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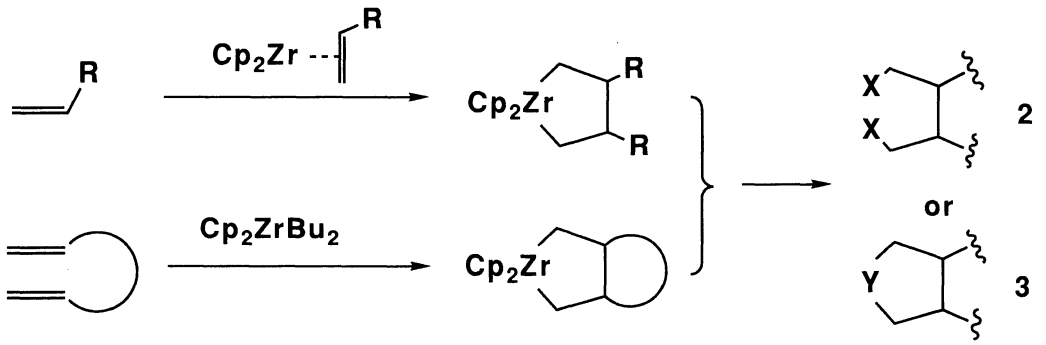
Monohalogenation of Zirconacyclopentane Complexes via Alkylalkoxyzirconocene

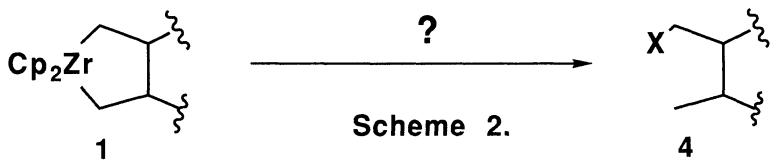
Tamotsu TAKAHASHI,* Koichiro AOYAGI, Ryuichiro HARA, and Noriyuki SUZUKI
Coordination Chemistry Laboratories, Institute for Molecular Science,
Nishigo-naka 38, Myodaiji, Okazaki, Aichi 444

Treatment of trans-3,4-diethylzirconacyclopentane complex, which was a selective butene-butene coupling product on zirconium, with methanol followed by bromine gave selectively monobromination product, 2-ethyl-3-methyl-1-bromopentane, in 89% yield with high stereoselectivity. Similarly, non-conjugated diene cyclization products on zirconium were also selectively converted into monohalogenated compounds. These selective monohalogenations proceeded via alkylalkoxyzirconocene complexes.

Zirconacyclopentane complexes **1** have been selectively prepared by alkene-alkene coupling or non-conjugated diene cyclization coupling on zirconium.[1-11] From the point of view of organic synthesis, functionalization of the coupling products on zirconium is also important and attractive. Although many reactions of zirconacyclopentanes with reagents such as I_2, Br_2, H^+, D^+, O_2, $SeCl_2$, Ph_2SnCl_2, S_2Cl_2,and CO have been investigated, most of the products were di-functionalized compounds **2** or cyclized compounds **3** as shown in Scheme 1.[1,2,4-11] Selective mono-functionalization of zirconacyclopentanes is very rare (Scheme 2). To the best of our knowledge, only one precedent is known for selective mono-functionalization reaction. It has been reported that transmetalation reaction of zirconacyclopentane compounds with ethylmagnesium bromide selectively converted the coupled products on zirconium into mono-Grignard compounds.[7] We would like to



Scheme 1.

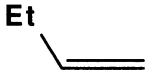
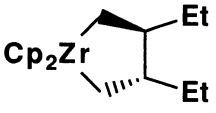
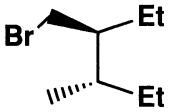
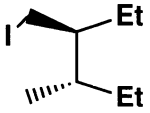
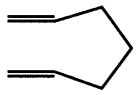
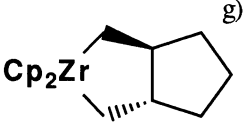
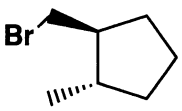
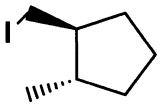
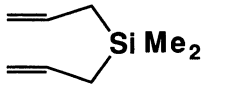
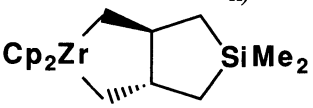
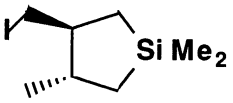
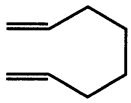
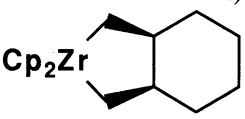
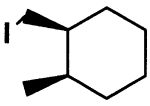


Scheme 2.

describe here selective monohalogenation of zirconacyclopentane compounds via alkylalkoxyzirconocene complexes.

Coupling reactions of alkenes or bicyclization of non-conjugated dienes were carried out as in the literatures.[6,9,10] Typical procedure is as follows. To a mixture of 1 mmol of Cp_2ZrCl_2 and 5 cm^3 of THF was added 2 equiv. of n-butyllithium (2 mmol) at -78 °C and the mixture was stirred for 1h at -78 °C. To this was added 1 mmol of 1,6-heptadiene. After stirring at room temperature for 1 h, bicyclization compound **6** was cleanly formed in 92% yield. The mixture was treated with 1 mmol of MeOH, and stirred for 1 h at room

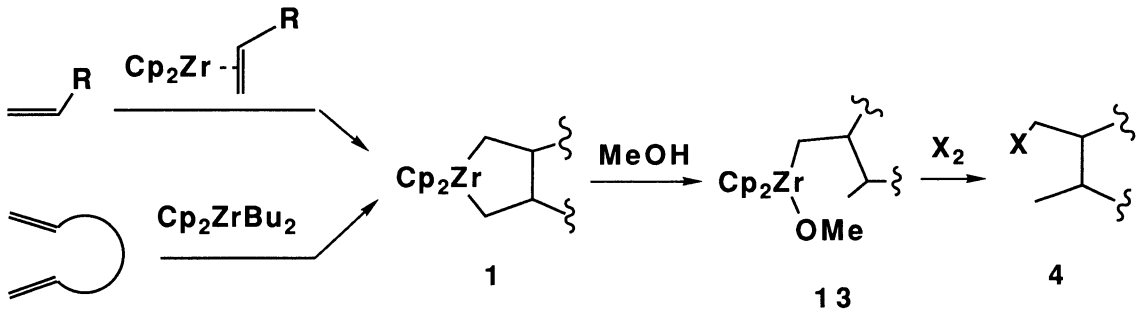
Table 1. Monohalogenation reactions of zirconacyclopentane compounds

Alkene	Zirconacyclopentane[a]	X_2[b]	Product[c]	Overall yield/%[d]	Stereo-selectivity/%[e]
	f)  **5**	Br_2	 **9a**	89	97
		I_2	 **9b**	73	94
	g)  **6**	Br_2	 **10a**	88	90
		I_2	 **10b**	64	94
	h)  **7**	I_2	 **11**	61	96
	i)  **8**	I_2	 **12**	77	83

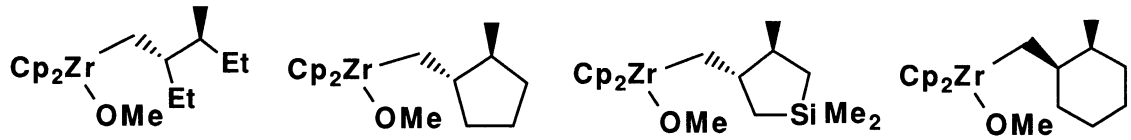
a)Zirconacyclopentanes were prepared from Cp_2ZrBu_2 and alkenes by the method in the literatures. b)X_2 was added to the mixture at 0 °C. c)Major stereoisomer is described. d)Based on zirconium metal. Yields were determined by GC. e)Selectivity for major stereoisomer. f)See Ref.6. g)See Ref.9. h)See Ref.10. i)See Ref.9.

temperature. Treatment of this reaction mixture with bromine at 0°C gave monobromination product **10a** in 88% overall yield. Formation of dibromination product was not observed.

Monohalogenation results obtained here for coupling products of 1-butene, 1,6-heptadiene, 1,7-octadiene, or dimethyldiallylsilane **5 - 8** are summarized in Table 1.



As shown in Table, monohalogenated products **9 - 12** were selectively obtained in good yields with high stereoselectivities of major isomers. Stereoselectivities obtained here were very similar to those for cyclization reactions as described in the corresponding literatures.[6,9,10] The key reaction of this monohalogenation of zirconacyclopentane compound is selective monoprotonation which gave alkylalkoxyzirconocenes **14**, **15**, **16**,and **17** in 80 - 90% overall yields as intermediate complexes. Formation of these complexes were observed by NMR spectroscopy. ^{1}H and ^{13}C NMR spectra of these complexes were consistent with these formulas.[12] It is noteworthy that alkyl moieties of alkylalkoxyzirconocene complexes **14 - 17** were inert for further protonation with MeOH. This inertness is very attractive for selective protonation reactions of coupling products on zirconium.



14 **15** **16** **17**

Selective monoprotonation of dialkylzirconocene such as Cp_2ZrMe_2 has been already reported to give $Cp_2ZrMe(OMe)$.[13] During the course of our study, we investigated this monoprotonation reaction with alcohols for other dialkylzirconocene $Cp_2Zr(CH_2CHRR')_2$ where alkyl group has a β-hydrogen such as dibutylzirconocene which were not stable at room temperature. Alkylalkoxyzirconocene such as $Cp_2ZrBu(OMe)$ **18**[14] and $Cp_2ZrBu(OiPr)$ **19**[15] were also selectively obtained in >99% yields within 1h even when treated with 2 equiv. of alcohols. This preparative method could be also used for preparing alkylalkoxyhafnocene $Cp_2HfR(OR')$ complexes which have not been reported yet. Hafnium complex, $Cp_2HfMe(OMe)$ (91%) **20** or $Cp_2HfBu(OMe)$ (>99%) **21** was similarly prepared.[16]

Further investigations are now in progress in this area.

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12) **14**: ^{1}H NMR (C_6D_6, TMS) δ 0.59 (dd, J = 4, 13 Hz, 1H), 0.74 - 1.18 (m, 11H), 1.22 - 1.64 (m, 4H), 1.77 - 1.84 (m, 1H), 3.64 (s, 3H), 5.74 (s, 5H), 5.77 (s, 5H). ^{13}C NMR (C_6D_6, TMS) δ 13.06, 13.17, 14.63, 26.90, 27.60, 38.27, 39.91, 48.39, 61.56, 110.42, 110.64. **15**: ^{1}H NMR (C_6D_6, TMS) δ 0.81-2.02 (m, 13H), 3.65 (s, 3H), 5.73 (s, 5H), 5.77 (s, 5H). ^{13}C NMR (C_6D_6, TMS) δ 19.28, 23.43, 34.99, 36.28, 45.26, 47.12, 53.28, 61.67, 110.26, 110.64. **16**: ^{1}H NMR (C_6D_6, TMS) δ 0.22 (s, 3H), 0.23 (s, 3H), 0.29 (dd, J = 15, 10 Hz, 1H), 0.46 (dd, J = 15, 10 Hz, 1H), 0.97 - 1.17 (m, 4H), 1.30 (d, J = 7 Hz, 3H), 1.36 - 1.55 (m, 1H), 1.73 - 1.87 (m, 1H), 3.66 (s, 3H), 5.74, 5.80 (s, 10H). ^{13}C NMR (C_6D_6, TMS) δ -0.47, -0.40, 23.27, 23.41, 24.40, 45.79, 48.37, 52.13, 61.62, 110.33, 110.64. **17**: ^{1}H NMR (C_6D_6, TMS) δ 0.67 (dd, J = 5, 13 Hz, 1H), 0.81 - 0.98 (m, 2H), 1.03 (d, J = 7 Hz, 3H), 1.07 - 1.86 (m, 8H), 2.05 - 2.09 (m, 1H), 3.62 (s, 3H), 5.73 (s, 5H), 5.74 (s, 5H). ^{13}C NMR (C_6D_6, TMS) δ 15.31, 23.23, 25.61, 32.24, 32.88, 36.48, 41.90, 44.17, 61.53, 110.35, 110.46.
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14) **18**: ^{1}H NMR (C_6D_6, TMS) δ 0.95 - 1.01 (m, 2H), 1.09 (t, J = 7 Hz, 3H), 1.49 (tq, J = 7, 7 Hz, 2H), 1.61 - 1.69 (m, 2H), 3.65 (s, 3H), 5.76 (s, 10H). ^{13}C NMR (C_6D_6, TMS) δ 14.27, 29.87, 36.01, 40.34, 61.40, 110.30.
15) **19**: ^{1}H NMR (C_6D_6, TMS) δ 0.90 - 1.05 (m, 8H), 1.12 (t, J = 7 Hz, 3H), 1.46-1.59 (m, 2H), 1.64 - 1.72 (m, 2H), 3.95-4.04 (m, 1H), 5.77 (s, 10H). ^{13}C NMR (C_6D_6, TMS) δ 14.32, 26.54, 30.13, 36.60, 39.71, 73.94, 110.15.
16) **20**: ^{1}H NMR (C_6D_6-THF, TMS) δ -0.08 (s, 3H), 3.73 (s, 3H), 5.93 (s, 10H). ^{13}C NMR (C_6D_6-THF, TMS) δ 20.47, 60.63, 109.91.; **21**: ^{1}H NMR (C_6D_6, TMS) δ 0.78-0.85 (m, 2H), 1.13 (t, J = 7 Hz , 3H), 1.49-1.64 (m, 2H), 1.66-1.73 (m, 2H), 3.69 (s, 3H), 5.72 (s, 10H). ^{13}C NMR (C_6D_6, TMS) δ 14.38, 30.91, 35.90, 41.90, 60.81, 109.65.

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