *312*, 257; b) Z. Huang, E. Rolfe, E. C. Carson, M. Brookhart, A. S. Goldman, S. H. El-Khalafy, A. H. R. MacArthur, *Adv. Synth. Catal.* **2010**, *352*, 125.  
[10] R. Ahuja, B. Punji, M. Findlater, C. Supplee, W. Schinski, M. Brookhart, A. S. Goldman, *Nat. Chem.* **2011**, *3*, 167.  
[11] T. W. Lyons, D. Guironnet, M. Findlater, M. Brookhart, *J. Am. Chem. Soc.* **2012**, *134*, 15708.  
[12] A (PSCOP)Ir complex containing *t*Bu phosphino substituents has also been prepared. Initial experiments on this system were carried out at the University of North Carolina and the Shanghai Institute of Organic Chemistry, and the complex showed poor dehydrogenation activity.  
[13] Determined by  $^{13}\text{C}$  NMR spectroscopy, the sum of COE and COD double bonds equals TON of TBE within 10% difference. Trace 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 maximum 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.
- [15] For reviews, see: a) G. E. Dobreiner, R. H. Crabtree, *Chem. Rev.* **2009**, *109*, 681; b) T. Suzuki, *Chem. Rev.* **2011**, *111*, 1825.
- [16] R. Yamaguchi, C. Ikeda, Y. Takahashi, K.-i. Fujita, *J. Am. Chem. Soc.* **2009**, *131*, 8410.
- [17] J. Wu, D. Talwar, S. Johnston, M. Yan, J. Xiao, *Angew. Chem.* **2013**, *125*, 7121; *Angew. Chem. Int. Ed.* **2013**, *52*, 6983.
- [18] Goldman et al. have reported that complex **1** catalyzes the dehydrogenation of pyrrolidines to pyrroles; see: X. Zhang, A. Fried, S. Knapp, A. S. Goldman, *Chem. Commun.* **2003**, 2060.
- [19] Two equivalents of NaOtBu relative to **3** were used in the dehydrogenation reactions of heterocycles.
- [20] In contrast, **1**-catalyzed transfer dehydrogenation of THF with TBE in a THF solution formed 2,3-dihydrofuran and furan as the major products, and 3,4-dihydrofuran as the minor product. See Ref. [4c].
- [21] F. Liebner, P. Schmid, C. Adelwöhrer, T. Rosenau, *Tetrahedron* **2007**, *63*, 11817.
-