Preparation and Characterization of Bis(cyclopentadienyl)zirconium(II) Complexes with a Tethered Olefin−Phosphine Ligand

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Unprecedented zirconium(II) complexes bearing tethered olefin−phosphine ligands were synthesized and characterized. The molecular structures of the newly synthesized complexes (η^5-1,2-$Me_2C_5H_3)_2Zr(CH_2{=}CHCH_2CH_2PPh_2)$ (**1c**) and $Cp_2Zr(CH_2{=}CHCH_2CH_2CH_2PPh_2)$ (**2a**) were determined by single-crystal X-ray diffraction methods. The stability and reactivity of the series of complexes $Cp_2Zr\{CH_2{=}CH(CH_2)_nPR_2\}$ (n = 2, 3; R = Et, Ph) were examined. The complex **2a** showed simultaneously both sufficient stability and high reactivity.

Introduction

Recently, zirconocene(II)−olefin complexes have attracted much attention, since these complexes have been found to be good reagents or catalysts in organic synthesis. In most cases, these complexes have been prepared in situ by the reaction of zirconocene dichloride with 2 equiv of alkyllithium[1] or -magnesium reagent.[2] To investigate the reaction mechanism of such zirconocene−olefin complexes, the use of isolated complexes as starting materials is necessary. In the past few decades, several zirconium(II)−olefin complexes were isolated and fully characterized by X-ray single-crystal analyses, such as $Cp_2Zr\{(E)$-PhCH=CHPh$\}$-(PMe_3),[3a] $Cp_2Zr(CH_2{=}CH_2)(PMe_3)$,[3b,c] $Cp_2Zr(CH_2{=}CHPh)$,[3b] and $Cp_2Zr(CH_2{=}CHEt)(PMe_3)$,[3d,e] which were stabilized with phosphine ligands. These complexes were found to be fairly stable in the solid state, but in solution, substantial decomposition still proceeds within a few hours. We have now turned our attention to the preparation of potentially more stable zirconium(II) complexes using tethered olefin−phosphine ligands. Although there are several examples of tethered alkene complexes for Ru, Rh, Ir, and W,[4−8] there is no example of zirconocene complexes with tethered olefin−phosphine ligands. We report here unprecedented zirconium(II) complexes bearing tethered olefin−phosphine ligands.

Experimental Section

All reactions were carried out under dry nitrogen with use of standard Schlenk techniques. Zirconocene dichloride and chlorodiphenylphosphine were obtained from Aldrich Chemical Co. Ltd. THF, diethyl ether, and hexane were distilled over sodium/benzophenone. 4-(Diethylphosphino)-1-butene, 4-(diphe-

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(1) (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (b) Swanson, D. R.; Negishi, E. *Organometallics* **1991**, *10*, 825.

(2) (a) Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, K.; Uchida, T. *Chem. Lett.* **1989**, 761. (b) Takahashi, T.; Nitto, Y.; Seki, T.; Saburi, M.; Negishi, E. *Chem. Lett.* **1990**, 2259. (c) Takahashi, T.; Suzuki, N.; Kageyama, M.; Nitto, Y.; Saburi, Y.; Negishi, E. *Chem. Lett.* **1991**, 1579. (d) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8950. (e) Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687. (f) Takahashi, T.; Kasai, K.; Suzuki, N.; Nakajima, K.; Negishi, E. *Organometallics* **1994**, *13*, 3413. (g) Takahashi, T.; Xi, Z.; Obora, Y.; Suzuki, N. *J. Am. Chem. Soc.* **1995**, *117*, 2665. (h) Xi, Z.; Fischer, R.; Hara, R.; Sun, W.-H.; Obora, Y.; Suzuki, N.; Nakajima, K.; Takahashi, T. *J. Am. Chem. Soc.* **1997**, *119*, 12842. (i) Kemp, M. I.; Whitby, R. J.; Steven, J. C. *Synthesis* **1998**, 552.

(3) (a) Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, Y.; Uchida, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761. (b) Alt, H. G.; Denner, C. E.; Thewalt, U.; Rausch, M. D. *J. Organomet. Chem.* **1988**, *356*, C83. (c) Binger, P.; Müller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Krüger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1031. (d) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (e) Goddard, R.; Binger, P.; Hall, S. R.; Müller, P. *Acta Crystallogr.* **1990**, *C46*, 998.

(4) Issleib, K.; Haftendorn, M. Z. *Anorg. Allg. Chem.* **1967**, *351*, 9−17.

(5) For *Rh* and *Ir*, see: (a) Curtis, J. L. S.; Hartwell, G. E. *J. Organomet. Chem.* **1974**, *80*, 119. (b) Clark, P. W.; Hartwell, G. E. *J. Organomet. Chem.* **1975**, *96*, 451. (c) Clark, P. W.; Hartwell, G. E. *J. Organomet. Chem.* **1975**, *102*, 387. (d) Ryan, R. R.; Schaeffer, R.; Clark, P.; Hartwell, G. *Inorg. Chem.* **1975**, *14*, 3039. (e) Bennett, M. A.; Johnson, R. N.; Tomkins, I. B. *J. Organomet. Chem.* **1976**, *118*, 205. (f) Bennett, M. A.; Johnson, R. N.; Tomkins, I. B. *J. Organomet. Chem.* **1977**, *133*, 231. (g) Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1978**, *152*, 347. (h) Clark, P. W.; Hanisch, P.; Jones, A. J. *Inorg. Chem.* **1979**, *18*, 2067. (i) Clark, G. R.; Marsden, K. *J. Organomet. Chem.* **1984**, *265*, 215. See also: (j) Aresta, M.; Quaranta, E.; Treglia, S.; Ibers, J. A. *Organometallics* **1988**, *7*, 577. (k) Krafft, M. E.; Wilson, L. J.; Onan, K. D. *Organometallics* **1988**, *7*, 2528.

(6) For *Ru*, see: (a) Reference 2i. (b) Irvine, D. J.; Preston, S. A.; Cole-Hamilton, D. J.; Barnes, J. C. *J. Chem. Soc., Dalton Trans.* **1991**, 2413. (c) Blake, A. J.; Easton, T.; Stephenson, T. A. *Acta Crystallogr.* **1992**, *C48*, 1567.

(7) For *Pt*, see: Simms, B. L.; Ibers, J. A. *J. Organomet. Chem.* **1987**, *327*, 125.

(8) For *W*, see: Wermer, P. H.; Dobson, C. B.; Dobson, G. R. *J. Organomet. Chem.* **1986**, *311*, C47.

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nylphosphino)-1-butene, 5-(diethylphosphino)-1-pentene, and 5-(diphenylphosphino)-1-pentene were prepared according to literature procedures.[9] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-400 spectrometer. GC analysis was performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector and a 25 m capillary column (CBP1-M25-025).

Preparation of $Cp_2Zr\{CH_2{=}CH(CH_2)_2PPh_2\}$ (1a). To a solution of Cp_2ZrCl_2 (292 mg, 1.0 mmol) in THF (5 mL) was added *n*-butyllithium (in hexane, 1.6 M, 1.25 mL, 2.0 mmol) at −78 °C. After the mixture was stirred for 1 h at the same temperature, 4-(diphenylphosphino)-1-butene (240 mg, 1.0 mmol) was added and the reaction mixture was warmed to room temperature and stirred for 1 h to give a dark red solution. The solvent was removed under vacuum, and a red residue was extracted with hexane (25 mL × 2). This was followed by filtration and concentration under vacuum. Crystallization from the hexane solution at −40 °C overnight gave 259 mg (56%) of the title compound. The NMR yield was 82%. ^{1}H NMR (C_6D_6, Me_4Si): δ 4.85 (d, J_{H-P} = 1.1 Hz, 5H), 5.19 (d, J_{H-P} = 1.5 Hz, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 31.76 (d, J_{C-P} = 34.1 Hz), 33.79 (d, J_{C-P} = 12.0 Hz), 39.53 (d, J_{C-P} = 35.8 Hz), 50.27, 99.56 (Cp), 100.35 (Cp), 128.30 (d, J_{C-P} = 32.7 Hz), 128.59 (d, J_{C-P} = 11.8 Hz), 128.66, 129.58, 130.63 (d, J_{C-P} = 9.0 Hz), 134.44 (d, J_{C-P} = 11.8 Hz), 139.94 (d, J_{C-P} = 12.2 Hz), 142.21 (d, J_{C-P} = 24.6 Hz). ^{31}P NMR (C_6D_6, H_3PO_4): δ 74.59. Anal. Calcd for $C_{26}H_{27}PZr$: C, 67.64; H, 5.89; P, 6.70. Found: C, 67.40; H, 5.90; P, 6.51.

Preparation of $Cp_2Zr\{CH_2{=}CH(CH_2)_2PEt_2\}$ (1b). NMR yield: 85%. Isolated yield: 46%. ^{1}H NMR (C_6D_6, Me_4Si): δ 0.50−0.62 (m, 1H), 0.71−0.82 (m, 3H), 0.84−0.96 (m, 3H), 1.13−1.67 (m, 8H), 2.21−2.33 (m, 1H), 3.05−3.20 (m, 1H), 5.00 (s, 5H), 5.11 (s, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 7.00 (d, J_{C-P} = 7.3 Hz), 9.63 (d, J_{C-P} = 5.2 Hz), 16.58 (d, J_{C-P} = 3.9 Hz), 19.29 (d, J_{C-P} = 12.1 Hz), 29.56, 33.35 (d, J_{C-P} = 13.8 Hz), 34.17 (d, J_{C-P} = 32.7 Hz), 51.25, 98.48 (Cp), 99.85 (Cp). Anal. Calcd for $C_{18}H_{27}PZr$: C, 59.13; H, 7.44; P, 8.47. Found: C, 58.85; H, 7.26; P, 8.25.

Preparation of $(1,2\text{-}Me_2C_5H_3)_2Zr\{CH_2{=}CH(CH_2)_2PPh_2\}$ (1c). This complex was prepared from $(1,2\text{-}Me_2C_5H_3)_2ZrCl_2$ by the same method as described above for **1a**. Isolated yield: 74%. ^{1}H NMR (C_6D_6, Me_4Si): δ 0.67 (dd, 1H, J = 5.5, 10.6 Hz), 0.86 (dd, J = 5.5, 11.7 Hz, 1H), 1.14 (s, 3H), 1.15−1.27 (m, 1H), 1.8−1.9 (m, 1H), 1.83 (s, 3H), 1.88 (s, 3H), 2.05 (s, 3H), 3.04−3.16 (m, 1H), 3.40−3.52 (m, 1H), 3.79 (q, J = 3.1 Hz, 1H), 4.65 (q, J = 2.7 Hz, 1H), 4.85 (q, J = 3.4 Hz, 1H), 4.93 (t, J = 2.6 Hz, 1H), 5.20 (q, J = 2.3 Hz, 1H), 5.28 (q, J = 2.9 Hz, 1H), 6.85−7.77 (m, 10H). ^{13}C NMR (C_6D_6, Me_4Si): δ 11.87, 12.82, 13.76, 13.89, 32.45 (d, J_{C-P} = 13.1 Hz), 40.00 (d, J_{C-P} = 37.2 Hz), 40.44 (d, J_{C-P} = 3.0 Hz), 56.12, 89.74, 94.27, 100.54, 100.87, 104.79, 105.43, 109.42, 111.98, 114.43, 114.91, 128.01, 128.05 (d, J_{C-P} = 7.0 Hz), 128.43 (d, J_{C-P} = 7.0 Hz), 129.43, 130.71 (d, J_{C-P} = 8.0 Hz), 134.45 (d, J_{C-P} = 12.1 Hz), 139.96 (d, J_{C-P} = 6.0 Hz), 142.86 (d, J_{C-P} = 23.1 Hz). ^{31}P NMR (C_6D_6, H_3PO_4): δ 88.76. Anal. Calcd for $C_{30}H_{35}PZr$: C, 69.59; H, 6.81; P, 5.98. Found: C, 69.33; H, 6.74; P, 6.08.

Preparation of $Cp_2Zr\{CH_2{=}CH(CH_2)_3PPh_2\}$ (2a). NMR yield: 91%. Isolated yield: 84%. ^{1}H NMR (C_6D_6, Me_4Si): δ 4.99 (d, J_{H-P} = 1.5 Hz, 5H), 5.15 (d, J_{H-P} = 1.5 Hz, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 19.54 (d, J_{C-P} = 5.0 Hz), 26.32, 29.12 (d, J_{C-P} = 21.1 Hz), 32.05 (d, J_{C-P} = 18.0 Hz), 39.07 (d, J_{C-P} = 4.0 Hz), 100.56 (Cp), 101.83 (Cp), 128.57 (d, J_{C-P} = 7.1 Hz), 128.74 (d, J_{C-P} = 11.8 Hz), 129.20, 129.22, 131.65 (d, J_{C-P} = 10.8 Hz), 138.89 (d, J_{C-P} = 22.2 Hz), 142.74 (d, J_{C-P} = 12.1 Hz). ^{31}P NMR (C_6D_6, H_3PO_4): δ 35.19. Anal. Calcd for $C_{27}H_{29}PZr$: C, 68.17; H, 6.14; P, 6.51. Found: C, 67.81; H, 6.08; P, 6.36.

Preparation of $Cp_2Zr\{CH_2{=}CH(CH_2)_3PEt_2\}$ (2b). NMR yield: 80%. Isolated yield: 37%. ^{1}H NMR (C_6D_6, Me_4Si): δ 0.33−0.45 (m, 1H), 0.68−0.77 (m, 3H), 0.80−0.92 (m, 3H), 0.92−1.02 (m, 2H), 1.17−1.71 (m, 8H), 1.73−1.90 (m, 1H), 3.38−3.49 (m, 1H), 5.03 (s, 5H), 5.12 (s, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 5.80 (d, J_{C-P} = 7.5 Hz), 8.76 (d, J_{C-P} = 5.4 Hz), 15.88 (d, J_{C-P} = 14.1 Hz), 18.19 (d, J_{C-P} = 4.9 Hz), 20.70 (d, J_{C-P} = 3.5 Hz), 25.42 (d, J_{C-P} = 21.8 Hz), 26.68 (d, J_{C-P} = 1.8 Hz), 29.52 (d, J_{C-P} = 18.2 Hz), 39.38 (d, J_{C-P} = 4.0 Hz), 99.81 (Cp), 100.47 (Cp).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 1c

Zr−P	2.680(2)	C2−C3	1.530(7)
Zr−C1	2.323(5)	C3−C4	1.542(8)
Zr−C2	2.357(4)	P−C4	1.842(4)
C1−C2	1.432(8)		
P−Zr−C1	100.9(2)	C1−Zr−C2	35.6(2)
P−Zr−C2	65.9(1)	Zr−P−C4	104.8(2)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 2a

Zr−P	2.696(1)	C2−C3	1.517(4)
Zr−C1	2.332(3)	C3−C4	1.520(3)
Zr−C2	2.390(3)	C4−C5	1.528(4)
C1−C2	1.435(3)	P−C4	1.841(3)
P−Zr−C1	108.91(7)	C1−Zr−C2	35.35(8)
P−Zr−C2	73.86(6)	Zr−P−C4	111.37(8)

Decomposition of Complexes 1a, 1b, 2a, 2b, and 3. THF solutions (0.4 mL, ca. 0.13 mM) of **1a, 1b, 2a, 2b**, and **3** were charged in a NMR tube. To each was added 0.2 mL of C_6D_6. Cyclopentadienyl hydrogens which appear in the region δ 4.6−5.5 were monitored by NMR with 1 equiv of mesitylene (δ 6.7) as a standard. The decomposition reaction was carried out at 27 °C for 6 and 24 h. The results are shown in Table 4.

Reactions of Complexes 1a, 1b, 2a, 2b and 3 with 5-Decyne. To solutions of complexes **1a, 1b, 2a, 2b** and **3** (1.0 mmol in 6 mL of a mixture of THF and hexane) was added 5-decyne (2.0 mmol), and the mixtures were stirred at room temperature for several hours. The reactions were monitored by GC after hydrolysis of the mixtures with 3 M aqueous HCl. The reaction of **2a** with 5-decyne for 20 h afforded the dimerization product 6,7-dibutyldodeca-5,7-diene in 95% yield after hydrolysis.

X-ray Crystal Structure Determinations of Complexes 1c and 2a. Single crystals of **1c** and **2a** suitable for X-ray diffraction study were obtained by recrystallization from hexane/ether solution at 5 °C. The single crystals were mounted in a glass capillaries and sealed under argon. X-ray data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Crystallographic data and experimental details are summarized in Table 3. Three standard reflections were monitored every 150 reflections during the data collection, and no significant crystal decay was detected. Absorption correction was applied on the basis of ψ-scans. The structures were readily solved using direct methods (SHELXS-86[10]), and refinement was performed with Xtal 3.2 software[11] by full-matrix least-squares techniques on F. All non-hydrogen atoms were refined anisotropically. For **1c**, hydrogen atoms attached to C(1), C(2), C(3), and C(4) were located from difference maps and the other hydrogen atoms were introduced at ideal positions. Each hydrogen atom was assigned an isotropic displacement parameter 20% greater than that of the carbon atom to which it was bonded. For **2a**, hydrogen atoms were located by difference maps and refined isotropically.

(9) Clark, P. W.; Curtis, J. L. S.; Garrou, P. E.; Hartwell, G. E. *Can. J. Chem.* **1974**, *52*, 1714.

(10) Sheldrick, G. M. SHELXS-86, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1986.

(11) Hall, S. R.; Flack, H. D.; Stewart, J. M. Xtal 3.2, Program for X-Ray Crystal Structure Analysis; Universities of Western Australia, Geneva, and Maryland, 1992.

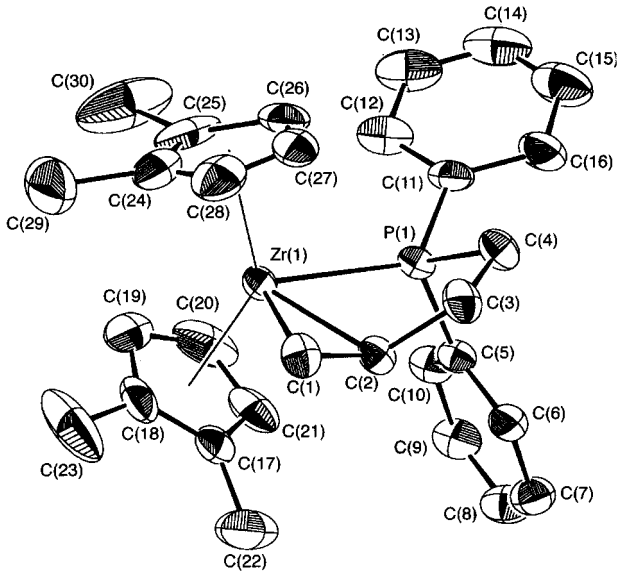


Figure 1. ORTEP drawing of complex **1c**.

Table 3. Crystal Data and Experimental Details for Complexes 1c and 2a

	1c	**2a**
formula	$C_{30}H_{35}PZr$	$C_{27}H_{29}PZr$
M_r	517.81	475.73
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	12.955(3)	8.469(5)
b (Å)	13.051(2)	30.821(6)
c (Å)	8.100(2)	9.236(5)
α (deg)	92.44(2)	
β (deg)	101.04(2)	110.33(4)
γ (deg)	74.30(2)	
Z	2	4
V (Å^3)	1294.0(5)	2261(2)
μ(Mo Kα) (cm^{-1})	4.9	5.6
transmissn factor	0.902−0.947	0.914−0.962
cryst size (mm^3)	0.20 × 0.20 × 0.40	0.20 × 0.30 × 0.40
D_{calcd} (g cm^{-3})	1.33	1.40
F(000)	540	984
diffractometer	Rigaku AFC7R	Rigaku AFC7R
λ(Mo Kα) (Å)	0.710 69	0.710 69
T (K)	298	298
scan range (deg)	1.42 + 0.30 tan θ	1.00 + 0.30 tan θ
scan mode	$\omega-2\theta$	$\omega-2\theta$
scan speed (deg min^{-1})	8	8
$2\theta_{max}$ (deg)	55	55
rflns measd	$0 \le h \le 15$	$0 \le h \le 11$
	$-16 \le k \le 16$	$0 \le k \le 11$
	$-10 \le l \le 10$	$0 \le l \le 11$
no. of data collected	6032	5504
no. of data ($\|F_o\| > 3\sigma(\|F_o\|)$)	4301	4085
no. of variables	289	378
R, %[a]	5.1	2.7
R_w, %[b]	6.6	3.2
S, goodness of fit[c]	2.52	1.34
$(\Delta/\delta)_{max}$	0.62	0.76
largest diff peak (e Å^{-3})	1.11	0.29
largest diff hole (e Å^{-3})	−0.61	−0.51

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$, $w = [\sigma^2(F_o) + \{0.015(F_o)\}^2]^{-1}$. [c] $S = [\sum w||F_o| - |F_c||^2/(m - n)]^{1/2}$ (m = no. of used reflections, n = no. of refined parameters).

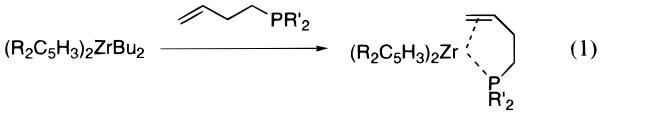
Results and Discussion

Olefin−phosphine ligands were readily prepared from the corresponding bromoolefins and chlorophosphines by a slight modification of the method reported by Clark.[9] Treatment of Cp_2ZrBu_2 (Negishi reagent),[1] which has most frequently been employed as a precursor of the "Cp_2Zr" equivalent, with olefin−phosphine ligands afforded the expected zirconocene complexes **1a**−**c** and **2a**,**b** in good yields (eqs 1 and 2).

Table 4. Proportion of Zr(II) Complexes vs Time in Solutions[a]

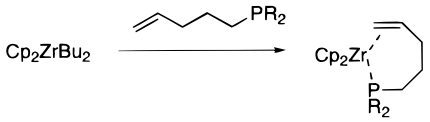
	amount/%				
time/h	**1a**	**1b**	**2a**	**2b**	**3**
0	100	100	100	100	100
6	88	96	93	94	74
24	86	93	91	93	68

[a] 0.13 mM solution of complexes in THF/C_6D_6 (2:1) were monitored by NMR. Proportions are obtained by observing cyclopentadienyl protons.



(1)

1a: R = H, R' = Ph
(82% NMR yield, 56% isolated yield)
1b: R = H, R' = Et
(85% NMR yield, 48% isolated yield)
1c: R = Me, R' = Ph
(74% isolated yield)



(2)

2a: R =Ph
(91% NMR yield, 84% isolated yield)
2b: R =Et
(80% NMR yield, 37% isolated yield)

The ^{1}H NMR spectrum of **1a** showed two sets of doublets at 4.85 (J_{H-P} = 1.1 Hz) and 5.19 (J_{H-P} = 1.5 Hz) ppm, and its ^{13}C NMR spectrum revealed two singlets at 99.56 and 100.35 ppm, which were assigned to cyclopentadienyl ligands. As expected, the two Cp ligands are not equivalent, since complex **1a** does not have a symmetric center. Similarly for **2a**, two sets of doublets appeared at 4.99 (J_{H-P} = 1.1 Hz) and 5.15 (J_{H-P} = 1.5 Hz) ppm in its ^{1}H NMR spectrum and two singlets at 100.56 and 101.83 ppm in the ^{13}C NMR. These NMR spectral data were consistent with other zirconocene−olefin complexes with phosphine ligands.

Though crystals of **1a** suitable for X-ray analysis could not be obtained, (1,2-$Me_2C_5H_3)_2Zr\{CH_2{=}CH(CH_2)_2$-$PPh_2\}$ (**1c**) with 1,2-dimethylcyclopentadienyl ligands, which was prepared by the same procedure, crystallized from the ether solution at 5 °C. A full characterization by a single-crystal X-ray analysis was successfully achieved.

The structure of **1c** is shown in Figure 1; selected bond distances and angles are given in Table 1. The structure clearly shows the simultaneous coordination of the olefin moiety and the phosphorus atom. The C(1)−C(2) distance of 1.432(8) Å is between that of typical C−C single and double bonds. Zr−C(1), Zr−C(2), and Zr−P distances were 2.323(5), 2.357(4), and 2.680(2) Å, respectively, and the C(1)−Zr−C(2) angle was 35.6(2)°.

All these values of **1c** are insignificantly different from those of other olefin−trimethylphosphine complexes as described below, despite the fact that the substituents on the phosphorus atom are phenyl groups. The reported distances of C(1)−C(2), Zr−C(1), Zr−C(2), and Zr−P and the C(1)−Zr−C(2) angle are as follows: for $Cp_2Zr\{(E)$-PhCH=CHPh$\}(PMe_3)$,[3a] 1.38(2), 2.36(2), 2.43(2), 2.715(5) Å and 33.4(5)°; for $Cp_2Zr(CH_2{=}CH_2)(PMe_3)$,[3c] 1.449(6), 2.354(3), 2.332(4), 2.695(1) Å and 36.0(1)°; for $Cp_2Zr(CH_2{=}CHPh)(PMe_3)$,[3c] 1.46(2), 2.35(1), 2.35(2), 2.679(4) Å and 36.2(5)°; for $Cp_2Zr(CH_2{=}CHEt)(PMe_3)$,[3e] 1.47(1), 2.35(1), 2.38(1), 2.689(3) Å and 36.1(3)°.

Complex **2a** was also isolated and recrystallized from the THF and hexane mixture. The structure of complex **2a** is shown in Figure 2; selected bond distances and angles are given in Table 2. The zirconium−olefin−phophorus moiety consists of seven members; however, the structure which comes from Zr−C(2)−C(3)−C(4)−C(5)−P appears as a typical chair conformation. C(1)−C(2), Zr−C(1), Zr−C(2), and Zr−P distances were 1.435(3), 2.332(3), 2.390(3), and 2.696(1) Å, respectively, and the C(1)−Zr−C(2) angle was 35.35(8)°.

Stability and Reactivity. To evaluate the stability of **1a**,**b** and **2a**,**b**, the decomposition of complexes in THF was monitored by an NMR study. The decomposition rates of complexes **1a**,**b** and **2a**,**b** were compared with that of $Cp_2Zr(CH_2{=}CHEt)(PMe_3)$ (**3**).[3d] The result is shown in Table 4. Within 6 h, 26% of complex **3** decomposed in THF at 27 °C. However, those of complexes **1b** and **2a**,**b** remained unreacted in 96%, 93%, and 94% amounts, respectively.

To evaluate the reactivity of these complexes, we chose the dimerization of 5-decyne as a representative organic reaction. Usually, zirconocene−olefin complexes prepared in situ, for example from Cp_2ZrBu_2 (Negishi reagent), give a very high yield of the dimerization product of 5-decyne after hydrolysis.

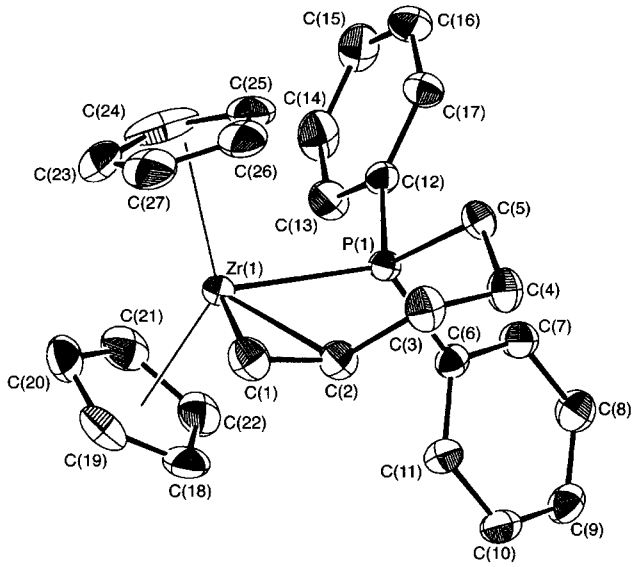


Figure 2. ORTEP drawing of complex **2a**.

It is interesting to report that the reaction of **2a** with 2 equiv of 5-decyne for 20 h at room temperature afforded the dimerization product 6,7-dibutyldodeca-5,7-diene in 95% yield after hydrolysis. This clearly indicated that the complex **2a**, which had a tethered olefin−phosphine ligand, showed simultaneously both sufficient stability and high reactivity.

Supporting Information Available: Tables giving X-ray analysis data for **1c** and **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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