# Syntheses, Characterization, and Structural Studies of Half-Open Zirconocenes

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The reaction of $Zr(C_5H_5)Cl_2Br$ with 3 equiv of $K(2,4\text{-}C_7H_{11})$ and 1 equiv of dmpe was found to lead to the 18-electron half-open zirconocene $Zr(C_5H_5)(2,4\text{-}C_7H_{11})$(dmpe) ($C_7H_{11}$ = dimethylpentadienyl; dmpe = $Me_2PC_2H_4PMe_2$), which has been fully characterized. A structural study has revealed that the Zr−C bond distances for the open dienyl ligand are significantly shorter than those for the $C_5H_5$ ligand. Alternatively, through a similar reaction involving the use of only 2 equiv of a more selective (pentadienyl)magnesium reagent, the two dienyl anions serve as one-electron reducing agents, and the Zr(II) complex $Zr(C_5H_5)$(Br)(dmpe)$_2$ is obtained, which has also been fully characterized. In the absence of dmpe, the reaction between $Zr(C_5H_5)BrCl_2$ and 3 equiv of the magnesium reagent leads to an unusual $Zr(C_5H_5)(C_{14}H_{21})$ complex. The $C_{14}H_{21}$ ligand was formed from the coupling of two $2,4\text{-}C_7H_{11}$ ligands, followed by the loss of one hydrogen atom, presumably abstracted by the third $2,4\text{-}C_7H_{11}$ ligand. The $C_{14}H_{21}$ ligand bonds to the zirconium center through both $\eta^5$-dienyl and $\eta^4$-“diene” coordination, leading to an 18-electron complex. The structural parameters indicate that the diene coordination can be more appropriately described as enediyl coordination, leading to a formal Zr(IV) instead of Zr(II) complex. The presence of a high formal metal oxidation state would seem to explain the fact that in this complex, as opposed to $Zr(C_5H_5)(2,4\text{-}C_7H_{11})$(dmpe) and many other related complexes, the M−C bond distances for the $C_5H_5$ ligand are much shorter than those for the open dienyl ligand.

## Introduction

Structural studies on a number of $M(C_5H_5)$(pentadienyl) and related complexes (“half-open metallocenes”) of early transition metals have revealed that the M−C distances for the open dienyl ligands tend to be dramatically shorter than those for the “stabilizing” $C_5H_5$ ligand.[1,2] Theoretical studies have supported the conclusion that the metal center in these compounds bonds more strongly to the open dienyl ligand rather than to the cyclopentadienyl ligand.[2] Furthermore, for at least the half-open titanocenes, the open dienyl ligands are quite susceptible to coupling reactions with alkynes, imines, nitriles, isonitriles, ketones, and aldehydes, so that the open dienyl ligands can be simultaneously both more strongly bound and more reactive than their cyclic counterparts.[3]

While the half-open titanocenes have already been found to be quite interesting, both structurally and chemically, there is reason to expect analogous zirconium compounds to be even more so. To begin with, the large girth of the open dienyl ligands leads to orbital overlap problems, especially for smaller metal centers.[4] The large girth, together with the resulting shorter M−ligand plane separations, also leads to greatly enhanced steric crowding. As zirconium is the largest transition metal (ignoring the arguable case of yttrium),[5] these problems should be minimized in its complexes. Thus, together with the fact that zirconium tends to form significantly stronger bonds than does titanium,[6] the bonding of the open dienyl ligands should be especially enhanced in zirconium complexes. As a result, we have for some time had an interest in preparing half-open zirconocenes. Herein we report on some of our results in this area, for which the use of $Zr(C_5H_5)Cl_2Br$[7] as a starting material appears to provide substantial advantages.

## Experimental Section

All preparations, reactions, and manipulations of these compounds were carried out under a prepurified nitrogen

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atmosphere, using either Schlenk techniques or a glovebox. Hydrocarbon, ethereal, and aromatic solvents were dried and deoxygenated by distillation from sodium benzophenone ketyl under a nitrogen atmosphere. Spectroscopic data were obtained as previously described.[8] The $^{13}C$ NMR spectra were not precisely integrated, but numbers of carbon atoms are reported in accord with their assignments. Elemental analyses were obtained from E & R Microanalytical Labs, Robertson Microanalytical Labs, or Desert Analytics. Pentadienyl anions[9] and $Zr(C_5H_5)Cl_2Br$[7] were prepared as previously described.

**$Zr(C_5H_5)(2,4\text{-}C_7H_{11})(dmpe)$ (1).** To a magnetically stirred solution of 0.70 g (2.3 mmol) of $Zr(C_5H_5)Cl_2Br$ in 30 mL of THF under nitrogen at −78 °C was added 0.38 mL (2.3 mmol) of dmpe, yielding a pale pink solution. To the resulting solution was added dropwise 0.92 g (6.9 mmol) of potassium 2,4-dimethylpentadienide dissolved in 30 mL of THF, after which the mixture was stirred for 30 min. The resulting red solution was warmed to room temperature, and a color change to bright red was observed. The solvent was removed in vacuo, the crude product was extracted with three 25 mL portions of pentane, and the extracts were filtered through a coarse frit. The red filtrate was concentrated to 10 mL and cooled to −90 °C, affording a red crystalline solid (40% yield, mp 131−132 °C).

Anal. Calcd for $C_{18}H_{32}P_2Zr$: C, 53.83; H, 8.03. Found: C, 54.02; H, 7.64. $^1H$ NMR (toluene-$d_8$, ambient temperature): $\delta$ 5.69 (s, 1H, H-3), 5.01 (s, 5H, Cp), 2.80 (br, 1H, H-1,5 exo), 2.02 (br, 1H, H-1,5 endo), 1.2−1.6 (multiplet, dmpe), 0.79 (s, 6H, $CH_3$ on $C_7H_{11}$). $^{13}C$ NMR (toluene-$d_8$, ambient temperature): $\delta$ 109.9 (d, C-3, $J$ = 151 Hz), 96.0 (d, $C_5H_5$, $J$ = 169 Hz), 93.2 (s, C-2,4), 84.2 (t, C-1,5, $J$ = 164 Hz), 30.1 (q, $CH_3$−Pdl), 24.3 (t, $PCH_2$), 15.6 (q, $PCH_3$). Mass spectrum (EI, 17 eV; $m/z$ (relative intensity)): 401 (97), 386 (15), 312 (62), 266 (24), 251 (100), 154 (56), 150 (62), 95 (13), 90 (65), 62 (40), 61 (22).

**$Zr(C_5H_5)(\eta^4{:}\eta^5\text{-}C_{14}H_{21})$ (2).** To a magnetically stirred solution of 0.90 g (4.9 mmol) of $MgBr_2$ in 30 mL of THF under nitrogen at −78 °C was added 0.66 g (4.9 mmol) of K(2,4-$C_7H_{11}$), forming a cloudy yellow solution. The resulting solution was warmed to room temperature. This mixture was added to 0.50 g of $Zr(C_5H_5)Cl_2Br$ (1.6 mmol) in 20 mL of THF under nitrogen at −78 °C. The resulting orange solution was warmed to room temperature. The solvent was removed in vacuo, the crude product was extracted with three 20 mL portions of pentane, and the extracts were filtered through a coarse frit. The filtrate was concentrated to 15 mL and cooled to −90 °C, affording an orange crystalline solid in 45% yield (mp 109−110 °C dec). This compound is very air- and moisture-sensitive, but it can be stored under nitrogen without any decomposition.

Anal. Calcd for $C_{19}H_{26}Zr$: C, 66.02; H, 7.58. Found: C, 65.88; H, 7.41. $^1H$ NMR (toluene-$d_8$, ambient temperature): $\delta$ 5.25 (s, 5H, $C_5H_5$), 4.00 (s, 1H), 3.79 (br, 1H), 3.68 (s, 1H), 3.53 (br, 1H), 3.41 (br, 1H), 2.86 (br, 1H), 2.32 (dd, 1H, $J$ = 2.0, 7.5 Hz), 1.89 (s, 3H), 1.78 (s, 3H), 1.70 (s, 3H), 1.41 (dd, 1H, $J$ = 2.0, 7.5 Hz). $^{13}C$ NMR (toluene-$d_8$, ambient temperature): $\delta$ 155.9 (s), 142.1 (s), 123.0 (s), 113.5 (d, $J$ = 150 Hz), 112.6 (s), 104.3 (d, $C_5H_5$, $J$ = 170 Hz), 100.9 (d, $J$ = 158 Hz), 83.4 (t, $J$ = 156 Hz), 69.2 (t, $J$ = 159 Hz), 47.5 (t, $J$ = 145 Hz), 42.6 (t, $J$ = 127 Hz), 41.8 (t, $J$ = 125 Hz), 32.0 (q, $CH_3$, $J$ = 125 Hz), 30.3 (q, $CH_3$, $J$ = 125 Hz), 28.5 (q, $CH_3$, $J$ = 125 Hz). Mass spectrum (EI, 17 eV; $m/z$ (relative intensity)): 345 (100), 344 (50), 330 (42), 315 (71), 220 (68), 205 (54), 204 (36), 190 (66), 125 (40), 66 (35).

**$Zr(C_5H_5)Br(dmpe)_2$ (3).** To a magnetically stirred solution of 0.60 g (3.3 mmol) of $MgBr_2$ in 30 mL of THF under nitrogen at −78 °C was added 0.44 g (3.3 mmol) of K(2,4-$C_7H_{11}$), forming a cloudy yellow solution. The resulting solution was warmed to room temperature. This mixture was added to a solution of 0.50 g of $Zr(C_5H_5)Cl_2Br$ (1.6 mmol) and 0.54 mL (3.3 mmol) of dmpe in 20 mL of THF under nitrogen at −78 °C. The resulting orange solution was warmed to room temperature. When the temperature was raised with stirring to room temperature, a distinct color change to a dark red solution occurred. The solvent was removed in vacuo, the crude product was extracted with three 25 mL portions of ether, and the extracts were filtered through a coarse frit. The red filtrate was concentrated to 15 mL and cooled to −90 °C, affording a red crystalline solid in 45% yield (mp 94−96 °C dec).

**Table 1. Crystal Data and Refinement Parameters for 1−3**

| | 1 | 2 | 3 |
|---|---|---|---|
| formula | $C_{18}H_{32}P_2Zr$ | $C_{16}H_{26}Zr$ | $C_{17}H_{37}BrP_4Zr$ |
| fw | 401.60 | 345.62 | 536.48 |
| temp (K) | 233 | 173 | 173 |
| $\lambda$, Å | 0.710 73 | 0.710 73 | 0.710 73 |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/n$ | $P2_1/n$ |
| unit cell dimens | | | |
| $a$, Å | 8.433(2) | 13.580(5) | 9.665(4) |
| $b$, Å | 14.381(4) | 8.169(2) | 15.154(6) |
| $c$, Å | 16.417(5) | 14.268(3) | 16.570(4) |
| $\beta$, deg | 99.08(2) | 93.29(2) | 98.49(3) |
| $V$ (Å$^3$); $Z$ | 1966(1); 4 | 1580(1); 4 | 2400(2); 4 |
| calcd density, g cm$^{-3}$ | 1.357 | 1.453 | 1.485 |
| abs coeff, cm$^{-1}$ | 7.16 | 6.85 | 23.9 |
| $\theta$ range, deg | 2.4−24.9 | 2.0−25.0 | 2.3−25.0 |
| limiting indices | $0 \le h \le 9$<br>$0 \le k \le 12$<br>$-19 \le l \le 19$ | $0 \le h \le 16$<br>$0 \le k \le 9$<br>$-16 \le l \le 16$ | $0 \le h \le 11$<br>$0 \le k \le 18$<br>$-19 \le l \le 19$ |
| no. of rflns collected | 3207 | 2901 | 4476 |
| no. of indep rflns; $n$ ($I > n\sigma(I)$) | 2999; 2 | 2777; 2 | 4213; 2 |
| $R(F)$ | 0.040 | 0.036 | 0.053 |
| $R_w(F^2)$ | 0.097 | 0.096 | 0.120 |
| max/min diff Fourier peak, e Å$^{-3}$ | 0.78/−1.02 | 0.74/−1.29 | 1.08/−1.50 |

Anal. Calcd for $C_{17}H_{37}BrP_4Zr$: C, 38.06; H, 6.95. Found: C, 38.02; H, 6.63. $^1H$ NMR (toluene-$d_8$, ambient temperature): $\delta$ 4.26 (m, 5H, $C_5H_5$, $J$(C−P) = 2 Hz), 1.49 (br, 12H, $CH_3$), 1.39 (m, 4H, $CH_2$), 0.95 (m, 4H, $CH_2$), 0.93 (br, 12H, $CH_3$). Mass spectrum (EI, 17 eV; $m/z$ (relative intensity)): 536 (80), 456 (100), 306 (40), 156 (69), 91 (30), 61 (44).

**Crystallographic Structural Determinations.** Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals were selected and mounted in thin-walled, nitrogen-flushed, glass capillaries. Each structure was solved by direct methods, subsequent difference Fourier syntheses, and least-squares refinements. Most hydrogen atoms were treated as idealized contributions, except for those attached to the metal-bound carbon atoms of the open dienyl ligand in **1**, and those in **2**, which were refined isotropically. All non-hydrogen atoms were refined anisotropically. The systematic absences in the diffraction data were uniquely consistent with the reported space groups. All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

## Results and Discussion

Earlier efforts to prepare a half-open zirconocene from the reactions of $Zr(C_5H_5)Cl_3$ with pentadienyl anions met with some success,[10] and the desired $Zr(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$ complex could be identified spectroscopically, but only as a mixture with significant quantities of $Zr(2,4\text{-}C_7H_{11})_2(PEt_3)$[11] ($C_7H_{11}$ = dimethylpentadienyl).

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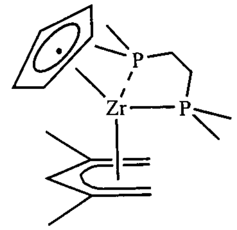
As $Zr(2,4\text{-}C_7H_{11})_2(PEt_3)$ is readily prepared from $ZrCl_4$ under similar conditions, it appeared possible that overchlorination of $Zr(C_5H_5)_2Cl_2$ in the attempted preparation of $Zr(C_5H_5)Cl_3$[12] could have led to the $ZrCl_4$. Indeed, others have observed that overchlorination of $Zr(C_5H_5)_2Cl_2$ can lead to significant quantities of $ZrCl_4$.[13] Alternatively, it is well-known that the aromatic cyclopentadienyl anion can often be readily displaced from its metal complexes by nonaromatic anions,[14] so that it would be possible that some initially formed half-open zirconocene complex could react with the $2,4\text{-}C_7H_{11}$ anion to yield $Zr(2,4\text{-}C_7H_{11})_2(PEt_3)$. Such displacements of the $C_5H_5$ ligand by pentadienyl anions have actually been observed, even for zirconium complexes.[15] If the problem indeed is due to the presence of $ZrCl_4$, then it would seem that bromination of $Zr(C_5H_5)_2Cl_2$ might provide a solution. In fact, we have already found that use of $Zr(C_5H_5)Cl_2Br$ does allow for the preparation of $Zr(C_5H_5)(6,6\text{-dmch})(PMe_3)_2$ [7] and related species (dmch = dimethylcyclohexadienyl). We have now found that $Zr(C_5H_5)Cl_2Br$ does also allow for the preparation and isolation of a nonedge bridged half-open zirconocene (eq 1; dmpe = $Me_2PC_2H_4PMe_2$). It is noteworthy that the

$$Zr(C_5H_5)Cl_2Br + dmpe + 3K(2,4\text{-}C_7H_{11}) \rightarrow \underset{\mathbf{1}}{Zr(C_5H_5)(2,4\text{-}C_7H_{11})(dmpe)} \quad (1)$$

dmpe ligand is bidentate, leading to an 18-electron complex, as half-open titanocenes typically incorporate only a single donor ligand site, and dmpe has been observed to bridge two half-open vanadocenes rather than chelate a single metal center.[16] The larger size of zirconium, the existence of dicarbonyl complexes of open zirconocenes and half-open titanocenes, and our earlier isolation of $Zr(C_5H_5)(dmch)(PMe_3)_2$ suggested that chelation of dmpe to the $Zr(C_5H_5)(2,4\text{-}C_7H_{11})$ unit should be possible, if not favored.

On the basis of the observed structure of $Zr(2,4\text{-}C_7H_{11})_2(CO)_2$,[11] **1** was expected to exist in a ground-state configuration in which the two phosphorus centers would be nonequivalent:



A single-crystal diffraction study was carried out and has confirmed this expectation. Pertinent bonding parameters are presented in Table 2, while the structure and numbering scheme can be seen in Figure 1. One can first observe that one phosphorus center, P2, is located by the open edge of the $2,4\text{-}C_7H_{11}$ ligand, whereas P1 is located to one side of the ligand. As the coordination of Lewis bases typically is favored to occur by the open edge of a pentadienyl ligand,[17] it is not surprising that the Zr−P2 distance is significantly shorter than that for P1: 2.6706(15) vs 2.8348(15) Å. The chelating nature of the dmpe ligand leads to a small P−Zr−P angle of 73.91(5)°, which may be compared to a OC−Zr−CO angle of 88.1(2)° in $Zr(2,4\text{-}C_7H_{11})_2(CO)_2$.[11]

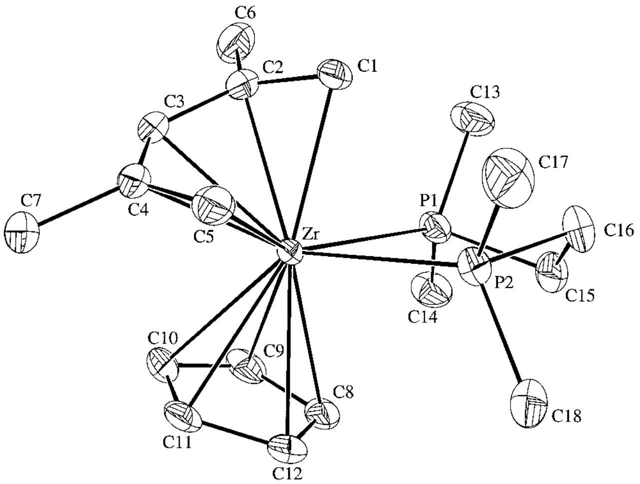


**Figure 1.** Perspective view of $Zr(C_5H_5)(2,4\text{-}C_7H_{11})(dmpe)$ (**1**). The ellipsoids are drawn at the 30% probability level.

**Table 2. Pertinent Bonding Parameters for $Zr(C_5H_5)(2,4\text{-}C_7H_{11})(dmpe)$ (1)**

| Bond Distances (Å) | | | |
|---|---|---|---|
| Zr−P1 | 2.8348(15) | Zr−P2 | 2.6706(15) |
| Zr−C1 | 2.403(5) | Zr−C8 | 2.510(4) |
| Zr−C2 | 2.402(5) | Zr−C9 | 2.510(5) |
| Zr−C3 | 2.428(5) | Zr−C10 | 2.546(5) |
| Zr−C4 | 2.464(5) | Zr−C11 | 2.578(5) |
| Zr−C5 | 2.418(5) | Zr−C12 | 2.568(5) |
| C1−C2 | 1.460(7) | C8−C9 | 1.416(7) |
| C2−C3 | 1.433(7) | C8−C12 | 1.399(7) |
| C2−C6 | 1.515(8) | C9−C10 | 1.393(7) |
| C3−C4 | 1.407(8) | C10−C11 | 1.417(8) |
| C4−C5 | 1.430(8) | C11−C12 | 1.397(7) |
| C4−C7 | 1.534(7) | C15−C16 | 1.521(8) |
| P1−C13 | 1.836(5) | P2−C16 | 1.851(6) |
| P1−C14 | 1.837(5) | P2−C17 | 1.828(6) |
| P1−C15 | 1.861(5) | P2−C18 | 1.837(6) |
| **Bond Angles (deg)** | | | |
| P1−Zr−P2 | 73.91(5) | C2−C3−C4 | 130.2(5) |
| C1−C2−C3 | 118.6(5) | C3−C4−C5 | 126.7(5) |

Of greatest interest are the relative Zr−C bond distances for the two dienyl ligands. As pentadienyl ligands can lead to both steric and orbital overlap problems in metal coordination spheres,[4] these problems should be minimized for large metal centers such as zirconium. As expected, the $Zr-C(2,4\text{-}C_7H_{11})$ bond distances average less than those for the $Zr-C(C_5H_5)$ bonds: 2.423 vs 2.542 Å. Taken together with similar though slightly smaller differences for half-open titanocenes, and with MO studies on such species, this provides a clear indication that the bonding to the open dienyl ligand is indeed significantly stronger than that for the “stabilizing” $C_5H_5$ ligand.

The individual Zr−C distances for the $2,4\text{-}C_7H_{11}$ ligand appear fairly regular, except that the Zr−C4 distance is longer than the Zr−C2 distance: 2.464(5) vs 2.402(5) Å. The difference may result from a steric

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[14] Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295.

[15] (a) Thus, $Zr[1,5\text{-}(Me_3Si)_2C_5H_5]_2$[15b] is obtained from the reaction of $Zr(C_5H_5)ClBr_2$ with $K[1,5\text{-}(Me_3Si)_2C_5H_5]$.[15c] (b) Gedridge, R. W.; Arif, A. M.; Ernst, R. D. *J. Organomet. Chem.* **1995**, *501*, 95. (c) Kulsomphob, V.; Ernst, R. D. Unpublished results.

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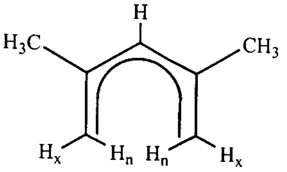
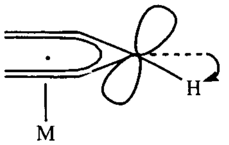
interaction between C7 and the $C_5H_5$ ligand, as C7 undergoes a substantially smaller tilt toward the zirconium center than C6: 0.7 vs 3.7° (vide infra). Notably, the Zr−C distances for the open dienyl ligand are shorter on average than those in $Zr(C_5H_7)_2(dmpe)$[18] (2.495 Å), while the Zr−C distances for the $C_5H_5$ ligand are on average longer than those in $Zr(C_5H_5)_2(PMe_3)_2$ [19] (2.486 Å). This could be explained either by the greater steric demands of the open dienyl ligands or, perhaps more likely, by the inherently stronger M−C bonding for the open dienyl ligands, which renders them stronger competitors for M−C bonding. Also of note is the fact that in $Zr(C_5H_5)(2,6,6\text{-tmch})(PMe_3)_2$ (tmch = trimethylcyclohexadienyl) there is less of a difference between the average Zr−C distances for the electronically open (2.474 Å) and closed (2.519 Å) dienyl ligands.[7] This might well be ascribed to additional steric influences brought about by the tmch ligand's edge bridge, which prevented phosphine coordination by the edge bridge, leading instead to coordination by the back end (C3) and side of the tmch ligand. However, it is also true that cyclohexadienyl ligands exhibit electronic properties intermediate between those of $C_5H_5$ and typical pentadienyl ligands,[20] which would therefore tend to offset the usual electronic preference generally found for the open pentadienyl ligands relative to $C_5H_5$.

The hydrogen substituents of the open dienyl ligand exhibit noticeable tilts out of the dienyl plane. Thus, for H3, there is a tilt of 2.2° toward Zr, with tilts in the same direction of 0.3 and 10.8°, respectively, for the exo-oriented substituents on C1 and C5.



For the endo-oriented substituents on C1 and C5, the respective tilts are 55.7 and 31.7° in the opposite direction. The downward tilts (toward the metal) have been attributed to an attempt to point the carbon atom p orbitals toward the metal center,



while the upward tilts of the endo substituents on C1 and C5 have been attributed both to a partial rehybridization toward $sp^3$ for C1 and C5[21] and to an attempt of the two hydrogen substituents to avoid pointing right at each other. In this case, the downward tilt of 0.3° by one of the C1 substituents appears unusually small, perhaps due to an interaction with C13 (separation 3.52 Å). Either the small degree of this tilt or some steric interaction with the dmpe ligand (e.g., $d$(C5−C17) = 3.49 Å) could be responsible for the large difference between the endo-oriented substituent tilts. The zirconium center lies 1.835 and 2.243 Å, respectively, out of the dienyl planes for the open and closed ligands. The smaller deviation for the open ligand is a geometric result of its large open edge, and this leads to the substantially greater steric demands exerted by the open dienyl ligands.[5] The dienyl planes are tilted out of a parallel orientation by 34.6°.

**Table 3. Pertinent Bonding Parameters for $Zr(C_5H_5)(\eta^4{:}\eta^5\text{-}C_{14}H_{21})$ (2)**

| Bond Distances (Å) | | | |
|---|---|---|---|
| Zr−C1 | 2.569(3) | C2−C6 | 1.513(5) |
| Zr−C2 | 2.587(3) | C3−C4 | 1.433(5) |
| Zr−C3 | 2.614(3) | C4−C5 | 1.368(5) |
| Zr−C4 | 2.701(3) | C4−C12 | 1.506(5) |
| Zr−C5 | 2.720(3) | C6−C7 | 1.538(5) |
| Zr−C8 | 2.382(3) | C7−C8 | 1.524(5) |
| Zr−C9 | 2.476(3) | C8−C9 | 1.442(4) |
| Zr−C10 | 2.495(3) | C8−C13 | 1.515(5) |
| Zr−C11 | 2.367(3) | C9−C10 | 1.404(5) |
| Zr−C15 | 2.513(4) | C10−C11 | 1.432(5) |
| Zr−C16 | 2.527(3) | C10−C14 | 1.517(5) |
| Zr−C17 | 2.533(4) | C15−C16 | 1.397(6) |
| Zr−C18 | 2.556(4) | C15−C19 | 1.398(6) |
| Zr−C19 | 2.544(4) | C16−C17 | 1.411(6) |
| C1−C2 | 1.387(5) | C17−C18 | 1.405(6) |
| C2−C3 | 1.399(5) | C18−C19 | 1.391(6) |
| Bond Angles (deg) | | | |
| C1−C2−C3 | 125.9(3) | C6−C7−C8 | 110.8(3) |
| C2−C3−C4 | 130.4(3) | C7−C8−C9 | 121.6(3) |
| C3−C4−C5 | 125.4(3) | C8−C9−C10 | 129.6(3) |
| C1−C2−C6 | 118.9(3) | C9−C10−C11 | 125.9(3) |
| C2−C6−C7 | 108.3(3) | | |

A variation of reaction 1 was also carried out in the absence of dmpe, using a magnesium pentadienyl reagent[22] generated in situ, to reduce the chance of any displacement of the cyclopentadienyl anion. In this case, a very unusual product (**2**, eq 2) could be isolated.

$$Zr(C_5H_5)Cl_2Br + 3Mg(2,4\text{-}C_7H_{11})Br \rightarrow \underset{\mathbf{2}}{Zr(C_5H_5)(C_{14}H_{21})} \quad (2)$$

Spectroscopic and structural data (Table 3, Figure 2) revealed that **2** was actually another example of a half-open zirconocene, except that an $\eta^4$-diene ligand was present instead of the dmpe in **1**, and a $C_2H_4$ bridge existed between the diene and open dienyl ligands. This bridge is clearly revealed from the $^{13}C$ NMR spectrum, which contains two triplets with $J(^{13}C{-}H)$ values of 125−127 Hz, consistent with formal $sp^3$ hybridization. The diene and open dienyl coordinations are both provided by the $C_{14}H_{21}$ ligand, derived from the coupling of two of the three anionic ligands in the reaction.

A possible mechanism for the formation of **2** is given in Scheme 1. In this process, two $2,4\text{-}C_7H_{11}$ ligands are initially incorporated, in their usually favored **U** conformations. Thereafter, an equilibration of one of these ligands with its sickle (**S**) isomer can occur, most likely through C−C bond rotation, although a hydrogen atom transfer could also lead to the same result. The second equilibrium involves a change in the allylic fragment bound to the zirconium center. This could be brought

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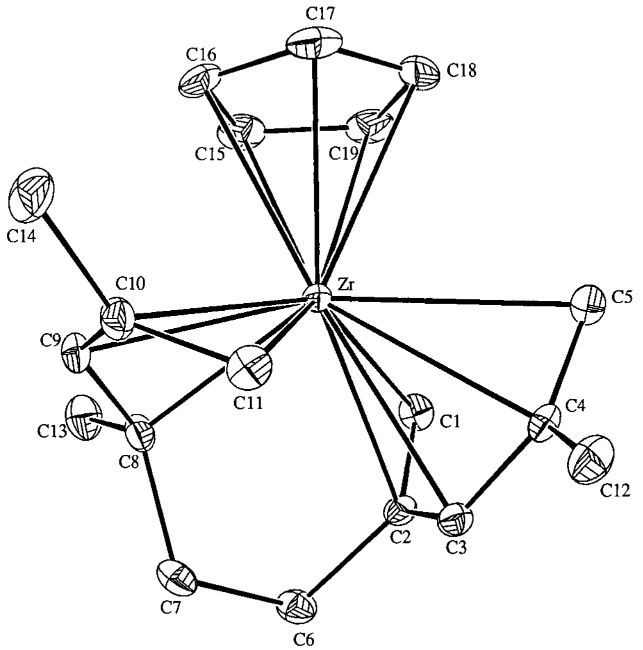


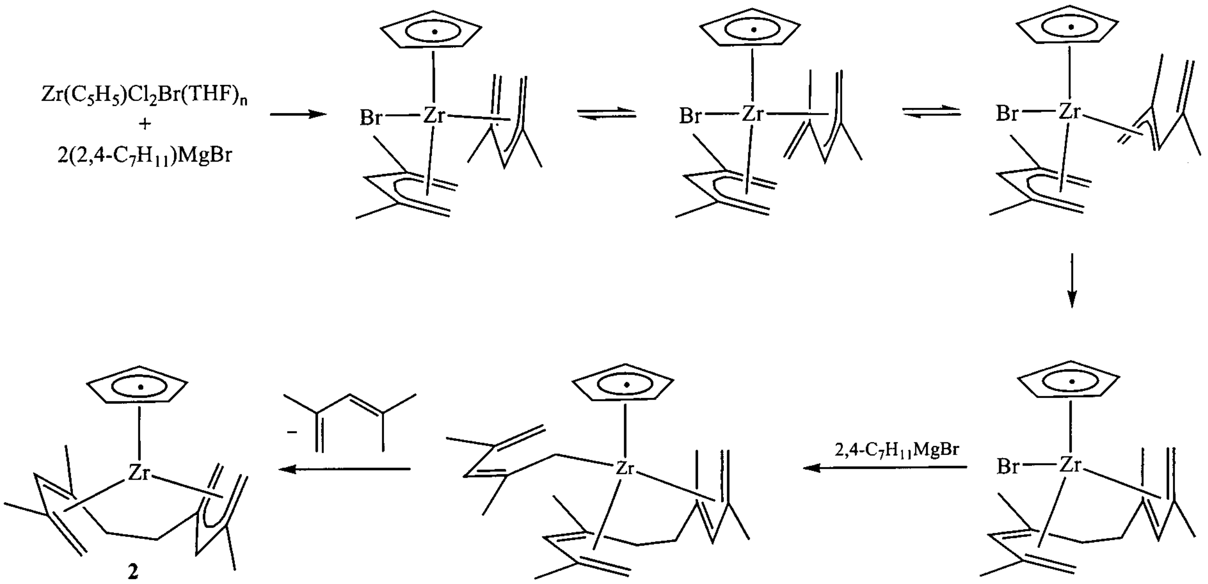
**Figure 2.** Perspective view of Zr($C_5H_5$)($\eta^4$:$\eta^5$-$C_{14}H_{21}$) (**2**). The ellipsoids are drawn at the 30% probability level.

about either through a 16-electron $\eta^1$ intermediate (bonding to the central dienyl carbon atom) or through an $\eta^5$-**S** intermediate with simultaneous adoption of $\eta^3$ coordination by the other 2,4-$C_7H_{11}$ ligand, to avoid a 20-electron configuration. Subsequent coupling would yield an 18-electron bis(diene) complex, whose remaining bromide ligand could then be replaced by the third dienyl ligand. Oxidative addition of a dienylic C−H bond, followed by its reductive elimination with the third dienyl ligand, would yield the observed product **2**. It is entirely possible that the timing of some of these processes, especially the incorporation of the third dienyl ligand and some of the isomerizations, could differ from the sequence shown in Scheme 1. Nonetheless, the scheme should depict the key transformations involved in the product's formation.

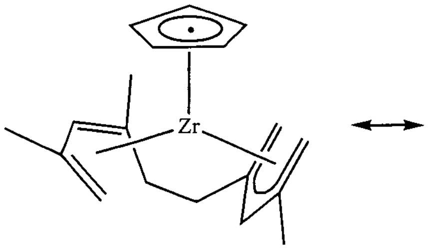
Remarkably, the Zr−C bonds for the diene ligand are the shortest of all Zr−C bonds (2.367(3)−2.495(3) Å), while those for the open dienyl ligand are the longest (2.569(3)−2.720(3) Å) and those for the $C_5H_5$ ligand are intermediate (2.513(4)−2.556(4) Å). The bonding parameters for the diene ligand actually reflect a high enediyl contribution, given that the terminal diene carbon atoms are significantly closer to Zr (2.374(4) vs 2.485(4) Å) and the carbon−carbon bonds adopt a long−short−long pattern (1.442(4), 1.404(5), and 1.432(5) Å). The formal presence of a 2− charge on this fragment would seem to explain the relative shortness of its Zr−C bonds. Even so, the observed C−C distances do not really signal full participation by the enediyl form. Most dramatically, the Zr−C(Cp) bonds (average 2.535 Å) are substantially *shorter* than those for the open dienyl ligand (average 2.638 Å). This trend is opposite to what one generally expects, as in Zr($C_5H_5$)(2,4-$C_7H_{11}$)(dmpe), for which respective averages of 2.542 and 2.423 Å were observed. It is first of all obvious that the Zr−Cp bond lengths are essentially identical in **1** and **2**, whereas the change from **1** to **2** resulted in what seems to be an unprecedented increase of over 0.2 Å in the Zr−C bonds for the open dienyl ligand. Thus, while the Zr−C bonds for the open dienyl ligand were favored by ca. 0.1 Å in **1**, they become disfavored in **2** by the same amount.

One might consider whether the bridge between the diene and open dienyl ligands might lead to less than optimal Zr−C bonding interactions, as indeed has been demonstrated in bridged bis(open dienyl) complexes of other metal centers,[23] but the angles about C6 and C7 do not deviate signficantly from the tetrahedral value. The actual cause of the dramatic change in Zr−open dienyl bonding must then be attributed to the diene/enediyl ligand. It has already been concluded that metal−pentadienyl complexes exhibit a substantial preference for low-oxidation-state metal centers, which has been attributed to the presence of a strong $\delta$ back-bonding interaction in low-oxidation-state complexes, signifying that pentadienyl ligands can serve as strong $\delta$ acids.[4] This $\delta$ acid character nicely explains a number of electronic influences brought about by pentadienyl ligands, as well as the generally much shorter M−C distances typically observed for pentadienyl ligands, as

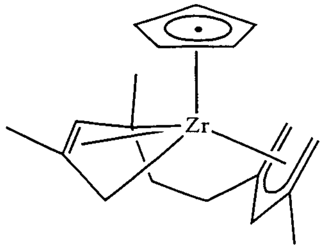
**Scheme 1**



compared to cyclopentadienyl ligands, in half-open metallocenes.[4,17] In the case of complex **2**, the enediyl contribution results in the zirconium center existing substantially in a formal 4+ oxidation state, which thereby would largely prevent the $\delta$ back-bonding interaction with the open dienyl ligand. In fact, complex **2** appears to be the first example of a simple (i.e., non edge bridged) $M^{IV}(\eta^5$-**U**-pentadienyl) complex. While a few $Ti^{IV}$ and $Zr^{IV}$ complexes with edge-bridged pentadienyl ligands are known,[24] the edge-bridged ligands, especially 6,6-dimethylcyclohexadienyl and related species, must be considered as special cases, as they have been shown to be intermediate electronically between typical pentadienyl ligands and the Cp ligand.[20] This most likely occurs as a result of the short lengths of separation between their terminal carbon atoms in their dienyl fragments, as compared to non-edge-bridged pentadienyl ligands.

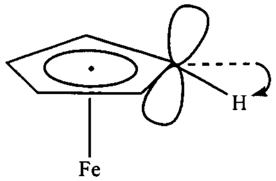


**2a**



**2b**

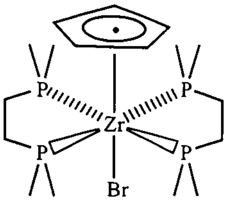
It is also interesting that the Zr−C bonds for the open dienyl ligand increase in length sequentially from C1 to C5. This trend may easily be attributed to the presence of the ethylene bridge connecting the open diene and dienyl units. The preferential bonding to one side of the open dienyl ligand also has affected the tilts of the dienyl substituents from the ligand plane. In particular, while the exo and endo hydrogen atoms on C1 have tilted 9.2° toward, and 25.4° away from, the metal center, the respective deviations for the C5 substituents, 4.1 and 23.8°, appear smaller, as would be expected in the case of a weaker interaction with the metal center. The corresponding deviations for H3, C6, and C12 are 3.4, 12.8, and 4.0°, respectively. The substantial deviation for C6 should reflect in part the stronger Zr−C2 vs Zr−C4 interaction. In addition, however, the large deviation may derive from an attempt to optimize the orientations of the two zirconium-bonded fragments of the $C_{14}H_{21}$ ligand. Overall, the tilts for the diene fragment are similar, being 10.8, 13.9, 8.6, and 5.4° for the downward-tilted substituents on C8, C9, C10, and C11, while the upward tilts by C7 and the endo-oriented substituent on C11 are 44.5 and 39.8°, respectively. In comparison to the tilts for the diene and open dienyl ligands, those for the $C_5H_5$ ligand are significantly smaller in magnitude but appear to reflect an approximate average tilt of 2° *away from* the metal center. This is opposite to what is observed for ferrocene and other complexes, in which a relatively small metal center is bonded to a $C_5H_5$ ligand.[25] For these smaller metal complexes, the tilts have been attributed to an attempt by the ligand to point its p orbitals toward the metal center:[26]



It could thus be expected that for a large enough metal center, as in **2**, tilts in the opposite direction should be observed.[4,17,26]

One other reaction was carried out, in which only 2 equiv of the 2,4-$C_7H_{11}$ anion was added to $Zr(C_5H_5)Cl_2Br$, in the presence of 2 equiv of dmpe. In this case, the two dienyl anion equivalents served as formal one-electron reductants, leading to the formation of $Zr(C_5H_5)Br(dmpe)_2$ (**3**; eq 3), analogous to the previously reported $Zr(C_5H_5)Cl(dmpe)_2$.[27] Notably, the magnesium reagents selectively removed the chloride, as opposed to bromide, ligands from $Zr(C_5H_5)Cl_2Br$, as indicated by both analytical and structural data. This appears reasonable, given the relative electronegativities and the higher charge/radius ratio of $Mg^{2+}$ compared to $Zr^{2+}$. Reaction 3 appears to offer some advantage over the previously reported preparation of $Zr(C_5H_5)Cl(dmpe)_2$, which required 10 days. Of course, reaction 3 is complicated by its utilization of pentadienyl reagents;

$$Zr(C_5H_5)Cl_2Br + 2Mg(2,4\text{-}C_7H_{11})Br + 2dmpe \rightarrow \underset{\mathbf{3}}{Zr(C_5H_5)Br(dmpe)_2} \quad (3)$$



**3**

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**Table 4. Pertinent Bonding Parameters for $Zr(C_5H_5)Br(dmpe)_2$ (3)**

| Bond Distances (Å) | | | |
|---|---|---|---|
| Zr−C1 | 2.457(7) | C1−C2 | 1.400(9) |
| Zr−C2 | 2.531(6) | C1−C5 | 1.414(10) |
| Zr−C3 | 2.533(6) | C2−C3 | 1.381(10) |
| Zr−C4 | 2.450(6) | C3−C4 | 1.396(10) |
| Zr−C5 | 2.411(6) | C4−C5 | 1.415(9) |
| Zr−P1 | 2.694(2) | Zr−P3 | 2.717(2) |
| Zr−P2 | 2.707(2) | Zr−P4 | 2.705(2) |
| P1−C6 | 1.847(6) | P3−C12 | 1.851(7) |
| P1−C8 | 1.836(7) | P3−C14 | 1.834(6) |
| P1−C9 | 1.834(6) | P3−C15 | 1.833(7) |
| P2−C7 | 1.860(6) | P4−C13 | 1.858(7) |
| P2−C10 | 1.838(7) | P4−C16 | 1.824(7) |
| P2−C11 | 1.839(7) | P4−C17 | 1.839(6) |
| C6−C7 | 1.526(9) | C12−C13 | 1.541(9) |
| Zr−Br | 2.8357(12) | | |

| Bond Angles (deg) | | | |
|---|---|---|---|
| Br−Zr−P1 | 78.00(5) | P1−Zr−P3 | 151.97(5) |
| Br−Zr−P2 | 73.34(5) | P1−Zr−P4 | 94.60(6) |
| Br−Zr−P3 | 74.48(5) | P2−Zr−P3 | 101.49(6) |
| Br−Zr−P4 | 78.35(5) | P2−Zr−P4 | 151.32(6) |
| P1−Zr−P2 | 75.24(6) | P3−Zr−P4 | 74.85(6) |

however, it seems quite possible that alternative reducing agents, such as lithium alkyls,[28] could function similarly, as has been demonstrated for a titanium analogue.[29]

The structural details for $Zr(C_5H_5)Br(dmpe)_2$ (**3**) appear in Table 4 and Figure 3. The complex exists with the $C_5H_5$ and Br ligands trans to one another, as found also for $Zr(C_5H_5)Cl(dmpe)_2$ and several titanium analogues.[29] The longer Zr−halogen distance for this compound (2.836(1) Å) vs the chloride analogue (2.629(2) Å) exceeds the difference of 0.15 Å between the covalent radii of bromine and chlorine.[5] This provides a clear indication, along with analytical and spectroscopic data, that the complex is free of any of the chloride analogue. The unexpectedly long Zr−Br distance may be an indication of steric crowding, and indeed the small values of the P−Zr−Br angles (two of ca. 74°, two of ca. 78°) reflect this expectation. Significant steric crowding has also been invoked in $Zr(C_5H_5)(CH_3)(dmpe)_2$.[29] In other respects the bonding parameters for **3** are quite similar to those for $Zr(C_5H_5)Cl(dmpe)_2$: e.g., the respective Zr−P distances of 2.706(1) and 2.708(2) Å and the respective Zr−Cp plane separations of 2.166(3) and 2.177(9) Å.

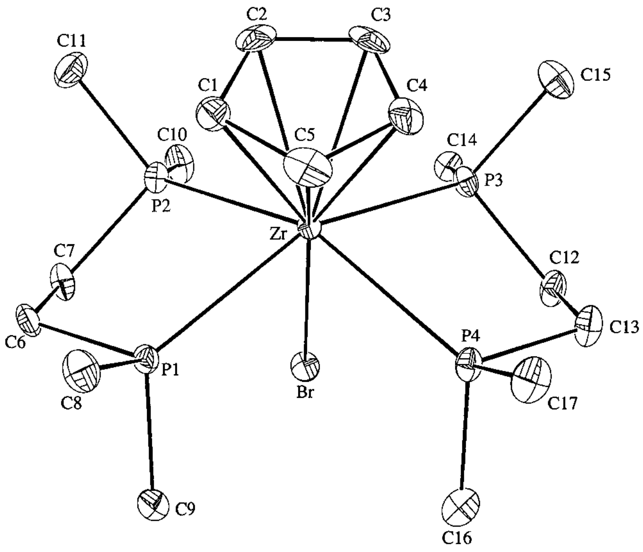

**Figure 3.** Perspective view of $Zr(C_5H_5)Br(dmpe)_2$ (**3**). The ellipsoids are drawn at the 30% probability level.

The utilization of $Zr(C_5H_5)Cl_2Br$ as a starting material has proven advantageous for the preparations of half-open zirconocenes and other low-valent organozirconium complexes. From this reagent one can readily isolate both a low-valent half-open zirconocene, $Zr(C_5H_5)(2,4\text{-}C_7H_{11})(dmpe)$, in which the Zr−C bonds are favored for the open dienyl ligand, and a formally tetravalent $Zr(C_5H_5)$(dienyl)(diene) complex, in which a dramatic reversal in the Zr−dienyl bonding preference occurs. The tendency for open pentadienyl ligands to bond to low-valent metal centers also shows up in the facile preparation of $Zr(C_5H_5)(Br)(dmpe)_2$ from $Zr(C_5H_5)Cl_2Br$. The availability of facile routes to these half-open zirconocenes now makes possible the study of the reaction chemistry of these species, and this is currently under investigation.

**Acknowledgment.** R.D.E. is grateful to the University of Utah and the National Science Foundation for partial support of this work.

**Supporting Information Available:** Tables giving positional coordinates, anisotropic thermal parameters, and additional bonding parameters for $Zr(C_5H_5)(2,4\text{-}C_7H_{11})(dmpe)$ (**1**), $Zr(C_5H_5)(\eta^4{:}\eta^5\text{-}C_{14}H_{21})$ (**2**), and $Zr(C_5H_5)Br(dmpe)_2$ (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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