

Hydrogen Transfer Hydrozirconation of Alkenes with *i*BuZrCp₂Cl Catalyzed by Lewis-Acidic Metal Compounds Containing Al, Zn, Si, Ag, and Pd

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The hydrozirconation reaction of monosubstituted alkenes with *i*BuZrCp₂Cl can be significantly accelerated by catalytic amounts of various Lewis acidic metal compounds, most

notably AlCl₃, Me₃SiI, and Pd complexes, such as Li₂PdCl₄ and Cl₂Pd(PPh₃)₂.

Hydrozirconation is commonly carried out with pre-formed HZrCp₂Cl.^[1] Although commercially available, its preparation requiring sluggish filtration under inert atmosphere is somewhat cumbersome. Various procedures for in situ generation of HZrCp₂Cl using metal hydrides, such as LiAlH₄, NaAlH₂(OCH₂CH₂OCH₃)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*BuZrCp₂Cl^{[2][5]} has also provided a convenient and potentially more economical alternative. Indeed, the reaction of both terminal and internal alkynes with *i*BuZrCp₂Cl^[5] is a clean and high-yielding process, albeit slower than hydrozirconation with HZrCp₂Cl. 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*Bu₃Al and a catalytic amount of Cl₂ZrCp₂,^[6,7] which was thought to involve hydrogen transfer hydrozirconation, suggested an intriguing possibility of catalyzing hydrozirconation with *i*BuZrCp₂Cl by Al and other Lewis acidic metal compounds.^[8]

We now report that the hydrozirconation reaction of monosubstituted alkenes with *i*BuZrCp₂Cl can be significantly accelerated by catalytic amounts of a variety of Lewis acidic metal compounds, most notably AlCl₃ (2 mol%), Me₃SiI (5 mol%), and Pd complexes, such as Li₂PdCl₄ and Cl₂Pd(PPh₃)₂, as indicated by the results summarized in Table 1. Under otherwise the same conditions, the uncatalyzed reaction of 1-decene with *i*BuZrCp₂Cl produced even after 15 h the desired hydrozirconation product only in 20% yield with about 70% of 1-decene remaining

(Entry 1). In the AlCl₃-catalyzed reaction, it is essential to evaporate ether used to generate *i*BuZrCp₂Cl before addition of AlCl₃, and the amount of AlCl₃ must be kept at a minimum, as alkylzirconocene chlorides and AlCl₃ are known to undergo transmetalation to produce Cp₂ZrCl₂ 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*BuZrCp₂Cl. 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 AlCl₃, several other metal compounds including ZnCl₂ (Entries 6 and 7), AgBF₄ (Entry 11), Me₃SiI (Entry 15), Li₂PdCl₄, and Cl₂Pd(PPh₃)₂ (Entries 18 and 19) exhibit significant and potentially useful catalytic activities. Unlike AlCl₃, 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, Me₃SiI (Entry 15) is decidedly more effective than Me₃SiCl (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 CH₂Cl₂ and ethereal solvents, e.g., THF, in most cases. Additionally, various other compounds including LiI, EtAlCl₂, Et₂AlCl, SnCl₄, Bu₃SnBr, Bu₃SnI, and SbCl₅ were tested, but none yielded satisfactory results. With EtAlCl₂ 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 Cl₂ZrCp₂^[10] took place, although its mechanistic details are unclear.

The synthetic utility of two procedures with AlCl₃ (2 mol%) and Me₃SiI (5 mol%) has been examined with several representative functionally substituted terminal alkenes. Either catalyst was satisfactory in converting 11-

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Table 1. Hydrogen transfer hydrozirconation of 1-decene with *i*BuZrCp₂Cl catalyzed by metal compounds^[a]

$\text{Cp}_2\text{ZrCl}_2 \xrightarrow{t\text{-BuMgCl}} i\text{-BuZrCp}_2\text{Cl} \xrightarrow[\text{catalyst}]{n\text{-C}_8\text{H}_{17}\text{CH}=\text{CH}_2} n\text{-C}_{10}\text{H}_{21}\text{ZrCp}_2\text{Cl} \xrightarrow{3\text{N HCl}} n\text{-C}_{10}\text{H}_{22} \text{ (2)}$ $n\text{-C}_{10}\text{H}_{21}\text{ZrCp}_2\text{Cl} \xrightarrow{\text{I}_2} n\text{-C}_{10}\text{H}_{21}\text{I} \text{ (3)}$									
Entry	Catalyst (%)	Solvent [b]	T [°C]	t [h]	Product yield [%]			1-Decene [%]	Cp ₂ ZrCl ₂ [%]
					1 [c]	2 [d]	3 [e]		
1	None	PhH-Et ₂ O	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 ₂ Cl 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 ₂ O	50	4	76	86	74	0	13
7	ZnCl ₂	(10) THF-Et ₂ O	50	4	79	81	71	0	8
8	ZnBr ₂	(10) THF-Et ₂ O	50	10	44	49	[f]	40	[f]
9	ZnI ₂	(10) THF-Et ₂ O	50	10	13	14	[f]	75	[f]
10	AgBF ₄	(10) PhH-Et ₂ O	50	8	58	72	60	20	3
11	AgBF ₄	(20) PhH-Et ₂ O	50	8	74	92	85	0	16
12	HgCl ₂	(5) PhH-Et ₂ O	50	10	62	68	61	15	12
13	HgI ₂	(5) PhH-Et ₂ O	50	10	39	53	[f]	20	[f]
14	Me ₃ SiCl	(5) PhH-Et ₂ O	50	8	61	64	52	20	5
15	Me ₃ SiI	(5) PhH-Et ₂ O	50	3	82	85	82	0	6
16	Me ₃ SiI	(5) THF-Et ₂ O	50	3	31	33	[f]	50	[f]
17	Bu ₃ SnCl	(5) PhH-Et ₂ O	50	8	38	34	[f]	47	4
18	Li ₂ PdCl ₄	(2.5) PhH-THF-Et ₂ O	50	3	71	88	80	0	10
19	Cl ₂ Pd(PPh ₃) ₂	(2.5) PhH-Et ₂ O	50	3	76	74	72	0	5

^[a] The reaction was carried out with *i*BuZrCp₂Cl generated in situ 90–95% yield by treatment of 1.1 equiv. each (relative to an alkene) of Cp₂ZrCl₂ with *t*BuMgCl at 50°C for 1 h. – ^[b] In cases where Et₂O is not shown, it was evaporated. – ^[c] By ¹H-NMR spectroscopy. – ^[d] By GLC. – ^[e] Yield of isolated product. – ^[f] Not determined.

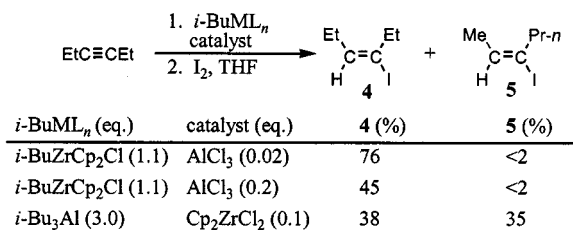
chloro-1-undecene into 1-iodo-11-chlorodecane in 70–80% yields. However, 11-benzyloxy-1-undecene, 11-(*tert*-butyldi-phenylsilyloxy)-1-undecene, and allyl phenyl ether all decomposed in the presence of AlCl₃. On the other hand, their reaction in the presence of 5 mol% of Me₃SiI gave, after iodinolysis, 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% Me₃SiI, whereas its yield observed with 2 mol% of AlCl₃ was 55%. With Cl₂Pd(PPh₃)₂ as a catalyst, even ester-containing alkenes can be chemoselectively hydrozirconated. Thus, for example, 9-decenyl benzoate reacted with *i*BuZrCp₂Cl and 5 mol% of Cl₂Pd(PPh₃)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 HZrCp₂Cl 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 AlCl₃ may be interpreted within the context of activation of *i*BuZrCp₂Cl by AlCl₃ through Zr-Cl-Al interaction to generate either *i*BuZr⁺Cp₂AlCl₄[−] or *i*BuZrCp₂^{δ+}–Cl–^{δ−}AlCl₃, which may be further converted to the corresponding zirconium hydrides as transient reactive species.^[8] Interestingly, however, the reaction of 3-hexyne with *i*BuZrCp₂Cl in the presence of 2 mol% of AlCl₃ 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 *i*Bu₃Al (3 equiv) in the presence of 10 mol% of Cp₂ZrCl₂ 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*BuZrCp₂Cl in the Presence of 2 mol% of AlCl₃: Ether was removed from an ethereal solution of *i*BuMgCl (2 M, 1.1 mL, 2.2 mmol) at room temperature under re-



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 Cp₂ZrCl₂ (642 mg, 2.2 mmol), and the reaction mixture was heated for 1 h at 50°C. The formation of *i*BuZrCp₂Cl in 94% yield was observed by ¹H-NMR spectroscopy. To this were added AlCl₃ (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 ¹H NMR spectroscopy indicated the formation of *n*C₁₀H₂₁ZrCp₂Cl (δ = 5.80 for Cp) in 87% yield along with 5% of Cp₂ZrCl₂ (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 *i*BuZrCp₂Cl in the Presence of Me₃SiI: To *i*BuZrCp₂Cl, generated in situ by treatment of *t*BuMgCl (2 M, 1.1 mL, 2.2 mmol) in Et₂O with Cp₂ZrCl₂ (642 mg, 2.2 mmol), and 5 mL of benzene at 50°C for 1 h were added Me₃SiI (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 ¹H-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 Cp₂ZrCl₂. 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 *i*BuZrCp₂Cl in the Presence of Cl₂Pd(PPh₃)₂: To *i*BuZrCp₂Cl generated in situ as described above from 2.2 mmol each of *t*BuMgCl and Cp₂ZrCl₂ were added Cl₂Pd(PPh₃)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 ¹H-NMR spectroscopy indicated that 10-(benzyloxy)-1-decylzirconocene chloride (δ = 5.81 for Cp) had been formed in 71% along with 5% of Cp₂ZrCl₂. 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.

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