Hydrogen Transfer Hydrozirconation of Alkenes with *i*BuZrCp$_2$Cl Catalyzed by Lewis-Acidic Metal Compounds Containing Al, Zn, Si, Ag, and Pd

Hidefumi Makabe[a] and Ei-ichi Negishi*[a]

Keywords: Hydrogen transfer / Zirconium / Alkenes / Isobutylzirconocene chloride / Lewis acid catalysis / Lewis acid catalysis

The hydrozirconation reaction of monosubstituted alkenes with *i*BuZrCp$_2$Cl can be significantly accelerated by catalytic amounts of various Lewis acidic metal compounds, most notably AlCl$_3$, Me$_3$SiI, and Pd complexes, such as Li$_2$PdCl$_4$ and Cl$_2$Pd(PPh$_3$)$_2$.

Hydrozirconation is commonly carried out with preformed HZrCp$_2$Cl.[1] Although commercially available, its preparation requiring sluggish filtration under inert atmosphere is somewhat cumbersome. Various procedures for in situ generation of HZrCp$_2$Cl using metal hydrides, such as LiAlH$_4$, NaAlH$_2$(OCH$_2$CH$_2$OCH$_3$)$_2$, and LiBH(*s*Bu)$_3$, have been devised.[2][3] However, these procedures can be complicated by the formation of by-products and their subsequent reactions, although solutions to some such problems have been devised.[4] Hydrogen transfer hydrozirconation with *i*BuZrCp$_2$Cl[2][5] has also provided a convenient and potentially more economical alternative. Indeed, the reaction of both terminal and internal alkynes with *i*BuZrCp$_2$Cl[5] is a clean and high-yielding process, albeit slower than hydrozirconation with HZrCp$_2$Cl. On the other hand, the corresponding reaction of terminal alkenes is generally sluggish, producing the desired products in variable yields, despite our earlier more favorable claim.[2] Another earlier report of Zr-catalyzed hydroalumination with *i*Bu$_3$Al and a catalytic amount of Cl$_2$ZrCp$_2$,[6,7] which was thought to involve hydrogen transfer hydrozirconation, suggested an intriguing possibility of catalyzing hydrozirconation with *i*BuZrCp$_2$Cl by Al and other Lewis acidic metal compounds.[8]

We now report that the hydrozirconation reaction of monosubstituted alkenes with *i*BuZrCp$_2$Cl can be significantly accelerated by catalytic amounts of a variety of Lewis acidic metal compounds, most notably AlCl$_3$ (2 mol%), Me$_3$SiI (5 mol%), and Pd complexes, such as Li$_2$PdCl$_4$ and Cl$_2$Pd(PPh$_3$)$_2$, as indicated by the results summarized in Table 1. Under otherwise the same conditions, the uncatalyzed reaction of 1-decene with *i*BuZrCp$_2$Cl produced even after 15 h the desired hydrozirconation product only in 20% yield with about 70% of 1-decene remaining (Entry 1). In the AlCl$_3$-catalyzed reaction, it is essential to evaporate ether used to generate *i*BuZrCp$_2$Cl before addition of AlCl$_3$, and the amount of AlCl$_3$ must be kept at a minimum, as alkylzirconocene chlorides and AlCl$_3$ are known to undergo transmetalation to produce Cp$_2$ZrCl$_2$ and alkylaluminum derivatives.[9]

The results presented above clearly established the feasibility of catalyzing hydrogen transfer hydrozirconation of alkenes with alkylzirconocene chlorides, e.g., *i*BuZrCp$_2$Cl. To further explore the scope of this novel catalytic protocol, various other metal compounds were tested. As the results shown in Table 1 indicate, an unexpectedly wide range of metal compounds display catalytic activities, and the following findings are particularly noteworthy. Firstly, in addition to AlCl$_3$, several other metal compounds including ZnCl$_2$ (Entries 6 and 7), AgBF$_4$ (Entry 11), Me$_3$SiI (Entry 15), Li$_2$PdCl$_4$, and Cl$_2$Pd(PPh$_3$)$_2$ (Entries 18 and 19) exhibit significant and potentially useful catalytic activities. Unlike AlCl$_3$, none of these other catalysts requires evaporation of ether. Secondly, metal chlorides containing Zn and Hg are more effective than the corresponding bromides and iodides. On the other hand, Me$_3$SiI (Entry 15) is decidedly more effective than Me$_3$SiCl (Entry 14), suggesting that more than one mechanism may be operative in the catalysis reported herein. Thirdly, selection of solvents is critically important. Somewhat unexpectedly, benzene and toluene are far superior to CH$_2$Cl$_2$ and ethereal solvents, e.g., THF, in most cases. Additionally, various other compounds including LiI, EtAlCl$_2$, Et$_2$AlCl, SnCl$_4$, Bu$_3$SnBr, Bu$_3$SnI, and SbCl$_5$ were tested, but none yielded satisfactory results. With EtAlCl$_2$ and tributyltin halides, extensive isomerization of 1-decene to a mixture of internal decenes similar to that observed in the reaction of 1-alkenes with *n*BuMgCl and Cl$_2$ZrCp$_2$[10] took place, although its mechanistic details are unclear.

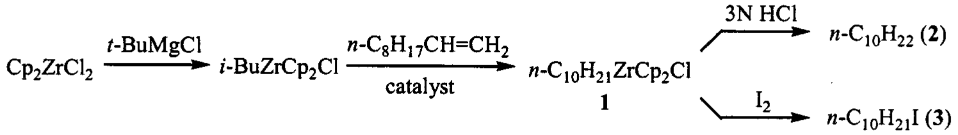
The synthetic utility of two procedures with AlCl$_3$ (2 mol%) and Me$_3$SiI (5 mol%) has been examined with several representative functionally substituted terminal alkenes. Either catalyst was satisfactory in converting 11-

---

[a] Department of Chemistry, Purdue University
West Lafayette, Indiana 47907-1393, USA
Fax: (internat.) +1-765/494-0239
E-mail: negishi@chem.purdue.edu

💻 Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/eurjoc or from the author.

Table 1. Hydrogen transfer hydrozirconation of 1-decene with iBuZrCp$_2$Cl catalyzed by metal compounds[a]



Entry	Catalyst (%)		Solvent [b]	T [°C]	t [h]	Product yield [%]			1-Decene [%]	Cp_2ZrCl_2 [%]
						1 [c]	**2** [d]	**3** [e]		
1	None		PhH-Et_2O	50	15	20	20	[f]	70	[f]
2	$AlCl_3$	(2)	PhH	50	3	87	91	84	0	5
3	$AlCl_3$	(2)	toluene	50	3	80	84	76	0	6
4	$AlCl_3$	(2)	CH_2Cl_2	reflux	3	51	71	[f]	28	6
5	BCl_3	(5)	PhH	50	8	45	52	[f]	30	10
6	$ZnCl_2$	(10)	PhH-Et_2O	50	4	76	86	74	0	13
7	$ZnCl_2$	(10)	THF-Et_2O	50	4	79	81	71	0	8
8	$ZnBr_2$	(10)	THF-Et_2O	50	10	44	49	[f]	40	[f]
9	ZnI_2	(10)	THF-Et_2O	50	10	13	14	[f]	75	[f]
10	$AgBF_4$	(10)	PhH-Et_2O	50	8	58	72	60	20	3
11	$AgBF_4$	(20)	PhH-Et_2O	50	8	74	92	85	0	16
12	$HgCl_2$	(5)	PhH-Et_2O	50	10	62	68	61	15	12
13	HgI_2	(5)	PhH-Et_2O	50	10	39	53	[f]	20	[f]
14	Me_3SiCl	(5)	PhH-Et_2O	50	8	61	64	52	20	5
15	Me_3SiI	(5)	PhH-Et_2O	50	3	82	85	82	0	6
16	Me_3SiI	(5)	THF-Et_2O	50	3	31	33	[f]	50	[f]
17	Bu_3SnCl	(5)	PhH-Et_2O	50	8	38	34	[f]	47	4
18	Li_2PdCl_4	(2.5)	PhH-THF-Et_2O	50	3	71	88	80	0	10
19	$Cl_2Pd(PPh_3)_2$	(2.5)	PhH-Et_2O	50	3	76	74	72	0	5

[a] The reaction was carried out with iBuZrCp$_2$Cl generated in situ in 90−95% yield by treatment of 1.1 equiv. each (relative to an alkene) of Cp$_2$ZrCl$_2$ with tBuMgCl at 50°C for 1 h. − [b] In cases where Et$_2$O is not shown, it was evaporated. − [c] By ^{1}H-NMR spectroscopy. − [d] By GLC. − [e] Yield of isolated product. − [f] Not determined.

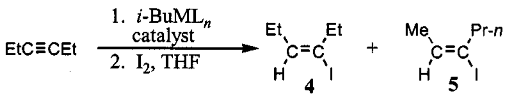
chloro-1-undecene into 1-iodo-11-chlorodecane in 70−80% yields. However, 11-benzyloxy-1-undecene, 11-(*tert*-butyldiphenylsilyloxy)-1-undecene, and allyl phenyl ether all decomposed in the presence of AlCl$_3$. On the other hand, their reaction in the presence of 5 mol% of Me$_3$SiI gave, after iodinolysis, the corresponding iodoalkanes in 74, 75, and 50% yields, respectively. 4-Vinylcyclohexene was similarly converted into 4-(2-iodoethyl)cyclohexene in 74% yield with 5 mol% Me$_3$SiI, whereas its yield observed with 2 mol% of AlCl$_3$ was 55%. With Cl$_2$Pd(PPh$_3$)$_2$ as a catalyst, even ester-containing alkenes can be chemoselectively hydrozirconated. Thus, for example, 9-decenyl benzoate reacted with iBuZrCp$_2$Cl and 5 mol% of Cl$_2$Pd(PPh$_3$)$_2$ to give, after protonolysis, decyl benzoate in 74% yield. No starting compound remained unchanged, and the extent of competitive ester reduction was about 5%. As the corresponding reaction with preformed HZrCp$_2$Cl in the absence of any catalyst gave 9-decenol in 40% yield along with the desired decyl benzoate only in 20% yield and the unchanged starting compounds (20%), the Pd-catalyzed hydrogen transfer hydrozirconation herein reported is expected to show a significantly different and more favorable chemoselectivity profile than the conventional hydrozirconation.

The catalytic activity of AlCl$_3$ may be interpreted within the context of activation of iBuZrCp$_2$Cl by AlCl$_3$ through Zr-Cl-Al interaction to generate either iBuZr$^+$Cp$_2$AlCl$_4$$^-$ or iBuZrCp$_2$ $^{\delta+}$−Cl−$^{\delta-}$AlCl$_3$, which may be further converted to the corresponding zirconium hydrides as transient reactive species.[8] Interestingly, however, the reaction of 3-hexyne with iBuZrCp$_2$Cl in the presence of 2 mol% of AlCl$_3$ produced, after iodinolysis, (*E*)-3-iodo-3-hexene (**4**) in 76% yield with no indication of the formation of (*E*)-3-iodo-2-hexene (**5**) (< 2%). As reported previously,[6] the corresponding reaction with iBu$_3$Al (3 equiv) in the presence of 10 mol% of Cp$_2$ZrCl$_2$ gave, after iodinolysis, **4** and **5** in 38 and 35% yields, respectively (Scheme 1). Further mechanistic studies are necessary to clarify mechanistic details.

Experimental Section

All reactions were run under Ar atmosphere with exclusion of light (Al foil).

Hydrozirconation of 1-Decene with *i*BuZrCp$_2$Cl in the Presence of 2 mol% of AlCl$_3$: Ether was removed from an ethereal solution of tBuMgCl (2 M, 1.1 mL, 2.2 mmol) at room temperature under re-



i-BuML$_n$ (eq.)	catalyst (eq.)	**4** (%)	**5** (%)
i-BuZrCp$_2$Cl (1.1)	AlCl$_3$ (0.02)	76	<2
i-BuZrCp$_2$Cl (1.1)	AlCl$_3$ (0.2)	45	<2
i-Bu$_3$Al (3.0)	Cp$_2$ZrCl$_2$ (0.1)	38	35

Scheme 1. Hydrogen transfer hydrometalation of 3-hexyne with isobutyl-containing Al−Zr reagents

duced pressure. To this were added 5 mL of benzene and Cp$_2$ZrCl$_2$ (642 mg, 2.2 mmol), and the reaction mixture was heated for 1 h at 50°C. The formation of iBuZrCp$_2$Cl in 94% yield was observed by ^{1}H-NMR spectroscopy. To this were added AlCl$_3$ (5.5 mg, 0.04 mmol) and 1-decene (0.38 mL, 2.0 mmol). The resulting mixture was stirred at 50°C for 3 h. Analysis by ^{1}H NMR spectroscopy indicated the formation of nC$_{10}$H$_{21}$ZrCp$_2$Cl (δ = 5.80 for Cp) in 87% yield along with 5% of Cp$_2$ZrCl$_2$ (δ 5.91). Its treatment with iodine (1.14 g, 4.5 mmol) in 10 mL of THF at 0 to 23°C followed by the usual extractive workup and bulb-to-bulb distillation (0.5 mm Hg, 70−75°C) afforded 451 mg (84%) of 1-iododecane.

Hydrozirconation of 11-(Benzyloxy)-1-decene with iBuZrCp$_2$Cl in the Presence of Me$_3$SiI: To iBuZrCp$_2$Cl, generated in situ by treatment of tBuMgCl (2 M, 1.1 mL, 2.2 mmol) in Et$_2$O with Cp$_2$ZrCl$_2$ (642 mg, 2.2 mmol), and 5 mL of benzene at 50°C for 1 h were added Me$_3$SiI (15 µL, 0.1 mmol) and 11-(benzyloxy)-1-undecene (521 mg, 2 mmol). The resulting mixture was heated for 3 h at 50°C. Analysis by ^{1}H-NMR spectroscopy indicated that 11-(benzyloxy)-1-undecylzirconocene chloride (δ = 5.81 for Cp) had been formed in 75% yield along with 6% yield of Cp$_2$ZrCl$_2$. After iodination and workup as above, column chromatography (5% EtOAc in hexane) provided 569 mg (76%) of 11-(benzyloxy)-1-iodoundecane.

Hydrozirconation of 9-Decenyl Benzoate with iBuZrCp$_2$Cl in the Presence of Cl$_2$Pd(PPh$_3$)$_2$: To iBuZrCp$_2$Cl generated in situ as described above from 2.2 mmol each of tBuMgCl and Cp$_2$ZrCl$_2$ were added Cl$_2$Pd(PPh$_3$)$_2$ (70 mg, 0.1 mmol) and 9-decenyl benzoate (520 mg, 2 mmol). The resulting mixture was heated for 3 h at 50°C. Analysis by ^{1}H-NMR spectroscopy indicated that 10-(benzoyloxy)-1-decylzirconocene chloride (δ = 5.81 for Cp) had been formed in 71% along with 5% of Cp$_2$ZrCl$_2$. After protonation with 3 N HCl and extractive workup, column chromatography (5% EtOAc in hexane) provided 384 mg (74%) of decyl benzoate along with a minor amount (ca. 5%) of decanol.

Acknowledgments

This research was supported by the US National Science Foundation (CHE 9704994) and Purdue University. H. M. is a Postdoctoral Fellow on funds provided by Japan Society for Promotion of Science for Research Abroad (1997−1999).

---

[1] [1a] D. W. Hart, J. Schwartz, *J. Am. Chem. Soc.* **1974**, *96*, 8115. – [1b] J. A. Labinger in *Comprehensive Organic Synthesis,* Vol. 8, B. M. Trost, I. Fleming, Eds., Pergamon Press, Oxford, **1991**, 667.

[2] E. Negishi, J. A. Miller, T. Yoshida, *Tetrahedron Lett.* **1984**, *25*, 3407.

[3] B. H. Lipshutz, R. Keil, E. L. Ellsworth, *Tetrahedron Lett.* **1990**, *31*, 7257.

[4] S. L. Buchwald, S. J. La Maire, R. B. Nielsen, B. T. Watson, S. M. King, *Tetrahedron Lett.* **1987**, *28*, 3895.

[5] D. R. Swanson, T. Nguyen, Y. Noda, E. Negishi, *J. Org. Chem.* **1991**, *56*, 2590.

[6] E. Negishi, D. Y. Kondakov, D. Choueiry, K. Kasai, T. Takahashi, *J. Am. Chem. Soc.* **1996**, *118*, 9577.

[7] E. Negishi, T. Yoshida, *Tetrahedron Lett.* **1980**, 1501.

[8] For a review discussing activation of Lewis acids by Lewis acids, see E. Negishi, *Chem. Eur. J.* **1999**, *5*, 411.

[9] D. B. Carr, J. Schwartz, *J. Am. Chem. Soc.*, **1979**, *101*, 3521.

[10] C. J. Rousset, E. Negishi, N. Suzuki, T. Takahashi, *Tetrahedron Lett.*, **1992**, *33*, 1965.

Received February 1, 1999
[99042]