

## Failure of Cyclopropyl Bromide to Add Oxidatively to $ZrCp_2(PMePh_2)_2$ : Reaction of $C_3H_5Br$ with $ZrCp_2(PMePh_2)_2$ in Toluene to Afford $ZrBr(CH_2Ph)Cp_2$

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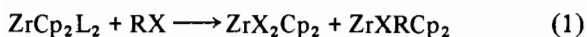
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### Abstract

Reaction of  $ZrCp_2(PMePh_2)_2$  (Cp =  $\eta^5$ -cyclopentadienyl) with cyclopropyl bromide in toluene, rather than affording  $ZrBr(C_3H_5)Cp_2$  as expected, affords  $ZrBr(CH_2Ph)Cp_2$  with the elimination of cyclopropane.

### Introduction

Reaction (1) summarizes a considerable body of chemistry that has been elucidated primarily by Schwartz and coworkers [1–4]



L =  $PMePh_2$ ,  $PMe_2Ph$ , R = alkyl, X = halide

If RX is a primary alkyl halide then  $ZrXRCp_2$  is the nearly exclusive Zr-containing product; if RX is a tertiary alkyl halide then  $ZrX_2Cp_2$  is the nearly exclusive Zr-containing product; if RX is a secondary alkyl halide then  $ZrX_2Cp_2$  and  $ZrXRCp_2$  form in roughly equivalent amounts. The reactions have been shown to proceed by radical processes [4].

In an attempt to prepare  $ZrBr(C_3H_5)Cp_2$  we reacted  $C_3H_5Br$  (cyclopropyl bromide), a secondary alkyl halide, with  $ZrCp_2(PMePh_2)_2$  in toluene. Neither  $ZrBr(C_3H_5)Cp_2$  nor  $ZrBr_2Cp_2$ , the expected products, was obtained. Rather, the major Zr-containing product is  $ZrBr(CH_2Ph)Cp_2$ .

### Experimental

All reactions were carried out under  $N_2$ . Infrared spectra were obtained from Nujol mulls on a Perkin-Elmer 283 Infrared Spectrophotometer.  $^1H$  NMR spectra at 270 MHz and  $^{31}P$  NMR spectra at 109.16

MHz were taken on a JEOL FX-270 FT-NMR spectrometer. Chemical shifts were obtained with reference to solvent peaks, and are given in ppm relative to TMS = 0.0. All spectra were recorded at 23 °C.

#### Preparation of $ZrCp_2(PMePh_2)_2$ [2]

A solution of 0.40 g (0.63 mmol) of  $[ZrH(CH_2C_6H_{11})Cp_2]_2$  [5] in 20 ml of degassed, dried toluene (distilled from titanocene), was treated with excess  $PMePh_2$  (0.75 ml, 3.8 mmol). The clear, almost colorless solution turned deep purple–black within a few seconds.

#### Preparation of $ZrBr(CH_2Ph)Cp_2$

The solution of  $ZrCp_2(PMePh_2)_2$  was allowed to stir for 30 min, then 0.43 ml (5.0 mmol) of  $C_3H_5Br$  (cyclopropyl bromide) was added. No visible change occurred at first. After 45 min some white solid had formed, and the mixture, now opaque, started to lighten in color. After 2 h the mixture, now yellow–orange, was filtered. A white solid and an orange filtrate resulted. The white solid was identified as  $[PMePh_2(C_3H_5)]Br$  by NMR and IR spectroscopy\*. The volume of the filtrate was reduced to ~3 ml by pumping, then 10 ml of dried, degassed hexane was added. The mixture was cooled to –30 °C in a freezer for several days. Orange crystals of  $ZrBr(CH_2Ph)Cp_2$  were obtained in 31% yield. The compound was identified through a crystal structure determination and by comparison with an authentic sample prepared by treating  $ZrBr_2Cp_2$  with  $PhCH_2MgBr$  [6]. IR: 1735(br, Ph CC overtone), 1590(s, Ph), 340(vs,  $\nu(Zr-Cp)$ ), 265(w, Cp ring tilt), and 243(w,  $\nu(Zr-Br)$ )  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  7.19(t, Ph),

\* $[PMePh_2(C_3H_5)]Br$ . White solid, slightly soluble in aromatic solvents, insoluble in alkanes, and very soluble in water.  $^{31}P$  NMR ( $CDCl_3$ ):  $\delta$  10.94 (free phosphine: –45.36) ppm.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.89(m), 7.75(m), 7.68(m), 2.86(d), 2.57(m), 1.50(m), 0.92(m), 0.86(m) ppm. IR (Nujol mull): 1685(w, br), 1588(m), 500(vs), 470(s), 422(m)  $cm^{-1}$ .

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6.98(d, Ph), 6.86(m, Ph), 5.64(s, Cp), 2.09(m, tol., CH<sub>3</sub>), and 1.96(s, CH<sub>2</sub>R) ppm.

The reaction was repeated, but with the use of toluene-d<sub>8</sub>, in order to monitor its progress through NMR spectroscopy.

#### Crystallographic Study of ZrBr(CH<sub>2</sub>Ph)Cp<sub>2</sub>

A suitable crystal was mounted directly into the cold stream (140 K) of a Picker FACS-1 X-ray diffractometer. Data collection proceeded smoothly until, as a result of a gas-flow problem, ice formed and the crystal was lost. Attempts to find other suitable crystals were unsuccessful. Crystal data and other details are given in Table I.

TABLE I. Crystal Data and Experimental Details for ZrBr-(CH<sub>2</sub>Ph)Cp<sub>2</sub>

Formula	C <sub>17</sub> H <sub>17</sub> BrZr
Formula weight	392.45
a (Å)	8.278(5)
b (Å)	11.149(5)
c (Å)	16.081(2)
β (°)	91.82(2)
V (Å <sup>3</sup> )	1483.5
Z	4
D <sub>calc</sub> (g/cm <sup>3</sup> )	1.757 (140 K) <sup>a</sup>
Space group	C <sub>2h</sub> <sup>5</sup> -P2 <sub>1</sub> /c
Crystal shape	Crystal bounded by faces {011}, {100}, and (110)
Crystal volume (mm <sup>3</sup> )	0.051
Radiation	Ni-filtered Cu Kα (λ(Cu Kα <sub>1</sub> ) = 1.540562 Å)
μ (cm <sup>-1</sup> )	92.0
Transmission factors	0.072 to 0.216
Take off angle	2.5°
Receiving aperture	4.0 wide by 5.0 high 32 cm from crystal
Scan speed (deg 2θ/min)	2.0
Scan width (°)	0.9 below Kα <sub>1</sub> to 1.0 above Kα <sub>2</sub>
Background counts	10 s with rescans option <sup>b</sup>
Data collected	h, k, ±l, 5 ≤ 2θ ≤ 80°; 25% of 80 ≤ 2θ ≤ 100°
No. of unique data	1044
p for calculation of σ(F <sub>o</sub> <sup>2</sup> )	0.03
No. unique data with F <sub>o</sub> <sup>2</sup> > 3σ(F <sub>o</sub> <sup>2</sup> )	996
Number of variables	77
R(F <sub>o</sub> )	0.083
R <sub>w</sub> (F <sub>o</sub> )	0.115

<sup>a</sup>The low-temperature system is based on a design by Huffman, ref. 8. <sup>b</sup>The diffractometer was run under the disk-oriented Vanderbilt system, ref. 9.

In the solution and refinement of this structure, procedures standard in this laboratory were employed [7]. The structure was solved from a Patterson function, followed by a combination of refinement and difference electron density calculations. The

structure was refined by full-matrix least-squares methods. Prior to the final cycle of refinement the positions of the H atoms were calculated assuming ideal geometry (C–H = 0.95 Å). These H positions were not varied in the final cycle of refinement. This final cycle was restricted to isotropic thermal motion for the non-hydrogen atoms, because of the limited number of data and the relatively small thermal motions of the atoms. Details on the refinement, including agreement indices, are given in Table I. Final positional and thermal parameters are given in Table II. See also 'Supplementary Material'.

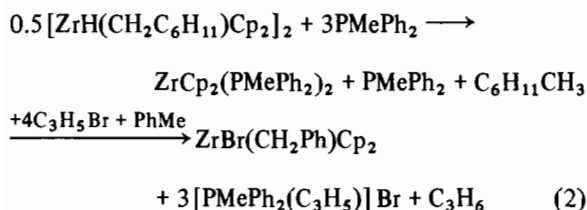
TABLE II. Positional and Thermal Parameters for ZrBr-(CH<sub>2</sub>Ph)Cp<sub>2</sub>

Atom	x	y	z	B (Å <sup>2</sup> )
Zr	0.66734(16)	0.17919(11)	0.614291(72)	0.60(7)
Br	0.51898(23)	0.00200(16)	0.67823(10)	2.00(8)
C(1)	0.5787(21)	0.3551(15)	0.52560(97)	1.5(4)
C(2)	0.4888(20)	0.2547(15)	0.49845(93)	1.6(4)
C(3)	0.3862(20)	0.2249(14)	0.56065(95)	1.4(3)
C(4)	0.4128(20)	0.3020(13)	0.62807(93)	1.0(3)
C(5)	0.5361(19)	0.3827(13)	0.60842(89)	0.8(3)
C(6)	0.8890(22)	0.1975(14)	0.5158(10)	1.7(4)
C(7)	0.9679(20)	0.1868(12)	0.59637(91)	0.9(3)
C(8)	0.9318(19)	0.0695(14)	0.62501(90)	1.0(3)
C(9)	0.8391(22)	0.0120(14)	0.5638(10)	1.2(4)
C(10)	0.8125(19)	0.0882(14)	0.49655(90)	1.1(3)
C(11)	0.7504(19)	0.2652(14)	0.73738(90)	1.0(3)
C(12)	0.8736(19)	0.2044(13)	0.79161(86)	0.6(3)
C(13)	1.0318(20)	0.2429(14)	0.80022(91)	1.3(3)
C(14)	1.1418(23)	0.1779(15)	0.8489(11)	2.6(4)
C(15)	1.0958(23)	0.0748(17)	0.8883(11)	2.7(4)
C(16)	0.9383(21)	0.0368(15)	0.8814(10)	2.0(4)
C(17)	0.8291(20)	0.1010(14)	0.83475(90)	1.2(3)
H1C(1)	0.662	0.398	0.495	2.6
H1C(2)	0.491	0.216	0.444	2.6
H1C(3)	0.309	0.160	0.558	2.4
H1C(4)	0.357	0.300	0.680	1.8
H1C(5)	0.582	0.444	0.644	1.9
H1C(6)	0.889	0.268	0.480	2.6
H1C(7)	1.034	0.247	0.625	1.7
H1C(8)	0.966	0.036	0.679	2.0
H1C(9)	0.796	-0.069	0.568	2.3
H1C(10)	0.751	0.069	0.446	2.1
H1C(13)	1.065	0.315	0.772	2.3
H1C(14)	1.255	0.205	0.854	3.4
H1C(15)	1.174	0.030	0.923	3.9
H1C(16)	0.905	-0.037	0.909	2.8
H1C(17)	0.718	0.075	0.830	2.1
H1C(11)	0.789	0.344	0.725	2.0
H2C(11)	0.654	0.275	0.770	2.0

## Results and Discussion

When ZrCp<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub> (prepared *in situ* [2]) reacts with C<sub>3</sub>H<sub>5</sub>Br in toluene the only Zr-containing product isolated is ZrBr(CH<sub>2</sub>Ph)Cp<sub>2</sub>, as character-

ized spectroscopically and from a crystal structure determination (see below). The reaction affords  $ZrBr(CH_2Ph)Cp_2$  only if toluene is used as the solvent and if four or more equivalents of  $C_3H_5Br$  are used. With solvents such as benzene, cyclohexane, or hexane only oligomeric Zr-containing products result. If three or less equivalents of  $C_3H_5Br$  are used only  $[PMePh_2(C_3H_5)]Br$  is formed. The overall reaction may be written:



That cyclopropane is produced in the reaction was established from the cyclopropane- $d_1$  resonances that appeared at 0.27 and 0.15 ppm when the reaction, monitored by NMR spectroscopy, was carried out with toluene- $d_8$  as the solvent.

The structure of  $ZrBr(CH_2Ph)Cp_2$  is shown in Fig. 1 while a short summary of bond distances and angles is given in Table III. The metrical details of the structure are unexceptional. The NMR data from a solution of  $ZrBr(CH_2Ph)Cp_2$  are consistent with the structure shown in Fig. 1.

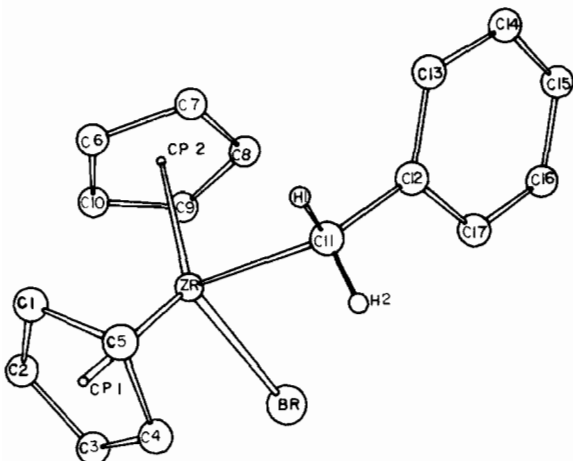


Fig. 1. A drawing of the structure of  $ZrBr(CH_2Ph)Cp_2$ . The spheres are of arbitrary size.

Probably the first step in the reaction is the abstraction of Br from  $C_3H_5Br$  to form  $[ZrBrCp_2]^+$  and  $[C_3H_5]^+$ . Abstraction of Br is known to be the first step in the oxidative addition of alkyl bromides to  $ZrCp_2(PMePh_2)_2$  [4]. For sterically hindered secondary bromides this step is faster than the capture of an alkyl radical by  $ZrCp_2(PMePh_2)_2$ . Probably  $[ZrBrCp_2]^+$  is too sterically hindered to capture  $[C_3H_5]^+$ . Hence the product originally sought,  $ZrBr-$

TABLE III. Brief Metrical Details for  $ZrBr(CH_2Ph)Cp_2$

Zr-Br	2.594(2) Å
Zr-Cp <sub>1</sub> <sup>a</sup>	2.21 Å
Zr-Cp <sub>2</sub>	2.19 Å
Zr-C(11)	2.29(1) Å
Zr-C(Cp)	2.47(2) to 2.53(2) Å
C(11)-C(12)	1.48(2) Å
C(Cp)-C(Cp)	1.37(2) to 1.44(2) Å
C(Ph)-C(Ph)	1.36(2) to 1.40(2) Å
Zr-C(11)-C(12)	120(1)°
Cp <sub>1</sub> -Zr-Cp <sub>2</sub>	131°
Cp <sub>1</sub> -Zr-Br	107°
Cp <sub>1</sub> -Zr-C(11)	104°
Cp <sub>2</sub> -Zr-Br	107°
Cp <sub>2</sub> -Zr-C(11)	105°
Br-Zr-C(11)	96.7(4)°

<sup>a</sup>Cp<sub>1</sub> = centroid of C(1)-C(5), Cp<sub>2</sub> = centroid of C(6)-C(10).

$(C_3H_5)Cp_2$ , is not obtained. The final product,  $ZrBr(CH_2Ph)Cp_2$ , could result from reaction of  $[ZrBrCp_2]^+$  either with toluene or with a benzyl radical produced by reaction of  $[C_3H_5]^+$  with toluene. Both pathways could account for formation of the observed cyclopropane- $d_1$  when the reaction is carried out in toluene- $d_8$ . However, if only three equivalents of  $C_3H_5Br$  are used, only  $[PMePh_2(C_3H_5)]Br$  is produced. The product  $ZrBr(CH_2Ph)Cp_2$ , would still be formed if  $[ZrBrCp_2]^+$  simply reacted with the solvent. Instead, we postulate that the initially produced equivalent of  $[C_3H_5]^+$  reacts quickly with  $PMePh_2$  to yield  $[PMePh_2(C_3H_5)]^+$ . This phosphonium radical then abstracts Br from  $C_3H_5Br$  to give  $[PMePh_2(C_3H_5)]Br$  and another equivalent of  $[C_3H_5]^+$ . This proceeds until all of the phosphine is converted into the phosphonium bromide. The remaining equivalent of  $[C_3H_5]^+$  then reacts with toluene to produce benzyl radicals. Solvents such as hexane, cyclohexane, and benzene, which form much less stable radicals than the benzyl radical, form only oligomeric Zr-containing products, further supporting this mechanism.

### Supplementary Material

Table IV listing structure amplitudes ( $\times 10$ ),  $10 |F_o|$  versus  $10 |F_c|$ , has been deposited with the Editor-in-Chief.

### Acknowledgement

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