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Reaction of 1-Zirconacyclopent-3-yne with "Zirconocene": Synthesis and Structure of Bimetallic 1,2,3-Butatriene Complexes[1]

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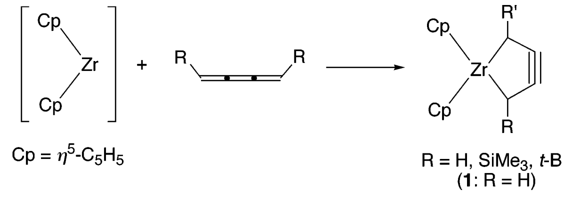
A 1-zirconacyclopent-3-yne complex (**1**) reacted with "zirconocene" to give a symmetrical, bimetallic 1,2,3-butatriene complex (**6**) in which butatriene coordinates to two equivalent zirconocene units. Treatment of **6** with trimethylphosphine gave the phosphine-stabilized zirconocene−**1** complex (**2**), which was transformed into **6** by addition of triethylborane.

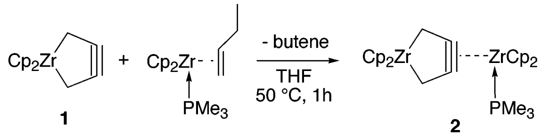
Introduction

Recently we reported that 1,2,3-butatrienes reacted with a low-valent zirconocene species to afford cyclic organozirconium compounds (eq 1).[2,3] These complexes can be regarded as a five-membered metallacyclic alkyne, 1-zirconacyclopent-3-yne, which is the smallest isolable cyclic alkyne. The unique structure of these compounds led us to an investigation of their reactivity.



(1)

In our previous paper, we demonstrated that the 1-zirconacyclopent-3-yne **1** (R = H) reacted with an equimolar amount of $Cp_2Zr(1\text{-butene})(PMe_3)$ to give a bimetallic complex **2** (eq 2).[3] In this complex, **1** coordinates to the other zirconocene unit by its triple bond to form an "alkyne complex" stabilized by a phosphine ligand.



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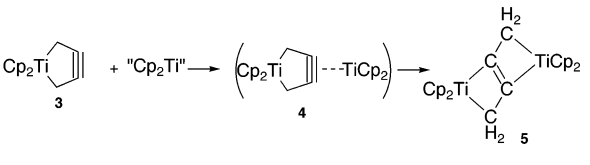
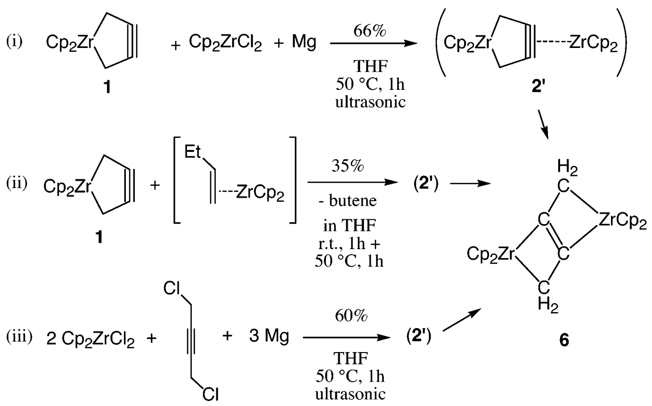


(3)

Scheme 1. Formation of Bimetallic Complex 6



In the course our study, Rosenthal and co-workers have reported very recently 1-titanacyclopentyne (**3**), the titanium analogue of **1**, and a related bimetallic complex **5** that was derived from **3** and titanocene, although the molecular structure of **3** was not shown (eq 3).[4] This prompted us to report here our results of the synthesis, structure, and reactivity of a symmetric, bimetallic zirconocene-1,2,3-butatriene complex.[1]

Results and Discussion

We studied the reaction of **1** with a low-valent zirconocene in the *absence* of a phosphine ligand (Scheme 1). Complex **1** and Cp_2ZrCl_2 were dissolved in THF in which dry magnesium powder was suspended [method (i)]. The mixture was sonicated at 50 °C for 1 h to form the bimetallic complex **6** in 66% yield. ^1H NMR observation of the solution indicated two singlets at 5.45 and 3.85 ppm assignable to Cp and CH_2, respectively, indicating the symmetrical structure of the product. In the ^{13}C NMR spectrum, methylene and quaternary

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[1] A part of this work has been orally presented. 84th Annual Meeting of the Chemical Society of Japan (1B7-09), March 2004 (Nishinomiya).

[2] Suzuki, N.; Nishiura, M.; Wakatsuki, Y. *Science* **2002**, *295*, 660−663.

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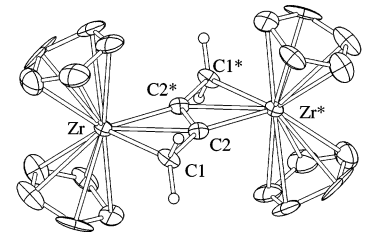
[4] (a) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Parameswaran, P.; Jemmis, E. D. *Chem. Commun.* **2004**, 2074−0275. (b) Rosenthal, U. *Angew. Chem., Int. Ed.* **2004**, *43*, 3882−3887. We recently reported the structural characterization of **3**, see: (c) Suzuki, N.; Watanabe, T.; Hirose, T.; Chihara, T. *Chem. Lett.* **2004**, *33*, 1488−1489.

10.1021/om049288h CCC: $30.25



Selected bond lengths (Å) and angles (deg)

Zr-C1	2.230(7)
Zr-C2	2.399(6)
Zr-C2*	2.196(6)
C1-C2	1.504(8)
C2-C2*	1.38(1)
Zr-C1-C2	77.3(3)
C1-Zr-C2*	72.3(2)
C1-C2-C2*	129.6(7)

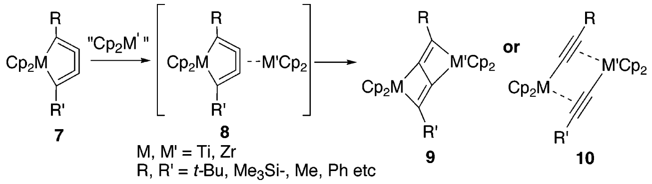
Figure 1. Molecular structure of **6** drawn with 50% probability. Hydrogen atoms are partly omitted for clarity.

carbons were observed at 76.35 and 167.57 ppm, respectively. Although the reaction of **1** with Cp_2ZrBu_2 (Negishi reagent) in the absence of phosphine ligands also gave **6**, the yield was lower (35%) [method (ii)]. Instead, **6** could be prepared from 1,4-dichloro-2-butyne and 2 equiv of Cp_2ZrCl_2 in the presence of magnesium in 60% yield [method (iii)]. The molecular structure of **6** was determined by X-ray diffraction analysis (Figure 1).

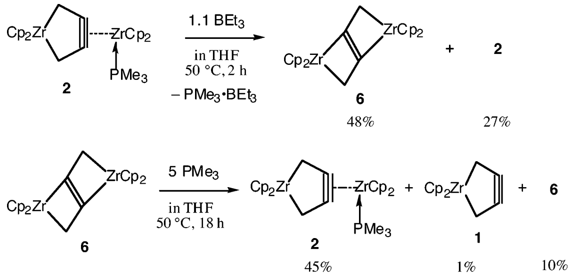
The molecule has a symmetrical center at the middle of the C2−C2* bond, and the butatriene molecule coordinates to two zircononium metals that are structurally equivalent. Four carbons in butatriene and two zirconium atoms are nearly coplanar. The bond lengths C1−C2 and C2−C2* are 1.504(8) and 1.38(1) Å, showing that the butatriene unit has single−double−single bonds. The molecular structure of **6** is nearly identical to the titanium analogue **5**. However, the bond lengths C1−C2 and C2−C2* are significantly longer in **6** than in **5** (1.443(4) and 1.325(5) Å, respectively), and the C1−C2−C2* angle is smaller in the zirconium complex (**6**: 129.6(7)°, **5**: 135.1(3)°). These suggest that butatriene coordinates to zirconium metals more closely than to titanium by π-back-donation from the metals. The structures of **6** and **5** are totally different from the known butatriene-diiron complex in which there is an Fe−Fe bond and the metals are located distant from the butatriene plane.[5]

Rosenthal and co-workers reported the synthesis of metallacyclocumulene complexes **7** derived from a low-valent group 4 metallocene and 1,3-diynes and their transformation into bimetallic η^4-butadiyne complexes **9** or σ,π-alkynyl-bridged complexes **10** via cleavage of the central single bond of 1,3-diynes (Scheme 2).[6,7] It should be emphasized that both Ti and Zr complexes **5** and **6** could be synthesized, while the zirconium derivative of **9** has not been reported.[7h] The structures of **6** and **5** are similar to that of **9**, in which the coordinated 1,3-diyne has double−single−double bonds. They proposed that the coordinated complex **8** as an intermediate in the reaction, and a few heterobimetallic analogues such as Zr−V, Ti−Ni, and Zr−Ni were reported.[8] However, to the best of our knowledge, direct interconversion between **8** and **9** (or **10**) has not been experimentally detected.

Scheme 2. Metallacyclocumulene and Bimetallic 1,3-Diyne Complexes



Scheme 3. Interconversion of 2 and 6



Our results and Rosenthal's report indicate that metallacyclopentyne complexes exhibit analogous reactivity. It is likely that **6** is formed from **1** and "Cp_2Zr" via **2′** (**2** without PMe_3) as an intermediate (Scheme 1). Low yield in the reaction from Cp_2Zr(1-butene) [method (ii)] can be rationalized by slow exchange between 1-butene and **1**. Rosenthal also suggested an intermediate **4**, the titanium analogue of **2′**, in the formation of **5** (eq 3), although no experimental data were shown. This led us to study the possibility of a transformation between **2** and **6** (Scheme 3).

Addition of 1.1 equiv of triethylborane to **2** brought about the formation of **6** in 48% yield at 50 °C after 2 h. Addition of excess (3-fold) triethylborane did not increase the yield, although the conversion of **2** was 98% after 1 h at 50 °C. Complex **6**, on the other hand, was converted into **2** in moderate yield (45%) in the presence of excess PMe_3. $Cp_2Zr(PMe_3)_2$,[9] a possible byproduct, was not observed. Thus the interconversion of **2** and **6** was experimentally detected. In this study we have succeeded in X-ray diffraction analysis of **1** (Figure 2). It should be noted that all these complexes—**1**, **2** and **6**—were structurally characterized. The structural parameters are compared in Table 1.

The following points are noteworthy. Both the C1−C2 and C2−C3 distances are longer in the order **6** > **2** > **1**. Accordingly, the C1−C2−C3 angles are smaller in the order **6** < **2** < **1**, and Zr−C1 lengths are shorter in this order. These results clearly show that the characters of C2 and C3(C2*) change from sp to sp^2 carbons with the transformation from **1** to **6**.

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[5] (a) Nakamura, A. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1868−1873. (b) Bright D.; Mills, O. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2465−2469.

[6] (a) Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1992**, *439*, C36−C41. (b) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1605−1607. (c) Rosenthal, U.; Ohff, A.; Tillack, A.; Baumann, W. *J. Organomet. Chem.* **1995**, *468*, C4−C8.

[7] The bimetallic titanium and zirconium complexes **10** prepared by different methods were also reported. (a) Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *17*, 87−93. (b) Sekutowski, D. G.; Stucky, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 1376−1382. (c) Wood, G. L.; Knolber, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1989**, *28*, 382−384. (d) Varga, V.; Mach, K.; Hiller, J.; Thewalt, U.; Sedmera, P.; Polásek, M. *Organometallics* **1995**, *14*, 1410−1416. (e) Erker, G.; Frömberg, W.; Mynott, R.; Gabor, B.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 463−465. (f) Metzler, N.; Nöth, H. *J. Organomet. Chem.* **1993**, *454*, C5−C7. (g) Kumar, P. N. V. P.; Jemmis, E. D. *J. Am. Chem. Soc.* **1988**, *110*, 125−131. (h) Jemmis, E. D.; Giju, K. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 606−608.

[8] (a) Danjoy, C.; Zhao, J.; Donnadieu, B.; Legros, J.-P.; Valade, L.; Choukroun, R.; Zwick, A.; Cassoux, P. *Chem. Eur. J.* **1998**, *4*, 1100−1105. (b) Pulst, S.; Arndt, P.; Heller, B.; Baumann, W.; Kempe, R.; Rosenthal, U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1112−1115.

[9] Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Honold, B.; Thewalt U. *J. Organomet. Chem.* **1987**, *320*, 37−46.

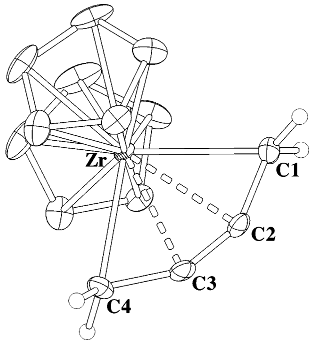

Figure 2. Molecular structure of **1** drawn with 50% probability. Hydrogen atoms are partly omitted for clarity.

Table 1. Bond Lengths (Å) and Angles (deg) of 1-Zirconacyclopent-3-yne 1 and the Bimetallic Complexes 2 and 6

complex	Zr−C1 (Zr−C4)	Zr−C2 (Zr−C3)	C1−C2 (C3−C4)	C2−C3	C1−C2−C3 (C2−C3−C4)
1	2.415(3)	2.314(3)	1.406(4)	1.237(5)	151.5(3)
	2.428(3)	2.320(3)	1.408(5)		151.3(3)
2[a]	2.279(4)	2.495(3)	1.490(4)	1.336(4)	136.7(3)
	2.270(3)	2.461(3)	1.480(4)		140.6(3)
6	2.230(7)	2.399(6)	1.504(8)	1.38(1)[b]	129.6(7)[c]
		2.196(6)[d]			

[a] Ref 3. [b] C2−C2*. [c] C1−C2−C2*. [d] Zr−C2*.

Although the mechanism for conversion between **2** and **6** is still unclear, a few possibilities can be raised. One is an associative route where a Zr metal moves along the butatriene unit and the terminal carbon migrates from Zr1 to Zr2. Another is a dissociative route; that is, the bimetallic complex **2** dissociates into butatriene and two low-valent zirconocenes and then reconstructs into the bimetallic structure of **6**. The latter would give rise to disproportionation if two zirconocenes are different.

To shed light on the mechanism, a reaction of **1** and (η^5-$C_5H_4Me)_2ZrCl_2$/Mg was studied in a manner similar to the preparation of **6**. It gave predominantly the unsymmetric bimetallic complex **11** in good yield (62%), accompanied by the two symmetric complexes **6** and **12** as minor products. Two signals for unequivalent CH_2 groups that coupled with each other were observed in the ^1H spectrum at 3.69 and 3.76 ppm, demonstrating that the structure of **11** is unsymmetric (Figure 3). The ratio of **11**, **6**, and **12** determined by NMR was 7:2:1, which does not accord with statistical distribution. This result suggests the associative mechanism, although its detail must await further investigation.

In 1,3-diyne-derived bimetallic complexes, Rosenthal reported that the unsymmetric complex **9** (R = $SiMe_3$, R′ = *t*-Bu) showed only one Cp signal in the ^1H NMR at ambient temperature, while it separated at low temperature.[10] This proposed fast exchange of the two metallocene units. It should be noted that, in complex **11**, two signals of methylene groups remained unchanged at −60 to 100 °C, indicating that, for this complex, the exchange of two zirconocenes either does not occur or occurs very slowly at this range of temperature.

In summary, we investigated the reaction of a 1-zirconacyclopent-3-yne complex (**1**) with a low-valent zirconocene in the absence of phosphine ligands. It gave a symmetrical bimetallic complex (**6**) in which the butatriene coordinates to the two equivalent metals. Interconversion of the bimetallic complex **6** and a zirconacyclopentyne-coordinated zirconocene (**2**) was experimentally detected. The molecular structure of **6** indicated sp^2-character of two quaternary carbons in the butatriene moiety, while they showed sp-character in the 1-zirconacyclopent-3-yne **1**. The NMR examination of an unsymmetric bimetallic complex suggested that its framework was more rigid compared to bimetallic 1,3-butadiyne complexes.

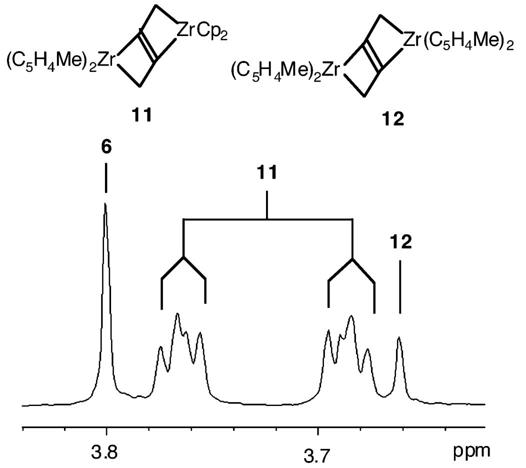

Figure 3. Methylene protons in the ^1H NMR spectrum for the bimetallic complexes **6**, **11**, and **12**.

Experimental Section

General Procedures. All manipulation was carried out under an argon atmosphere. Anhydrous THF and hexane were purchased from Kanto Kagaku and degassed prior to use. Dichlorobis(cyclopentadienyl)zirconium and triethylborane (1.0 M hexane solution) were purchased from Kanto Kagaku. Dichlorobis(methylcyclopentadienyl)zirconium was purchased from Acros Organics and used as received. 1,4-Dichloro-2-butyne was purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. Complexes **1** and **2** were prepared as previously reported.[2,3] IR spectra were recorded on TravelIR total reflection infrared spectroscopy equipment (SensIR Technologies). ^1H and ^{13}C NMR were recorded on JEOL AL-300 and AL-400 spectrometers.

Preparation of the Bimetallic Complex 6. Method (i). Magnesium powder was thoroughly heated in vacuo prior to use. To the dry magnesium powder (4.8 mg, 0.2 mmol) in THF (1 mL) were added dichlorobis(cyclopentadienyl)zirconium (29.2 mg, 0.1 mmol) and **1** (27.4 mg, 0.1 mmol), and the mixture was sonicated at 50 °C for 1 h. The formation of **6** in 66% yield was observed by ^1H NMR spectroscopy.

Method (ii). To a solution of Cp_2ZrCl_2 (87.6 mg, 0.3 mmol) in THF (2 mL) was added *n*-butyllithium (1.58 M in hexane, 0.6 mmol) dropwise at −78 °C, and the mixture was stirred for 1 h at −78 °C. Then **1** (77 mg, 0.28 mmol) was added and the mixture was warmed to room temperature. After stirring at room temperature for 1 h, the mixture was stirred at 50 °C for additional 1 h and examined by ^1H NMR spectroscopy. Complex **6** was formed in 35% yield.

Method (iii). To a suspension of dry magnesium powder (72 mg, 3.0 mmol) in THF (5 mL) were added dichlorobis(cyclopentadienyl)zirconium (Cp_2ZrCl_2, 292 mg, 1.0 mmol) and 1,4-dichloro-2-butyne (61.5 mg, 0.5 mmol). The mixture was sonicated in an ultrasonic bath at 50 °C for 1 h. ^1H NMR spectroscopy revealed the formation of **6** in 60% yield at this

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[10] Baumann, W.; Pellny, P.-M.; Rosenthal, U. *Magn. Reson. Chem.* **2000**, *38*, 515−519.

Table 2. Crystallographic Data of 1 and 6

	1	**6**
empirical formula	$C_{14}H_{14}Zr$	$C_{24}H_{24}Zr_2$
fw	273.48	494.89
cryst color, habit	colorless, plate	dark brown, block
cryst dimens	0.50 × 0.15 × 0.05 mm	0.20 × 0.20 × 0.10 mm
radiation	Mo Kα ($\lambda = 0.71073$ Å)	Mo Kα ($\lambda = 0.71073$ Å)
cryst syst	monoclinic	monoclinic
lattice params	$a = 12.1150(4)$ Å	$a = 8.7249(6)$ Å
	$b = 9.2921(3)$ Å	$b = 7.9789(6)$ Å
	$c = 9.9839(2)$ Å	$c = 13.8141(8)$ Å
	$\beta = 91.525(2)°$	$\beta = 91.116(3)°$
	$V = 1123.52(5)$ Å^3	$V = 961.5(1)$ Å^3
space group	*Cc* (#9)	$P2_1/n$ (#14)
Z value	4	2
D_{calc}	1.617 g/cm^3	1.709 g/cm^3
F_{000}	552.00	496.00
μ(Mo Kα)	9.39 cm^{-1}	10.88 cm^{-1}
temperature	113 K	93 K
$2\theta_{max}$	60.1°	50.0°
no. of reflns measd	total: 3688	total: 8284
	unique: 2965 ($R_{int} = 0.017$)	unique: 1812 ($R_{int} = 0.056$)
corrections	Lorentz−polarization	Lorentz−polarization
	absorption	absorption
	(transmn factors: 0.7741−0.9541)	(transmn factors: 0.5124−0.8969)
no. of reflns (all)	2965	1687
no. of variables	153	126
residuals (all data): R; R_w	0.045; 0.068	0.069; 0.135
residuals ($I > 2\sigma(I)$): R_1	0.024	0.056
goodness of fit indicator	0.93	1.58
max. shift/error in final cycle	0.002	0.000
max. peak in final diff map	0.38 e Å^{-3}	0.76 e Å^{-3}
min. peak in final diff map	−1.18 eÅ^{-3}	−1.20 e Å^{-3}

stage. Dioxane (0.3 mL) was added to this dark purple mixture to precipitate magnesium salts. The solution was then filtered, and the solvent was slowly evaporated under argon flow from the filtrate. Complex **6** was obtained as a dark brown solid (yield 33% crude). This solid was practically pure **6**, although it contained a small amount of **1**, magnesium salts, and unidentified products.

6. ^{1}H NMR (C_6D_6/THF): δ 3.85 (s, 4H), 5.45 (s, 20H). ^{13}C NMR (C_6D_6): δ 76.35 (CH_2), 105.80 (Cp), 167.57 (q). IR (neat): 2898, 1437, 1009 (cm^{-1}). Mp: 265−270 °C (dec under Ar). Neither elemental analysis nor high-resolution mass spectrometry gave satisfactory results presumably because the complex was extremely sensitive toward air and moisture. A ^{13}C NMR spectrum is shown in the Supporting Information.

Interconversion of 2 and 6. To a solution of **2** (57 mg, 0.1 mmol) in THF-d_8 (1 mL) was added triethylborane (1.0 M hexane solution, 0.11 mmol) at room temperature. The mixture was stirred at 50 °C for 2 h and observed by ^{1}H NMR spectroscopy. Complex **6** was formed in 48% yield. The conversion of **2** was 73%. The formation of trimethylphosphine−triethylborane complex (55%) was observed, whose methyl groups appeared at 1.15 ppm ($J_{PH} = 9.2$ Hz) as a doublet. Addition of 3-fold BEt_3 did not increase the yield, although the conversion of **2** was 98% after 1 h at 50 °C.

On the other hand, trimethylphosphine (76 mg, 1 mmol) was added to a THF-d_8 (1 mL) solution of **6** (0.12 mmol) at room temperature. After stirring the mixture at 50 °C for 18 h, the formation of **2** (45%) and the unreacted **6** (10%) was observed by ^{1}H NMR. Formation of $Cp_2Zr(PMe_3)_2$ was not detected.

Preparation of 11. Dry magnesium powder (7.2 mg, 0.3 mmol) was suspended in THF-d_8 (1 mL), and **1** (27.3 mg, 0.1 mmol) and $(C_5H_4Me)_2ZrCl_2$ (32.0 mg, 0.1 mmol) were added. The mixture was sonicated at 50 °C for 1 h. ^{1}H NMR spectroscopy of the dark purple solution exhibited the formation of **11** in 62% yield, accompanied by the formation of **6** and **12**, in 18% and 7% yield, respectively. In **11** and **12**, one singlet for methyl groups and four multiplets assignable to hydrogens on methylcyclopentadienyl rings were observed. This is presumably because of slow rotation of Cp rings for steric reasons. To measure NMR at variable temperatures, the solvent was removed in vacuo, and the residue was dissolved in toluene-d_8. ^{1}H NMR spectra were fundamentally unchanged over the temperature range −60 to 100 °C.

11: ^{1}H NMR (THF-d_8): δ 2.02 (s, 6H, CH_3), 3.69 (dd, $J =$ 4.6, 2.7 Hz, 2H, CH_2), 3.76 (dd, $J = 4.6$, 2.7 Hz, 2H, CH_2), 5.04 (m, 2H), 5.18 (m, 2H), 5.37 (m, 2H), 5.49 (s, 10H, Cp), 5.51 (m, 2H). ^{13}C NMR (THF-d_8): δ 15.24 (CH_3), 75.35 (CH_2), 78.13 (CH_2), 105.35, 105.35 (CH ×2), 106.12 (C_5H_5), 107.40 (CH), 108.23 (CH), 119.63 (q), 166.44, 171.37 (q).

For comparison, the bimetallic complex **12** was prepared and spectroscopically observed. The reaction was carried out similarly to the preparation of **6** by method (iii) using bis(methylcyclopentadienyl)zirconium dichloride (88% by ^{1}H NMR). **12**: ^{1}H NMR (THF-d_8): δ 2.05 (s, 12H, CH_3), 3.61 (s, 4H, CH_2), 4.99 (m, 4H), 5.14 (m, 4H), 5.33 (m, 4H), 5.48 (m, 4H). ^{13}C NMR (THF-d_8): δ 15.30 (CH_3), 76.78 (CH_2), 105.03, 105.12 (CH ×2), 107.16 (CH), 108.09 (CH), 119.620 (q), 166.44, 169.40 (q).

X-ray Crystallographic Analysis of 1. Single crystals were obtained by recrystallization from a hexane solution. A colorless plate crystal (0.50 × 0.15 × 0.05 mm) was mounted in a nylon loop and coated with liquid paraffin. Data were collected on a Rigaku RAXIS-CS imaging plate diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 113 K. The structure was solved by direct methods[11] and expanded using Fourier techniques.[12] The non-hydrogen atoms were refined anisotropically. Some of hydrogen atoms (H1a,b and H4a,b) were found by the difference Fourier syntheses, and the others were placed at calculated positions and not refined. The final cycle of full-matrix least-squares refinement was based on all 2965 reflections ($2\theta < 60.06$) and 193 variable parameters. All calculations were performed using the

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[11] SIR97: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

[12] DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 program system*, Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1994.

teXsan[13] crystallographic software package of Molecular Structure Corporation. Crystal data are summarized in Table 2. See the deposited CIF data for details.

X-ray Crystallographic Analysis of 6. Single crystals were obtained from a THF solution by slow evaporation of the solvent. A dark brown crystal of dimensions 0.2 × 0.1 × 0.1 mm was mounted in a nylon loop and coated with liquid paraffin. Data were collected on a Rigaku RAXIS-CS imaging plate diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 93 K. The structure was solved by direct methods[11] and expanded using Fourier techniques[12] and then refined on F^2 by full-matrix least-squares techniques. The hydrogen atoms of Cp rings were placed at the calculated positions and not refined. The other hydrogen atoms (H1a and H1b) were found by difference Fourier syntheses, and their coordinates and isotropic parameters were refined. All calculation were performed using the teXsan software package.[13] Crystallographic parameters are summarized in Table 2. See the deposited CIF file for details.

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Supporting Information Available: Spectroscopic data for **6**, **11**, and **12**; crystallographic data for **1** and **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) *teXsan*: Crystal Structure Analysis Package; Molecular Structure Corporation, 1985 and 1999.