

Synthesis and characterization of phosphine adducts of the open zirconocene $Zr(C_5H_7)_2$

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Abstract

Reactions of either $P(CH_3)_2C_6H_5$ or *dmpe* ($dmpe = (CH_3)_2PC_2H_4P(CH_3)_2$) adducts of $ZrCl_4$ with four equivalents of KC_5H_7 lead to the formation of the respective 16 or 18 electron mono(ligand) adducts of the open zirconocene $Zr(C_5H_7)_2$. Both complexes were found to exist in the expected symmetric conformations, as confirmed for the *dmpe* complex by a single crystal X-ray diffraction study.

Keywords: Zirconium; Phosphines; Pentadienyl; Crystal structure; Early transition metals; Open metallocene

1. Introduction

In the area of metal pentadienyl chemistry, the use of the 2,4-dimethylpentadienyl ($2,4-C_7H_{11}$) ligand has tended to dominate [1]. To some extent, this may derive from the fact that even as the free anion this group favors the adoption of the U conformation (I), as opposed to the otherwise more normal S (sickle) and W conformations [2]. In some circumstances, however, it is actually clear that the $2,4-C_7H_{11}$ complexes are more stable than their analogs with fewer methyl groups [3]. Naturally there will be situations in which the presence of other substitution patterns is required, particularly for applications in organic synthesis [4]. It is therefore important to be able to incorporate other pentadienyl ligands into metal coordination spheres of particular interest. Herein we report on the isolation of phosphine adducts of an unmethylated open zirconocene, $Zr(C_5H_7)_2$.

2. Experimental

All operations were carried out under a nitrogen atmosphere. Solvents were distilled from benzophenone ketyl to ensure complete removal of oxygen and water.

Spectroscopic data were obtained as previously described [5]. The numbers of carbon atoms are given for the ^{13}C NMR data in accord with the given assignments, but the spectra were not precisely integrated. KC_5H_7 and $ZrCl_4(dmpe)_2$ were prepared according to standard procedures [6].

2.1. $Zr(C_5H_7)_2(dmpe)$

To a three-neck flask equipped with a nitrogen inlet, magnetic stirring bar, and a pressure equalizing addition funnel was added 1.00 g (1.86 mmol) of $ZrCl_4(dmpe)_2$ and 30 ml of THF. The resulting pale pink solution was cooled to $-78^\circ C$ and 0.81 g (7.69 mmol) of potassium pentadienide in 45 ml of THF was added dropwise over 15 min to give a reddish colored solution. Warming of the reaction mixture to approx. $-15^\circ C$ resulted in an abrupt color change to dark purple and the reaction mixture was warmed to room temperature and stirred for an additional 1 h at this temperature. The solvent was removed in vacuo at the end of this period yielding a dark purple solid which was extracted with four 50 ml portions of hexanes and filtered through a Celite pad on a coarse frit. Concentration of the dark purple filtrate in vacuo to approx. 50 ml and subsequent cooling to $-30^\circ C$ resulted in 0.75 g of purple/black needles of the bis(pentadienyl)zirconium complex, $Zr(C_5H_7)_2(dmpe)$. The supernatant was transferred to a clean flask and further concentrated to approx. 20 ml and cooled to

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–30 °C overnight giving an additional 0.16 g of product for an overall yield of 65%. This compound forms well-formed rod shaped crystals (m.p. 148–152 °C, dec.) which ignite readily upon exposure to air but may be stored at ambient temperature under a nitrogen atmosphere for several months without apparent decomposition. However, several attempts to obtain analytical data led to low carbon values, even for samples of large well-formed single crystals.

¹H NMR (benzene-*d*₆, ambient): δ 6.61 (app. quintet, 2H, *J* = 6.5 Hz, H-2 or 4), 4.34 (d of d, 2H, *J* = 11.3 Hz, 7.9 Hz, H-2 or 4), 4.00 (t, 2H, *J* = 7.9 Hz, H-3), 2.60 (d, 2H, *J* = 11.1 Hz, H₁ or _{5exo}), 1.68 (d, 2H, *J* = 13.4 Hz, H₁ or _{5exo}), 1.37 (d, 4H, *J* = 6.7 Hz, “PCH₂”), 1.13 (s, 6H, PCH₃), 0.82 (s, 6H, PCH₃), –0.44 (m, 2H, H₁ or _{5endo}). One signal is obscured.

¹³C NMR (benzene-*d*₆, ambient): δ 105.1 (d, 2C, *J* = 160 Hz), 100.8 (d, 2C, *J* = 159 Hz), 98.0 (d, 2C, *J* = 153 Hz), 54.8 (t, 2C, *J* = 154 Hz, C-1 or 5), 52.4 (t, 2C, *J* = 154 Hz, C-1 or 5), 30.0 (t, *J* = 132 Hz, PCH₂), 16.0 (q, 2C, *J* = 134 Hz, PCH₃), 15.8 (q, 2C, *J* = 132 Hz, PCH₃).

IR (Nujol mull): 2910 (vs, br), 1460 (vs), 1372 (s), 1294 (w, br), 1270 (w,sh), 1150 (w, br), 1073 (vw), 930 (m), 920 (m, shoulder), 905 (w, shoulder), 882 (m), 796

(m), 708 (m, shoulder), 690 (w, sh) cm⁻¹.

Anal. Calc. for C₁₆H₃₀P₂Zr: C, 51.23; H, 8.06. Found: C, 49.33; H, 8.14.

2.2. Zr(C₅H₇)₂[P(CH₃)₂(C₆H₅)]

A three-neck flask equipped with a nitrogen inlet, addition funnel and magnetic stirring bar was charged with 1.00 g (2.65 mmol) of ZrCl₄(THF)₂ [7] and 30 ml of THF. Dimethylphenylphosphine (0.37 ml, 2.65 mmol) was added via syringe and the resulting pale pink solution was cooled to –78 °C prior to the addition of 1.15 g (10.9 mmol) of potassium pentadienide in 30 ml of THF. The resulting red solution was warmed to room temperature over the next 45 min during which time the color became a dark green/brown. After an additional 90 min at room temperature the solvent was removed in vacuo. Extraction of the green/brown solids with four 50 ml portions of hexane and filtration of the combined extracts through a Celite pad on a coarse frit gave a dark green solution. The filtrate was concentrated in vacuo to approx. 45 ml and then cooled to –5 °C overnight during which time the complex Zr(C₅H₇)₂[P(CH₃)₂(C₆H₅)] precipitated as a bright green powder. Removal of the supernatant via syringe and drying in vacuo resulted in 0.36 g of product (37% yield based on ZrCl₄(THF)₂, m.p. 136–138 °C (d)).

¹H NMR (benzene-*d*₆, ambient): δ 7.3–6.98 (m, 5H, Ph), 4.96 (app q, 4H, *J* ≈ 12Hz, 4H, H-2 and 4), 4.48 (t, 2H, *J* = 9.1 Hz, H-3), 2.64 (d, 4H, *J* = 11.4 Hz, H_{1,5exo}), 1.49 (d, 6H, *J* = 5.4 Hz, PCH₃), 0.18 (d of t, 4H, *J* = 14.2 Hz, 4.2 Hz, H_{1,5endo}).

Table 1
Crystallographic data for C₁₆H₃₀P₂Zr

(a) Crystal parameters			
Formula	C ₁₆ H ₃₀ P ₂ Zr	Z	4
Formula weight	375.6	cryst dimens, mm	0.21 × 0.21 × 0.33
Crystal system	orthorhombic	cryst color	purple
Space group	<i>Pbcn</i>	<i>D</i> (calc) (g cm ⁻³)	1.359
<i>a</i> (Å)	12.180(7)	<i>μ</i> (Mo Kα) (cm ⁻¹)	7.60
<i>b</i> (Å)	11.195(6)	temp. (K)	298
<i>c</i> (Å)	13.458(7)	<i>T</i> (max)/ <i>T</i> (min)	0.577/0.534
<i>V</i> (Å ³)	1835(2)		
(b) Data collection			
Diffractometer	Siemens P4	rflns. collected	1892
Monochromator	graphite	indpt. rflns.	1634
Radiation	Mo Kα (λ = 0.71073 Å)	indpt. obsvd. rflns. <i>F</i> ₀ ≥ 5σ(<i>F</i> ₀)	1016
2θ scan range (deg)	4.0–50.0	std. rflns., std./rfln.	3 std./197 rflns.
data collected (h, k, l)	+15, +14, +17	var. in stds. (%)	1
(c) Refinement ^a			
<i>R</i> (<i>F</i>) (%)	3.21	Δ(<i>ρ</i>) (e Å ⁻³)	0.36
<i>R</i> (<i>wF</i>) (%)	4.23	<i>N</i> _o / <i>N</i> _v	6.91
Δ/σ(max)	0.025	GOF	0.976

^a Quantity minimized = Σ*w*Δ²; *R* = ΣΔ/Σ(*F*₀); *R*(*w*) = ΣΔ*w*^{1/2}/Σ(*F*₀ · *w*^{1/2}), Δ = |(F_o – F_c)|.

Table 2
Atomic coordinates and isotropic thermal parameters (\AA^2)

Atom	x	y	z	U^*
Zr	0.5000	0.09405(5)	0.7500	0.0297(2)
P	0.5147(1)	0.2874(1)	0.62794(9)	0.0380(4)
C(1)	0.3040(4)	0.1590(5)	0.7352(4)	0.048(2)
C(2)	0.3189(4)	0.0615(5)	0.6711(4)	0.049(2)
C(3)	0.3547(4)	-0.0491(5)	0.7046(5)	0.050(2)
C(4)	0.3872(4)	-0.0807(4)	0.8030(5)	0.051(2)
C(5)	0.3942(4)	-0.0091(5)	0.8879(4)	0.053(2)
C(6)	0.5341(6)	0.4241(4)	0.7033(5)	0.062(2)
C(7)	0.6320(5)	0.3031(7)	0.5433(5)	0.069(3)
C(8)	0.4027(6)	0.3280(7)	0.5434(6)	0.059(2)

^{13}C NMR (benzene- d_6 , ambient): δ 130.0–127.7 (m, 6C, PPh), 106.2 (d, 4C, $J = 156$ Hz, C-2 and 4), 97.7 (d, 2C, $J = 162$ Hz, C-3), 52.6 (t, 4C, $J = 154$ Hz, C-1 and 5), 19.1 (q of d, 2C, $J = 130$ Hz, 16 Hz, PCH_3).

IR (Nujol mull): 2910 (vs, br), 1460 (vs), 1372 (s), 1290 (w, br), 1155 (m), 1070 (w, br), 935 (m), 918 (m), 880 (m), 780 (w), 718 (s, sh), 705 (w, sh), 685 (s) cm^{-1} .

^{31}P NMR (benzene- d_6 , ambient): δ 32.6 (s).

Anal. Calc. for $\text{C}_{18}\text{H}_{25}\text{PZr}$: C, 59.46; H, 6.93. Found: C, 59.11, H, 7.14.

2.3. Crystallographic studies

Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals were selected and mounted with epoxy cement to glass fibers. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20^\circ \leq 2\theta \leq 24^\circ$).

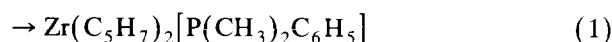
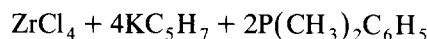
The systematic absences in the diffraction data are uniquely consistent for space group $Pbcn$. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Semi-empirical ellip-

oid absorption correction was applied to the data set. The molecule is located on a two-fold axis. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.1 Eclipse 32K version) program library (G. Sheldrick, Siemens XRD, Madison, WI). Pertinent data collection and refinement parameters are presented in Table 1, while atomic coordinates are given in Table 2, and bond distances and angles are given in Table 3. Additional information and the structure factor tables may be obtained from the authors.

3. Discussion

The reaction of ZrCl_4 with four equivalents of KC_5H_7 in the presence of $\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$ led to the spontaneous reduction of the zirconium center, and isolation of $\text{Zr}(\text{C}_5\text{H}_7)_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ (Eq. (1)). This reaction is quite analogous to ones observed for the 2,4- C_7H_{11} ligand [8], and thus indicates that many of the preferences (e.g., for metal ions in low oxidation states) exhibited by the 2,4- C_7H_{11} ligand also do carry over to analogs with lesser substitution patterns.

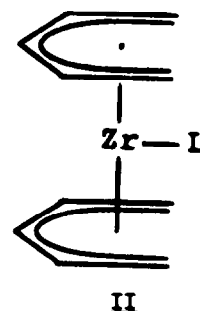


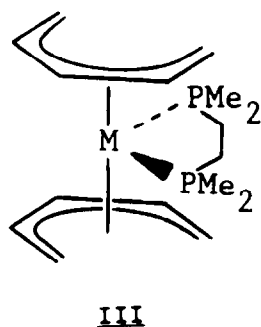
As was the case for the $\text{Zr}(2,4\text{-C}_7\text{H}_{11})_2(\text{PR}_3)$ complexes, one would expect $\text{Zr}(\text{C}_5\text{H}_7)_2\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ to exist in a syn-eclipsed conformation, as in **II**. Indeed, the ^1H and ^{13}C NMR spectra contain respectively four and three resonances attributable to the C_5H_7 ligand, in accord with this formulation. The chemical shifts and coupling constants are very much consistent with those of related compounds [8].

One interesting observation concerning the synthesis of this compound is that while the isolated solid product is green, the initial reaction solution is red. This suggested the possibility of an equilibrium between the green 16 electron complex, and 18 electron bis(phos-

Table 3
Pertinent bonding parameters for $\text{Zr}(\text{C}_5\text{H}_7)_2(\text{dmpe})$

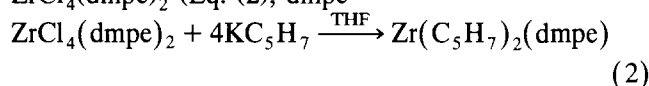
Bond lengths (\AA)			
Zr–P	2.724(1)	C(1)–C(2)	1.403(8)
Zr–C(1)	2.504(5)	C(2)–C(3)	1.389(8)
Zr–C(2)	2.475(5)	C(3)–C(4)	1.426(9)
Zr–C(3)	2.464(5)	C(4)–C(5)	1.399(8)
Zr–C(4)	2.494(5)	P–C(6)	1.851(6)
Zr–C(5)	2.538(6)	P–C(7)	1.836(6)
C(6)–C(6')	1.507(13)	P–C(8)	1.833(8)
Bond angle (deg.)			
P–Zr–P'	74.7(1)	Zr–P–C(6)	109.6(2)
C(1)–C(2)–C(3)	122.4(5)	Zr–P–C(7)	120.1(2)
C(2)–C(3)–C(4)	127.5(5)	Zr–P–C(8)	121.5(2)
C(3)–C(4)–C(5)	129.4(5)	C(6)–P–C(7)	99.3(3)
P–C(6)–C(6')	112.7(4)	C(6)–P–C(8)	103.3(3)
		C(7)–P–C(8)	99.8(3)





phine) complex [9]. Indeed, addition of a second equivalent of $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ to the complex in solution, followed by cooling, regenerated the red solution, which became green on warming to room temperature. A ^1H NMR spectrum of the red solution at -90°C showed a set of resonances entirely different from those of the 16 electron complex, consistent with the formation of a bis(ligand) adduct [10].

As the above data suggest that phosphine coordination is enthalpically favored, and decoordination entropically driven, the use of an appropriate chelating diphosphine ligand would be expected to allow for isolation of a bis(phosphine) adduct. Indeed, the reaction of $\text{ZrCl}_4(\text{dmpe})_2$ (Eq. (2), $\text{dmpe} =$



1,2-bis(dimethylphosphinoethane), led again to spontaneous reduction of the metal center, and formation of the deep purplish $\text{Zr}(\text{C}_5\text{H}_7)_2(\text{dmpe})_2$. The ^1H and ^{13}C NMR spectra contain respectively seven and five resonances for the pentadienyl fragments, indicating that the two ligands are equivalent but that there is no symmetry within the individual C_5H_7 groups. This implicates a structure such as **III**, with a C_2 axis of symmetry in the molecule. Analogous species are known for both allyl [11] and butadiene [12] complexes; however, $\text{Zr}(\text{2,4-C}_7\text{H}_{11})_2(\text{CO})_2$ has been shown to exist in a low symmetry structure, the probable cause being the presence of the methyl groups which disfavor a second CO coordination by an open dienyl edge [8].

An X-ray diffraction study has confirmed the structure as being that of **III** (Fig. 1), and in fact the molecule has crystallographically imposed C_2 symmetry. The $\text{Zr}-\text{C}$ bond lengths range from 2.464(5) to 2.538(6) Å, averaging 2.495 Å. The distances are greatest for the terminal CH_2 groups, which reside near the phosphorus centers, and shortest for the central carbon atoms. The $\text{Zr}-\text{C}(1,2)$ bond lengths are significantly shorter than the $\text{Zr}-\text{C}(4,5)$ counterparts, quite possibly a result of the C(4) and C(5) atoms being approx. 0.8–0.9 Å closer to the other dienyl plane than are the C(1) and C(2) atoms. For comparison, the $\text{Zr}-\text{C}$ bond lengths in $\text{Zr}(\text{2,4-C}_7\text{H}_{11})_2(\text{CO})_2$ range from 2.485(4) to 2.569(4)

Å, averaging 2.520 Å. The bonding in the dmpe complex may be favored by the absence of methyl groups on the dienyl ligand, and the fact that the pentadienyl ligands appear to be good acceptors, and as a result have their bonding enhanced by the inclusion of donating rather than accepting ligands in their coordination spheres [13].

There is an angle of 147.7° between the two C_5H_7 planes, compared to the value of 140.7° for $\text{Zr}(\text{2,4-C}_7\text{H}_{11})_2(\text{CO})_2$ [8]. The $\text{P}-\text{Zr}-\text{P}$ bite angle is $74.7(1)^\circ$, naturally smaller than the $\text{OC}-\text{Zr}-\text{CO}$ angle of $87.6(2)^\circ$ in $\text{Zr}(\text{2,4-C}_7\text{H}_{11})_2(\text{CO})_2$. The dienyl $\text{C}-\text{C}-\text{C}$ angles are rather unusual, with a value of only $122.4(5)^\circ$ around C(2), but much larger angles (approx. 128.5°) around C(3) and C(4). These deformations may minimize steric interactions between the dmpe and dienyl ligands.

Some evidence of the dmpe -dienyl steric interactions can be found in the placement of the dienyl hydrogen atoms, whose positions were successfully refined. In general, the dienyl substituents tend to tilt out of the dienyl plane towards the metal center, except for the “endo” positioned substituents on the terminal carbon atoms, which tilt away from the metal center. The former tilts reflect an attempt to point the dienyl p orbitals more toward the metal atom, which typically appears to be too small for effective overlap with these wide dienyl ligands [14]. However, zirconium(II) is a rather large transition metal ion, and should not have nearly the difficulty in achieving effective overlap as compared to the much smaller Fe(II) ion. In fact, the respective tilts [15] in the present case of 7.9° and 12.1° for the hydrogen atoms on C(2) and C(4) are reasonable, especially compared to the tilts of approx. 20.6° observed for $\text{Fe}(\text{1-Me}_3\text{Si-3-CH}_3\text{C}_5\text{H}_5)_2$ [16]. The tilt for the hydrogen atom on C(3) is smaller, at 2.5° , also in accord with earlier observations. One typically finds even greater tilts toward the metal center by the *exo* oriented substituents on the terminal carbon atoms, and

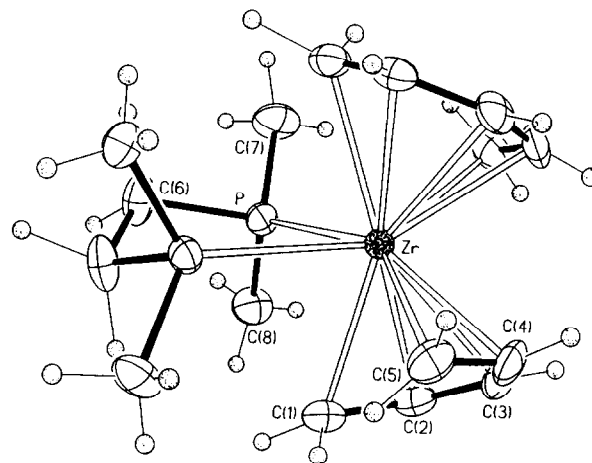


Fig. 1. Perspective view and numbering scheme for $\text{Zr}(\text{C}_5\text{H}_7)_2\text{[(CH}_3)_2\text{PC}_2\text{H}_4\text{P(CH}_3)_2]$.

that is indeed found for C(5), 17.3°. However, for C(1), the *exo* oriented hydrogen atom tilts away from the metal center, by 5.7°, an apparent result of its proximity to P', P, and C(8) (3.22, 3.28, and 3.42 Å, respectively). Regarding the *endo* hydrogen atoms on C(1) and C(5), as expected, they tilt away from the Zr(II) center, by 45.3° and 27.9°, respectively. Tilts of this sort have been attributed to a rehybridization of carbon atom orbitals, in order to improve overlap [14], and to a need to minimize H(*endo*)–H(*endo*) repulsions [17]. For a large metal ion like Zr(II), it would again be expected that there would be less of a need for such distortions. In fact, for Fe(1-Me₃Si-3CH₃C₅H₅)₂, a tilt of 48.9° was observed for the *endo* hydrogen atoms (cf., 42° for Fe(2,3,4-C₈H₁₃)₂) [18]. The tilt in the present structure of 45.3° for the *endo* hydrogen atom on C(1) would thus seem excessive, most likely occurring again in response to the proximity of P', P, and C(8). The tilt of 27.9° by the *endo* hydrogen atom on H(5) seems reasonable in this regard, and perhaps its tilt is actually reduced somewhat in response to the greater tilt by the other *endo* hydrogen atom.

While the Zr(2,4-C₇H₁₁)₂(CO)₂ and Zr(C₅H₇)₂(dmpe) complexes demonstrate that it is possible to prepare bis(ligand) adducts of open metallocenes, there is clearly a great deal of steric crowding that must be accommodated, as revealed by the facile loss of CO by the former, and from the structural data of the latter. As noted before, the wideness of the open dienylic ligands necessitates a much closer approach of its plane to the metal atom, as compared to C₅H₅ or C₅Me₅ ligands. As a result, the open ligands have larger cone angles and require much more room on metal coordination spheres.

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