Homogeneous Catalysis

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An Agostic Iridium Pincer Complex as a Highly Efficient and Selective Catalyst for Monoisomerization of 1-Alkenes to *trans*-2-Alkenes

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Abstract: *A unique Ir complex (^{tBu}NC^{C}P)Ir with the pyridine–phosphine pincer as the sole ligand, featuring a dual agostic interaction between the Ir and two σ C–H bonds from a tBu substituent, has been prepared. This complex exhibits exceptionally high activity and excellent regio- and stereoselectivity for monoisomerization of 1-alkenes to trans-2-alkenes with wide functional-group tolerance. Reactions can be performed in neat reactant on a more than 100 gram scale using 0.005 mol% catalyst loadings with turnover numbers up to 19000.*

Alkenes are versatile intermediates for the synthesis of value-added chemicals and materials, including pharmaceutical intermediates and polymers.[1] Among them, terminal alkenes can be readily prepared with high regioselectivity by several methods, such as olefin oligomerization,[2] elimination reactions,[3] and Wittig reactions.[4] The stereoselective formation of 2-alkenes,[5] however, is much more difficult relative to 1-alkene synthesis. In this regard, the monoisomerization of widely accessible 1-alkenes is attractive as an atom-economic route to 2-alkenes.

The ultimate challenge for the monoisomerization process is the simultaneous control of stereo- and regioselectivity because both *trans* and *cis* isomers can be formed, and overisomerization often occurs for linear hydrocarbon substrates (for example, linear α-olefins) that lack heteroatoms or branches to prevent from producing 3-alkenes or higher homologues.[6] For example, RajanBabu reported regioselective isomerizations of 1-alkenes to 2-alkenes using a Pd or Ni complex of triarylphosphine (5 mol%), but the processes gave moderate stereoselectivity (ca. 3.5:1 *E*/*Z*) when using linear 1-alkenes.[7] Skrydstrup applied an in situ generated bulky Pd hydride (0.5–1 mol%) for selective isomerization of various 1-alkenes. Note that in some cases of linear 1-alkenes, the *E*/*Z* selectivities (2.3:1–4:1) are close to the thermodynamic ratio.[8] Similarly, a number of transition-metal catalysts (for example, Fe,[9] Ru,[10] Co,[11] Mo,[12] and Ir[13]) offer regioselectivities for 2-alkenes; unfortunately the stereoselectivities demonstrated in these works are moderate or low. In 2012, Grotjahn disclosed an imidazolyl-phosphine Ru complex for *E*-selective isomerizations of linear allyl substrates (for example, *O*-, *N*-allyl substrates and allylarenes). However, in the hydrocarbon case (for example, 4-methyl-1-pentene), overisomerization occurred to give 3-alkene (9%).[14] More recently, the same group reported an improved system using a mixture of (C_5Me_5)Ru complexes (1 mol%) that enables selective isomerization of linear α-olefins to *trans*-2-alkenes at 40 °C. The reactions could be performed at RT, albeit with higher catalyst loadings (5 mol%) and longer reaction times (97 h). Alcohols and silyl ethers proved compatible with the catalyst, but other substrate types were not tested.[15] High *E*-selectivity (40:1 *E*/*Z*) was also achieved in the isomerization of linear 1-alkenes by a Co carbene complex (5 mol%). However, the reactions employ a Grignard reagent as an additive (0.5–1 equiv), which may pose a challenge in the isomerization of substrates bearing reactive functional groups.[16] Thus, despite the significant advances in this field, it is of great interest to develop highly efficient and widely functional-group-tolerant catalysts for selective alkene isomerizations.

Our group recently reported that NC^{O}P-type Ir pincer complexes of pyridine–phosphinite ligands (**1**; Figure 1) are very active for alkene isomerizations at 60 °C, but give low regio- and stereoselectivity.[17] We envisioned that a pyridine-based pincer Ir catalyst with a more sterically hindered ligand

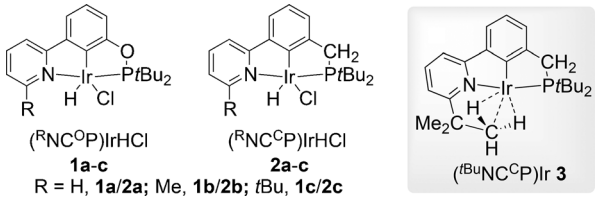

Figure 1. ^{R}NC^{O}P and ^{R}NC^{C}P iridium complexes.

might offer the combination of efficiency and selectivity in the isomerization. Early studies by Goldman and Brookhart on PCP-type pincer Ir complex-catalyzed olefin isomerization established a π-allyl methanism,[18] and revealed that the nature of the linkers connecting the P atoms and the aryl backbone have large impact on the steric properties.[18,19] In this context, we sought to develop more bulky pyridine-phosphine Ir complexes (^{R}NC^{C}P)IrHCl (**2**) with a methene (CH_2) linker in place of the O-linker in **1**. A novel *t*Bu-substituted complex (^{tBu}NC^{C}P)Ir (**3**; Figure 1) that possesses a dual agostic interaction between the metal and two σ C–H bonds in the *t*Bu$_{(py)}$ group (*t*Bu on the pyridine ring) is further generated. This complex, which requires no activator, is extremely active for isomerization of 1-alkenes, including challenging linear α-olefins, producing *trans*-2-alkenes with high positional and stereochemical selectivity.

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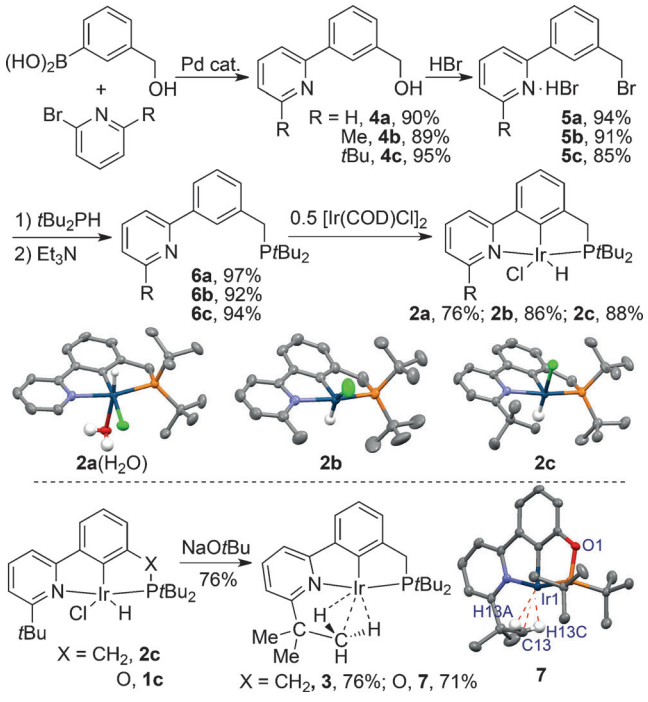


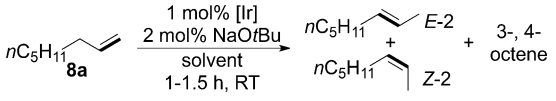
Figure 2. Synthesis of (^{R}NC^{C}P)IrHCl (**2**), (^{tBu}NC^{C}P)Ir (**3**), and (^{tBu}NC^{O}P)Ir **7**, and the crystal structures of **2a**(H_2O), **2b**, **2c**, and **7**.

The synthesis of the ^{R}NC^{C}P Ir complexes is outlined in Figure 2. Suzuki couplings of 2-bromopyridines with 3-(hydroxymethyl)phenyl boronic acid formed (3-(pyridin-2-yl)phenyl)methanols, which were brominated with HBr to give the HBr salts of ((bromomethyl)phenyl)pyridines (**5a–c**). Reactions of **5a–c** with tBu$_2$PH, followed by treatment with Et_3N, formed the ^{R}NC^{C}P ligands **6a–c**. Metalations of **6a–c** with $[Ir(COD)Cl]_2$ then generated the hydrido chloride complexes (^{R}NC^{C}P)IrHCl (R = H, **2a**; Me, **2b**; tBu, **2c**) in high yields. The Ir^{III} complexes were fully characterized. The characteristic Ir–H resonance for **2a** appears at −39.36 ppm in the ^{1}H NMR spectrum, which is close to that observed for the classical pincer hydrido chloride complexes adopting a square pyramidal geometry with the hydride *trans* to a vacant coordination site.[20] In contrast, the Ir–H resonance for the tBu-substituted complex **2c** appears at −21.98 ppm, implying that the site *trans* to the hydride is occupied. The Me-substituted complex **2b** has a Ir–H signal (−30.99 ppm) in the middle of those for **2a** and **2c**. The single crystal structures of **2c** and **2b** are consistent with the NMR data. The Cl atom in **2c** is located at the apical site rather than the equatorial position (∡ Cl-Ir-H: 169.0(11)°),[21] whereas **2b** adopts a geometry between square pyramidal and trigonal bipyramidal (∡ Cl-H-Ir: 152.2(19)°). Growing crystals of **2a** resulted in the formation of crystals of a H_2O-bound six-coordinate Ir complex **2a**(H_2O) (Figure 2).[22]

Three-coordinate 14-e$^-$ Ir species ligated only by the pincer ligand have been well documented as the key intermediates in various catalytic transformations,[19a,23] although as of yet such complexes have never been isolated, or even spectroscopically detected. Significantly, the reaction of the tBu-substituted complex (^{tBu}NC^{C}P)IrHCl (**2c**) with NaOtBu in toluene formed an Ir complex (^{tBu}NC^{C}P)Ir (**3**, 76% yield) without the coordination of any other ligands except for the ^{tBu}NC^{C}P pincer (Figure 2). MALDI-TOF-MASS and elemental analysis confirmed the proposed formulation. No hydride signal is detected and the tBu$_{(py)}$ group appears as a singlet resonance at 1.40 ppm in the ^{1}H NMR spectrum. Attempts to grow single crystals of **3** have been unsuccessful. A closely related complex (^{tBu}NC^{O}P)Ir (**7**) with a "O" linker was obtained in 71% yield using the same procedure, and its structure was revealed by X-ray crystallography. The data were of sufficient quality such that the σ carbon–hydrogen bonds adjacent to the metal center could be located in difference maps and refined freely. Strikingly, the solid-state structure of **7** shows an unusual dual agostic interaction between two σ C–H bonds from the tBu group and the Ir center (Ir1–C13 2.393, Ir1–H13A 2.149, Ir1–H13C 2.174 Å; Figure 2).[24,25] Note that this type of dual agostic interaction has been reported for a few late transition-metal complexes.[26] Similar to **3**, the tBu$_{(py)}$ group in **7** was observed as a singlet ^{1}H NMR resonance at 25 °C, or even at −75 °C, indicating the nine protons are in fast exchange. Taken together, the results suggest **3** most likely contains a dual agostic interaction with the C–H bonds from the tBu$_{(py)}$ group coordinated to the metal. Treatment of **2a** and **2b** with NaOtBu cannot form the corresponding (^{R}NC^{C}P)Ir complex,[27] which further supports the vital role of tBu$_{(py)}$ on stabilizing the Ir center in **3** and **7**.

The new ^{R}NC^{C}P-ligated Ir complexes **2a–c** and **3** were evaluated for the isomerization of a linear alkene, 1-octene (Table 1). Upon activation with NaOtBu, **2a** (1 mol%) exhibited low activity in toluene, giving only 3% conversion after 1.5 h at RT (entry 1). The Me-substituted complex **2b** is much more active than **2a**, affording 68% (*E*)-2-octene in 5:1 *E*/*Z* selectivity, along with 10% 3- and 4-octenes (entry 2). High conversion and high regio- and stereoselectivity for (*E*)-2-octene was obtained using the most sterically demanding complex **2c**, furnishing the desired product in 90% yield and 22:1 *E*/*Z* selectivity (entry 3). Catalysis using **2c**/NaOtBu also occurred efficiently in tBuOH and acetone (entries 4, 5). A

Table 1: Iridium catalysts for isomerization of 1-octene.[a]



Entry	Cat.	Solvent	Conv. [%]	E-2 yield [%]	E:Z	3-,4-octene
1[b]	**2a**/NaOtBu	toluene	3	ND	ND	ND
2[b]	**2b**/NaOtBu	toluene	93	68	5:1	10
3[b]	**2c**/NaOtBu	toluene	95	90	22:1	<2
4[c]	**2c**/NaOtBu	acetone	98	92	30:1	3
5[c]	**2c**/NaOtBu	tBuOH	98	93	26:1	<2
6[c]	**2c**	toluene	0	0	–	0
7[c]	**3**	toluene	97	94	51:1	1
8[d]	**3**	C_6D_6	97	93	35:1	1
9[c]	**7**	toluene	40	24	2:1	8

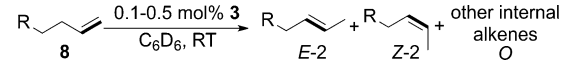
[a] Conditions: **8a** (0.5 mmol), [Ir] (5 μmol), NaOtBu (11 μmol), solvent (1 mL). Yields and *E*/*Z* ratios were determined by GC analysis. ND = not determined. [b] 1.5 h. [c] 1 h. [d] **8a** (0.25 mmol), **3** (0.1 mol%), C_6D_6 (0.4 mL), 8 h.

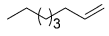
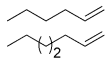
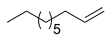
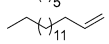
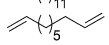
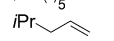
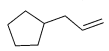
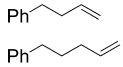
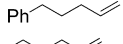
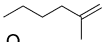
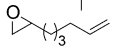
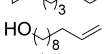
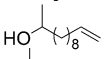
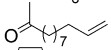
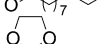
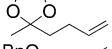
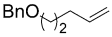
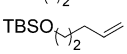
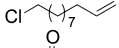
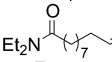
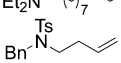
control experiment without NaO*t*Bu indicated that an activator is required in the run using **2c** (entry 6).

We expected that the η^2 C–H bonds in the agostic complex ($^{t\mathrm{Bu}}$NC$^{\mathrm{C}}$P)Ir (**3**) would dissociate readily to generate the catalytically active 14-e$^-$ species. Indeed, the catalysis using **3** without an external activator occurred smoothly at RT, giving 94% (*E*)-2-octene in 51:1 *E*/*Z* selectivity in 1 h (entry 7). The loading of **3** could be reduced to 0.1 mol% without affecting the yield of (*E*)-2-octene; the sum of all other isomers (3-, 4-octenes) constitutes only 1% of total alkenes (entry 8). The related agostic complex ($^{t\mathrm{Bu}}$NC$^{\mathrm{O}}$P)Ir (**7**) with the O-linker displayed low activity and selectivity (entry 9).

The substrate scope of the Ir-catalyzed isomerization was explored (Table 2). For the sake of convenience in NMR analysis, the reactions were carried out in C_6D_6. Most reactions proceeded at 25 °C using 0.1 mol% of **3** to form the desired (*E*)-2-alkenes in high yields (>90%) with both regio- and stereocontrol at a level of more than 20:1. The challenging linear hydrocarbon alkenes, C_6, C_7, C_{10}, C_{16} α-olefins (**8b–e**) were converted into (*E*)-2-alkenes in high selectivities, and in all cases ≤2% of other internal alkenes were detected. Two terminal C–C double bonds in 1,9-decadiene were both selectively isomerized, giving (*E*)-2-(*E*)-8-decadiene in 93% yield. The isomerization of 1-alkenes with branches in the homoallylic positions (**8g**, **8h**) gave (*E*)-2-alkenes in high yields. The reactions of 4-phenyl- and 5-phenyl-substituted 1-alkenes (**8i**, **8j**) occurred selectively; the overisomerized, thermodynamically more stable conjugated isomers were hardly observed. Disubstituted terminal olefin (**8k**) is unreactive, which reflects the steric effects of the substrates on the isomerization. Importantly, this catalyst system is tolerant of various functional groups. Terminal alkenes with free alcohol (**8m**, **8n**), ketone (**8o**), ester (**8z**, see below), epoxy (**8l**), ketal (**8p**), ether (**8q**), silicon ether (**8r**), and chloride (**8t**) groups undergo selective isomerizations. *N*-containing functionalities, such as amide (**8u**), tertiary amine (**8v**), and secondary amine (**8w**), can also be tolerated. Allylbenzene **8x** and its derivative **8y** were converted into (*E*)-2-isomers quantitatively.

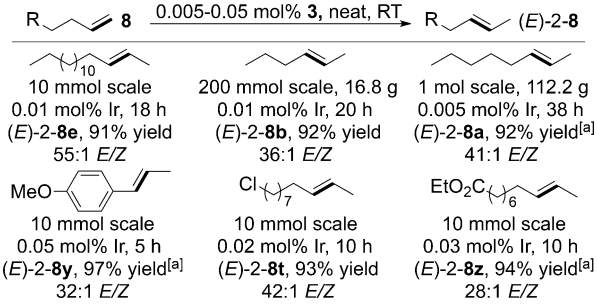
Table 2: Ir-catalyzed selective isomerization of various 1-alkenes.[a]



substrate		3 mol %	*t* (h)	conv. (%)	*E*-2 yield (%)	*E*:*Z*	*O* yield (%)
	**8a**	0.1	8	97	94	36:1	1
	**8b**	0.1	8	96	91	25:1	2
	8c	0.1	8	98	91	23:1	2
	**8d**	0.1	8	97	93	29:1	1
	**8e**	0.1	8	97	93	25:1	1
	**8f**	0.1	10	95	93	38:1	<1
	**8g**	0.1	30	93	85	10:1	ND[b]
	**8h**	0.1	30	91	87	20:1	0
	8i	0.1	30	95	78	20:1	3
	**8j**	0.1	10	91	87	28:1	1
	**8k**	0.1	8	0	0	-	-
	**8l**	0.2	10	93	92	27:1	2
	**8m**	0.5	5	96	92	26:1	1
	**8n**	0.5	2.5	96	91	31:1	2
	8o	0.5	1.5	96	94	31:1	2
	**8p**	0.3	8	97	92	31:1	0
	**8q**	0.1	32	95	87	19:1	1
	**8r**	0.2	36	96	90	22:1	2
	**8s**	0.2	4	96	95	42:1	1
	**8t**	0.1	8	96	93	31:1	1
	**8u**	0.5	3	98	93	38:1	<1
	8v	0.5	8	96	94	25:1	<1
	**8w**	0.2	0.5	96	93	37:1	-
	**8x**	0.1	8	99	98	99:1	-
	**8y**	0.1	8	>99	99	>99:1	-

[a] Conditions: **8** (0.25 mmol) and **3** (0.1–0.5 mol%) in C_6D_6 (0.4 mL) at 25 °C. Yields and *E*/*Z* ratios were determined by ^{1}H NMR analysis. [b] Not determined owing to overlap of ^{1}H NMR signals.

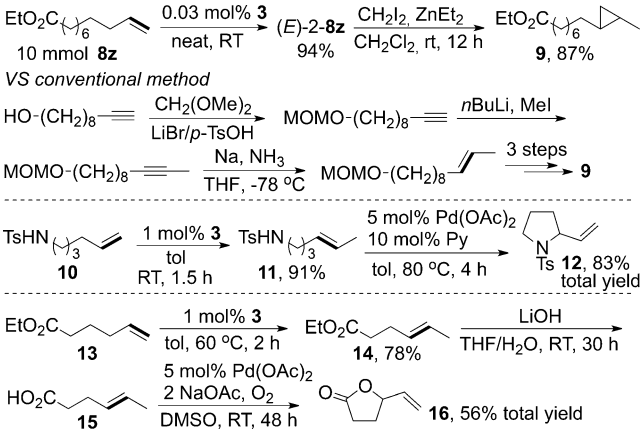
The isomerization reactions proceed efficiently on large scales under solvent-free conditions using a minimal amount of Ir (Scheme 1). The reaction with 0.01 mol% **3** in neat 1-hexadecene (10 mmol) yielded 91% (*E*)-2-hexadecene with very high *E*/*Z* selectivity (55:1) after 18 h. Catalysis on an even larger scale can be accomplished as shown by the conversion of 0.2 mol of 1-hexene (16.8 g) into 92% (*E*)-2-hexene (36:1 *E*/*Z*). Remarkably, using only 0.005 mol% of **2** (86 ppm Ir metal), the run with 1 mol of 1-octene (112.2 g) afforded (*E*)-2-octene in 92% yield (41:1 *E*/*Z*) with 19000 TONs. Furthermore, the reactions of allylarene **8y**, and 1-alkenes bearing ester (**8z**) and chloride (**8t**) functionalities using 0.02–0.05 mol% **3** gave the corresponding (*E*)-2-alkenes in high yields. We note that the *E*-selectivity obtained in neat olefin is in general higher than that obtained in solution, and in all cases only trace amounts (≤1%) of other internal isomers are present. A further advantage of the procedures is the easy isolation of the products: a quick pass of the reaction mixture through a short pad of silica gel (1–



Scheme 1. Large-scale preparation of (*E*)-2-alkenes. Yields and *E*/*Z* ratios were determined by ^{1}H NMR analysis, except: [a] determined by GC analysis.

2 cm) led to isolation of alkene products in high yields (> 90 %).

The selective isomerization creates access to a range of biologically active molecules and synthetically useful building blocks (Scheme 2). McLaughin reported that a tigliane diterpene containing a cyclopropyl fatty acid ester isolated from *Euphorbia poissonii* has strong bioactivities and selectivity for



Scheme 2. Derivatizations of (*E*)-2-alkenes.

the human kidney carcinoma.[28] The conventional synthesis of the cyclopropyl fatty acid ester unit (**9**, Scheme 2) requires multiple steps involving the synthesis of 2-alkyne as the intermediate, which is reduced by Na/NH_3 to give (*E*)-2–**8z**.[29] By comparison, the (*E*)-2-alkene can be prepared on a large scale from the comercially available **8z** via our Ir- catalyzed isomerization. Cyclopropanation of (*E*)-2–**8z** with Et_2Zn and CH_2I_2 afforded **9** in 87 % yield. Furthermore, *p*- toluenesulfonamide- and carboxylic acid-substituted (*E*)-2-alkenes (**11**, **15**) derived from the readily accessible terminal alkenes undergo Pd-catalyzed oxidative cyclization to form five-membered vinylic *N*-heterocycle (**12**) and lactone (**16**).[30,31]

In summary, the agostic pincer iridium complex ($^{tBu}NC^{C}P$)Ir (**3**) is a remarkably practical and general catalyst system for alkene isomerization. Its selectivies for *trans*-2-alkenes are exceptionally high and comparable to those of the most selective catalysts reported to date, and the activities far surpass those of the known selective isomerization catalysts. Mechanistic studies are underway, including attempts to understand the steric and electronic effects on the selectivity of the isomerization process.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: agostic interactions · alkenes · iridium · isomerization · pincer ligands

[1] a) P. W. N. M. van Leeuwen, *Homogeneous Catalysis*, Kluwer Academic Publishers, Dordrecht, **2004**, pp. 101–105; b) B. Cornils, W. A. Herrmann, *Applied Homogeneous Catalysis with Organometallic Compounds*, Wiley, New York, **2002**, pp. 980–991.
[2] D. S. McGuinness, *Chem. Rev.* **2003**, *103*, 27.
[3] a) T. Kobayashi, H. Ohmiya, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2008**, *130*, 11276; b) A. C. Bissember, A. Levina, G. C. Fu, *J. Am. Chem. Soc.* **2012**, *134*, 14232.
[4] B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863.
[5] For examples of (*E*)-2-alkene synthesis, see: a) T. Okazoe, K. Takai, K. Utimoto, *J. Am. Chem. Soc.* **1987**, *109*, 951; b) T. L. Underiner, S. D. Paisley, J. Schmitter, L. Lesheski, H. L. Goering, *J. Org. Chem.* **1989**, *54*, 2369; c) R. Riveiros, L. Saya, J. P. Sestelo, L. A. Sarandeses, *Eur. J. Org. Chem.* **2008**, 1959.
[6] For Reviews, see: a) R. Uma, C. Crévisy, R. Grée, *Chem. Rev.* **2003**, *103*, 27; b) N. Kuznik, S. Krompiec, *Coord. Chem. Rev.* **2007**, *251*, 222; c) S. Krompiec, M. Krompiec, R. Penczek, H. Ignasiak, *Coord. Chem. Rev.* **2008**, *252*, 1819; d) E. Larionov, H. Li, C. Mazet, *Chem. Commun.* **2014**, *50*, 9816.
[7] H. J. Lim, C. R. Smith, T. V. RajanBabu, *J. Org. Chem.* **2009**, *74*, 4565.
[8] D. Gauthier, A. T. Lindhardt, E. P. K. Olsen, J. Overgaard, T. Skrydstrup, *J. Am. Chem. Soc.* **2010**, *132*, 7998.
[9] a) M. Mayer, A. Welther, A. J. von Wangelin, *ChemCatChem* **2011**, *3*, 1567; b) R. Jennerjahn, R. Jackstell, I. Piras, R. Franke, H. Jaio, M. Bauer, M. Beller, *ChemSusChem* **2012**, *5*, 734.
[10] a) S. Krompiec, J. Suwinski, J. Grobelny, *Pol. J. Chem.* **1996**, *70*, 813; b) A. Sivaramakrishna, P. Mushonga, I. L. Rogers, F. Zheng, R. J. Haines, E. Nordlander, J. R. Moss, *Polyhedron* **2008**, *27*, 1911; c) S. Perdriau, M. C. Chang, E. Otten, H. J. Heeres, J. G. de Vries, *Chem. Eur. J.* **2014**, *20*, 15434.
[11] Some Co complexes offer *Z*-selectivity (5:1–7:1 *Z*/*E*); see: a) C. Chen, T. R. Dugan, W. W. Brennessel, D. J. Weix, P. L. Holland, *J. Am. Chem. Soc.* **2014**, *136*, 945; b) A. Schmidt, A. R. Nödling, G. Hilt, *Angew. Chem. Int. Ed.* **2015**, *54*, 801; *Angew. Chem.* **2015**, *127*, 814; c) F. Pünner, A. Schmidt, G. Hilt, *Angew. Chem. Int. Ed.* **2012**, *51*, 1270; *Angew. Chem.* **2012**, *124*, 1296.
[12] R. Castro-Rodrigo, S. Chakraborty, L. Munjanja, W. W. Brennessel, W. D. Jones, *Organometallics* **2016**, *35*, 3124.
[13] A. R. Chianese, S. E. Shaner, J. A. Tendler, D. M. Pudalov, D. Y. Shopov, D. Kim, S. L. Rogers, A. Mo, *Organometallics* **2012**, *31*, 7359.
[14] C. R. Larsen, D. B. Grotjahn, *J. Am. Chem. Soc.* **2012**, *134*, 10357.
[15] C. R. Larsen, G. Erdogan, D. B. Grotjahn, *J. Am. Chem. Soc.* **2014**, *136*, 1226.
[16] T. Kobayashi, H. Yorimitsu, K. Oshima, *Chem. Asian J.* **2009**, *4*, 1078.
[17] X. Jia, L. Zhang, C. Qin, X. Leng, Z. Huang, *Chem. Commun.* **2014**, *50*, 11056. The $NC^{O}P$ Ir complexes are much more active than the classical PCP pincer Ir complexes for alkene isomerization.
[18] S. Biswas, Z. Huang, Y. Choliy, D. Y. Wang, M. Brookhart, K. Krogh-Jespersen, A. S. Goldman, *J. Am. Chem. Soc.* **2012**, *134*, 13276.

[19] a) J. Choi, A. H. R. MacArthur, M. Brookhart, A. S. Goldman, *Chem. Rev.* **2011**, *111*, 1761; b) W. Yao, Y. Zhang, X. Jia, Z. Huang, *Angew. Chem. Int. Ed.* **2014**, *53*, 1390; *Angew. Chem.* **2014**, *126*, 1414.

[20] a) 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; b) B. Punji, T. J. Emge, A. S. Goldman, *Organometallics* **2010**, *29*, 2702.

[21] The closest distance between the Ir center and the H atom from the *t*Bu group on the pyridine ring is 2.311 Å in **2c**.

[22] CCDC 1515756 (**2a**(H_2O), 1515757 (**2b**), 1515758 (**2c**), and 1515759 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[23] a) K. Krogh-Jespersen, M. Czerw, N. Summa, K. B. Renkema, P. D. Achord, A. S. Goldman, *J. Am. Chem. Soc.* **2002**, *124*, 11404; b) K. Zhu, P. D. Achord, X. Zhang, K. Krogh-Jespersen, A. S. Goldman, *J. Am. Chem. Soc.* **2004**, *126*, 13044; c) I. Göttker-Schnetmann, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 9330.

[24] a) M. Brookhart, M. L. H. Green, G. Parkin, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 6908; b) M. Brookhart, M. L. H. Green, *J. Organomet. Chem.* **1983**, *250*, 395; c) C. Y. Tang, A. L. Thompson, S. Aldridge, *J. Am. Chem. Soc.* **2010**, *132*, 10578.

[25] The optimized structure of **7** shows a dual agostic interaction consistent to the experimental results (Ir1−C13 2.428, Ir1−H13A 2.010, Ir−H13C 2.158 Å). Y. Wang, Y. Li, Z. Huang, unpublished results.

[26] a) H. Urtel, C. Meier, F. Eisenträger, F. Rominger, J. P. Joschek, P. Hofmanna, *Angew. Chem. Int. Ed.* **2001**, *40*, 781; *Angew. Chem.* **2001**, *113*, 803; b) S. H. Crosby, G. J. Clarkson, J. P. Rourke, *J. Am. Chem. Soc.* **2009**, *131*, 14142; c) W. Baratta, P. Da Ros, A. Del Zotto, A. Sechi, E. Zangrando, P. Rigo, *Angew. Chem. Int. Ed.* **2004**, *43*, 3584; *Angew. Chem.* **2004**, *116*, 3668; d) W. Baratta, E. Herdtweck, P. Rigo, *Angew. Chem. Int. Ed.* **1999**, *38*, 1629; *Angew. Chem.* **1999**, *111*, 1733.

[27] Reactions of **2a** and **2b** with NaO*t*Bu in C_6D_6 formed unidentifed species.

[28] M. O. Fatope, L. Zeng, J. E. Ohayaga, G. Shi, J. L. McLaughlin, *J. Med. Chem.* **1996**, *39*, 1005.

[29] G. Villorbina, L. Roura, F. Camps, J. Joglar, G. Fabriàs, *J. Org. Chem.* **2003**, *68*, 2820.

[30] S. R. Fix, J. L. Brice, S. S. Stahl, *Angew. Chem. Int. Ed.* **2002**, *41*, 164; *Angew. Chem.* **2002**, *114*, 172.

[31] R. C. Larock, T. R. Hightower, *J. Org. Chem.* **1993**, *58*, 5298.

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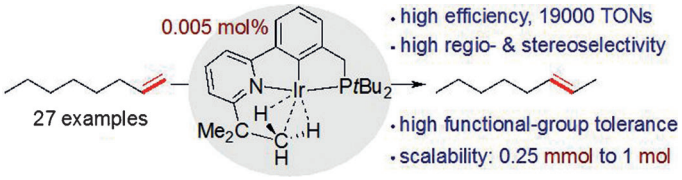
Communications

Homogeneous Catalysis

Y. Wang, C. Qin, X. Jia, X. Leng, Z. Huang* ——— ■■■■–■■■■

An Agostic Iridium Pincer Complex as a Highly Efficient and Selective Catalyst for Monoisomerization of 1-Alkenes to *trans*-2-Alkenes



An agostic pincer iridium complex is extremely efficient for isomerization of various terminal alkenes, including very challenging linear α-olefins, to *trans*-2-alkenes with high positional and stereochemical selectivity.

