# 1,3-Diphenylindenyl zirconium complexes. Synthesis, structure, and reduction reactions

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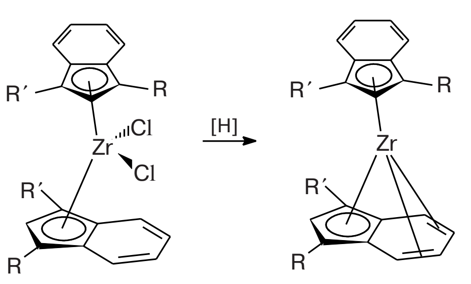
New zirconium sandwich complexes $(\eta^5\text{-}C_9H_5Ph_2)_2ZrCl_2$ (**1**) and $(\eta^5\text{-}C_9H_5Ph_2)(\eta^5\text{-}C_5(CH_3)_5)ZrCl_2$ (**2**) were synthesized and characterized. The molecular structures of complexes **1** and **2** were established by X-ray diffraction. The reduction of **1** and **2** does not stop at the formation of the $Zr^{II}$ derivatives with the $\eta^9$-coordinated indenyl ligand; instead the reaction results in the destruction of the metallocene structure.

**Key words:** 1,3-diphenylindenyl ligand, zirconium, reduction, X-ray diffraction study.

The recently synthesized[1—4] $Zr^{II}$ derivatives with the sterically crowded indenyl ligands are rare examples of thermally stable divalent zirconium compounds. The reactive metal centers in such complexes are stabilized through an additional reversible coordination of the six-membered ring to the metal atom (the $\eta^9$-coordination mode) (Scheme 1). Derivatives of $Zr^{II}$ with the 1,3-disubstituted ligands containing bulky alkyl ($Bu^t$ or $Pr^i$) or silyl ($SiMe_3$ or $SiPhMe_2$) substituents have been studied. With the aim of examining the possibility of the use of diaryl-substituted indenyl ligands for the preparation of divalent zirconium compounds, we synthesized the new bis-indenyl complexes $(\eta^5\text{-}1,3\text{-}C_9H_5Ph_2)_2ZrCl_2$ (**1**) and $(\eta^5\text{-}1,3\text{-}C_9H_5Ph_2)(\eta^5\text{-}C_5(CH_3)_5)ZrCl_2$ (**2**) and studied their reduction reactions.

**Scheme 1**



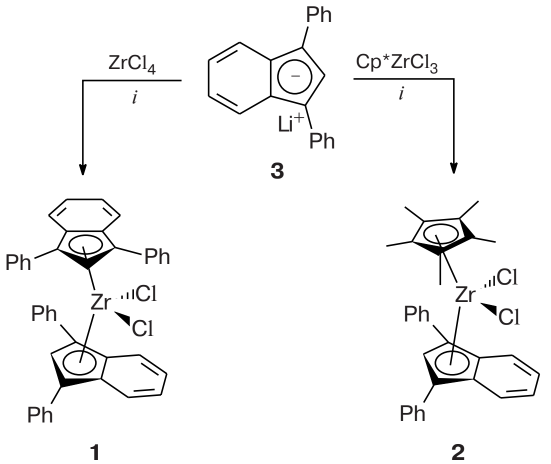
$R,R' = Pr^i, Bu^t, SiMe_3, SiMe_2Ph$

## Results and Discussion

Lithium 1,3-diphenylindenide (**3**) required for the synthesis of the target complexes was prepared by metallation of 1,3-diphenylindene with *n*-butyllithium. The pure product was isolated as an orange compound, which is extremely sensitive to atmospheric oxygen and moisture and is readily soluble in toluene, diethyl ether, and THF (unlike the first two solvents, a solution of compound **3** in THF exhibits strong fluorescence).

Sandwich complexes **1** and **2** were synthesized by heating compound **3** with $ZrCl_4$ and $Cp^*ZrCl_3$, respectively,

**Scheme 2**



*i*, Toluene, 100 °C.

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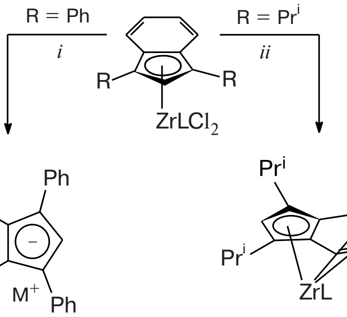
in toluene (Scheme 2). The target compounds, which are moderately stable in air, were isolated in the crystalline state and characterized. The molecular structures of complexes **1** and **2** were established by X-ray diffraction.

Studies of the reduction of **1** and **2** with magnesium amalgam in THF or with sodium in benzene showed that this reaction always affords magnesium or sodium 1,3-diphenylindenide, respectively, as the major product, *i.e.*, this reaction is accompanied by destruction of the metallocene structure. At the same time, the reactions of their isopropyl analogs $(\eta^5\text{-}1,3\text{-}C_9H_5Pr^i_2)_2ZrCl_2$ (see Ref. 2) and $(\eta^5\text{-}1,3\text{-}C_9H_5Pr^i_2)(\eta^5\text{-}Cp^*)ZrCl_2$ (see Ref. 4) with sodium amalgam give the thermally stable $Zr^{II}$ derivatives, *viz.*, $(\eta^9\text{-}1,3\text{-}C_9H_5Pr^i_2)(\eta^5\text{-}1,3\text{-}C_9H_5Pr^i_2)Zr$ and $(\eta^9\text{-}1,3\text{-}C_9H_5Pr^i_2)(\eta^5\text{-}Cp^*)Zr$, respectively (Scheme 3). Attempts to reduce compounds **1** and **2** with isobutyllithium[2] also failed. These reactions afforded mixtures of unidentified products. This difference in the results is apparently attributed to a much higher stability of the 1,3-diphenylindenyl anion compared to the diisopropyl-substituted analog, which substantially facilitates the reductive decomposition of the probable $Zr^{II}$ intermediates.

**Scheme 3**



M = 1/2 Mg, Na; L = $C_5Me_5$, $1,3\text{-}C_9H_5R_2$
*i*, Mg/Hg in THF or Na/Hg in $C_6D_6$; *ii*, Na/Hg, toluene.

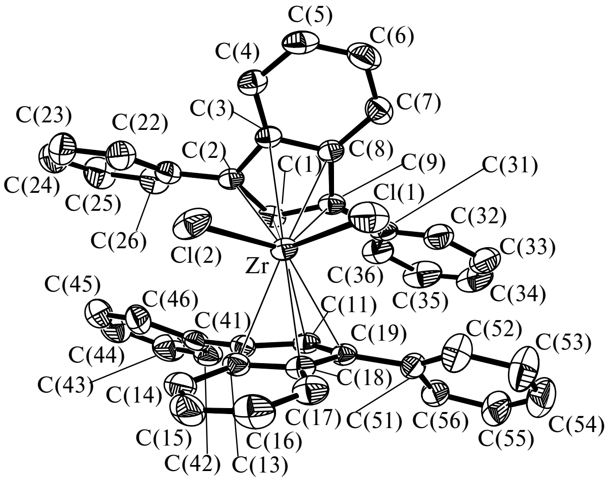


**Fig. 1.** Molecular structure of complex **1**. Hydrogen atoms are omitted.

**Table 1.** Selected bond lengths (*d*) and bond angles (ω) in the structure of compound **1***

| Bond | *d*/Å | Parameter | Value |
|---|---|---|---|
| Zr—Cl(1) | 2.4021(13) | Bond | *d*/Å |
| Zr—Pl(1)* | 2.255(2) | Zr—C(19) | 2.564(4) |
| Zr—C(1) | 2.500(4) | Zr—C(18) | 2.617(4) |
| Zr—C(9) | 2.510(4) | Zr—Cl(2) | 2.4147(14) |
| Zr—C(2) | 2.565(4) | Zr—C(11) | 2.486(3) |
| Zr—C(3) | 2.613(3) | | |
| Zr—C(8) | 2.632(4) | Angle | ω/deg |
| Zr—C(12) | 2.501(4) | Cl(1)—Zr—Cl(2) | 94.45(5) |

* The parameters Pl(1) and Pl(2) are the mean planes of the five-membered indenyl rings.

### Molecular structures of complexes 1 and 2

The molecular structure of bis-indenyl complex **1** is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 1. Compound **1** is a skewed metal sandwich. The angle between the $\eta^5$-coordinated five-membered rings is 61.5(1)°. The indenyl ligands adopt a staggered conformation. The phenylene moieties of the indenyl fragments are directed outward the zirconocene wedge. Both ligands are planar within 0.084(3) Å. The geometric parameters of **1** are, on the whole, similar to those found earlier in bis-indenyl zirconocene dichlorides (Cambridge Structural Database, version 5.28, 2007).[5]

The molecular structure of the mixed pentamethylcyclopentadienyl indenyl zirconocene **2** is shown in Fig. 2. Selected bond lengths and bond angles are given in Table 2. Compound **2** is a skewed metal sandwich. The angle between the $\eta^5$-coordinated five-membered rings is 54.6(2)°. The five-membered rings are in the mutually staggered conformation. The phenylene moiety of the indenyl ligand, like that in compound **1**, is directed outward the zirconocene wedge. It should be noted that this conformation has not been described earlier for mixed cyclopenta-

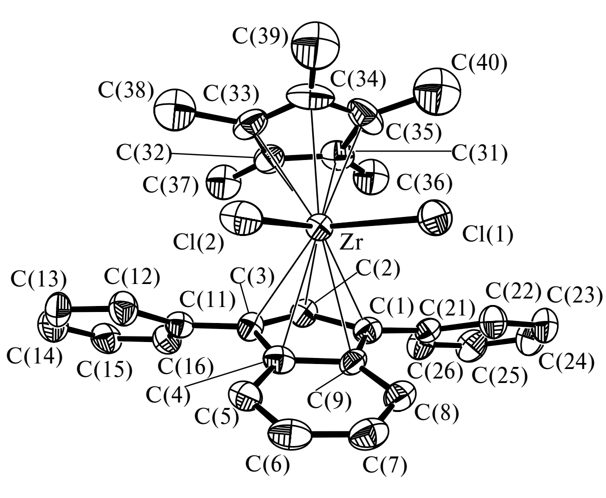


**Fig. 2.** Molecular structure of complex **2**. Hydrogen atoms are omitted.

**Table 2.** Selected bond lengths (*d*) and bond angles (ω) in the structure of compound **2***

| Bond | $d$/Å | Parameter | Value |
|---|---|---|---|
| Zr—Cl(1) | 2.4239(16) | Bond | $d$/Å |
| Zr—Pl(1)* | 2.211(2) | Zr—C(33) | 2.497(5) |
| Zr—Pl(2)* | 2.264(2) | Zr—C(31) | 2.513(6) |
| Zr—C(2) | 2.500(3) | Zr—C(32) | 2.519(6) |
| Zr—C(3) | 2.540(6) | Zr—C(35) | 2.532(6) |
| Zr—C(1) | 2.550(6) | | |
| Zr—C(4) | 2.630(6) | Angle | ω/deg |
| Zr—C(9) | 2.637(5) | Zr—Cl(2) | 2.4219(15) |
| Zr—C(34) | 2.495(5) | Cl(1)—Zr—Cl(2) | 94.80(7) |

* The parameters Pl(1) and Pl(2) are the mean planes of the five-membered cyclopentadienyl and indenyl rings, respectively.

dienyl indenyl zirconocenes. Both ligands are planar within 0.072(3) Å. As in most of the known indenyl complexes of $Zr^{IV}$, the Zr—C(2) distance (2.500(3) Å) is the shortest Zr—$C_{ind}$ distance.[5] The geometric parameters of **2** are, on the whole, similar to those found earlier in the related pentamethylcyclopentadienyl indenyl zirconium complexes $(Me_5C_5)(Ind)ZrCl_2$ (see Ref. 6) and $(Me_5C_5)$-(2-Ph-Ind)$ZrCl_2$.[7]

## Experimental

All operations, including the preparation of samples for NMR spectroscopy, were carried out under an inert atmosphere or in sealed evacuated Schlenk-type glassware. All solvents, including deuterated solvents, were purified according to standard procedures,[8] degassed, and recondensed under high vacuum ($10^{-3}$ Torr) directly into a reaction vessel or an NMR tube. Commercial $ZrCl_4$ (Fluka) was used without additional purification. Magnesium amalgam,[9] 1,3-diphenylindene,[10] and $Cp^*ZrCl_3$[11] were synthesized according to procedures described in the literature.

The $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 and 100 MHz, respectively) at 27 °C using the chemical shifts of the signals of the corresponding deuterated solvents (7.15 and 128.0 ppm for $C_6D_6$ and 1.73 and 25.3 ppm for THF-$d_8$, respectively) as the internal standard. The elemental analysis was carried out on an automated Carlo-Erba analyzer.

**Lithium 1,3-diphenylindenide, (1,3-IndPh$_2$)Li (3).** A 2.45 *M* *n*-BuLi solution in hexane (7.2 mL) was added with vigorous stirring and strong cooling to a solution of 1,3-diphenylindene (4.7 g, 17.5 mmol) in diethyl ether (50 mL). The yellow crystals that precipitated were separated by decantation, washed with diethyl ether, and dried under high vacuum. The mother liquor was concentrated, hexane was added, and the orange precipitate was separated, washed with a mixture of hexane and diethyl ether, and dried under high vacuum. The total yield was 3.94 g (14.4 mmol, 82%). $^1H$ NMR (THF-$d_8$), δ: 6.53 and 7.75 (both br.m, 2 H, H(4)—H(7)); 6.63 (br.t, 2 H, *p*-H); 7.07 (br.t, 4 H, *m*-H); 7.17 (s, 1 H, H(2)); 7.60 (br.d, 4 H, *o*-H). $^{13}C\{^1H\}$ NMR, δ: 111.77, 119.55 (C(1,3,3a,7a)); 115.19, 118.12 (C(4)H—C(7)H); 119.36 (*p*-CH); 125.14 (*o*-CH); 128.52 (*m*-CH); 131.65 (C(2)H); 144.46 (*ipso*-C).

**Bis(η$^5$-1,3-diphenylindenyl)dichlorozirconium (adduct with one toluene molecule), $(\eta^5\text{-}1,3\text{-}C_9H_5Ph_2)_2ZrCl_2 \cdot C_6H_5CH_3$ (1).** A mixture of $ZrCl_4$ (300 mg, 1.29 mmol) and salt **3** (790 mg, 2.88 mmol) in toluene was heated for 16 h in a boiling water bath. The solution was separated from the precipitate by decantation and concentrated to dryness. The residue was washed with hexane and dried under high vacuum. The product was obtained as an orange powder in a yield of 740 mg (0.94 mmol, 73%). Found (%): C, 75.01; H, 5.10. $C_{49}H_{38}Cl_2Zr$. Calculated (%): C, 74.60; H, 4.85. $^1H$ NMR ($C_6D_6$), δ 2.10 (s, 3 H, $PhC\underline{H}_3$); 6.70 (s, 2 H, H(2)); 6.85 (m, 4 H, H(4,7) or H(5,6)); 6.99—7.12 (m, 5 H, $\underline{Ph}CH_3$); 7.04 (m, 12 H, *m*-H, *p*-H); 7.44 (m, 8 H, *o*-H); 7.82 (m, 4 H, H(5,6) or H(4),H(7)). $^{13}C\{^1H\}$ NMR, δ: 21.36 ($Ph\underline{C}H_3$); 116.38 (CH(2)); 119.30 (C(1),C(3) or C(3a), C(7a)); 125.64 (*p*-CH in $PhCH_3$); 124.58, 127.10, 127.39 (*p*-CH, CH(4—7)); 128.51 (*m*-CH in $PhCH_3$); 128.56, 128.73 (*o*-CH, *m*-CH); 129.28 (*o*-CH in $PhCH_3$); 133.92 (*ipso*-C); 137.86 (*ipso*-C в $PhCH_3$).

Single crystals suitable for X-ray diffraction were grown by crystallization from hexane.

**(η$^5$-1,3-Diphenylindenyl)(η$^5$-pentamethylcyclopentadienyl)-dichlorozirconium, $(\eta^5\text{-}1,3\text{-}C_9H_5Ph_2)(\eta^5\text{-}C_5(CH_3)_5)ZrCl_2$ (2).** A mixture of $Cp^*ZrCl_3$ (640 mg, 1.92 mmol) and salt **3** (710 mg, 2.59 mmol) in toluene was heated for 16 h in a boiling water bath. The solution was separated from the precipitate by decantation and concentrated to dryness. The residue was washed with hexane and dried under high vacuum. The product was obtained as an orange powder in a yield of 1.03 g (1.82 mmol, 95%). Found (%): C, 66.13; H, 5.40. $C_{31}H_{30}Cl_2Zr$. Calculated (%): C, 65.94; H, 5.35. $^1H$ NMR (THF-$d_8$), δ: 1.64 (s, 15 H, $C_5Me_5$); 7.12 (s, 1 H, H(2)); 7.30 (m, 2 H, H(4),H(7) or H(5),H(6)); 7.34 (t, 2 H, *p*-H, $^3J_{H,H}$ = 7.4 Hz); 7.47 (t, 4 H, *m*-H, $^3J_{H,H}$ = 7.6 Hz); 7.95 (m, 6 H, *o*-H, H(5),H(6) or H(4),H(7)). $^{13}C\{^1H\}$ NMR, δ: 12.25 ($C_5\underline{Me}_5$); 115.20 (CH(2)); 117.46, 130.53 (C(1),C(3),C(3a),C(7a)); 125.03, 126.77, 128.07 (*p*-CH, C(4)H—C(7)H); 125.86 ($\underline{C}_5Me_5$); 129.16, 130.65 (*o*-CH, *m*-CH); 134.48 (*ipso*-C).

$^1H$ NNMR ($C_6D_6$), δ: 1.53 (s, 15 H, $C_5Me_5$); 6.58 (s, 1 H, H(2)); 7.13 (m, 4 H, *p*-H, H(4),H(7) or H(5),H(6)); 7.27 (t, 4 H, *m*-H, $^3J_{H,H}$ = 7.3 Hz); 7.85 (d, 4 H, *o*-H, $^3J_{H,H}$ = 7.6 Hz); 8.06 (m, 2 H, H(5),H(6) or H(4),H(7)). $^{13}C\{^1H\}$ NMR, δ: 12.16 ($C_5\underline{Me}_5$); 113.83 (CH(2)); 116.82 (C(1),C(3) or C(3a),C(7a)); 124.54, 126.84, 127.49 (*p*-CH, C(4)H-C(7)H); 125.24 ($\underline{C}_5Me_5$); 128.63 (*m*-CH); 130.15 (*o*-CH, C(3a),C(7a) or C(1),C(3)); 133.90 (*ipso*-C).

Single crystals suitable for X-ray diffraction were grown by crystallization from hexane.

**Reduction of complexes 1 and 2 with activated manganese.** A solution of complex **1** or **2** (~50 mg) in THF-$d_8$ (0.6 mL) was stirred with Mg/Hg (30 mg, ~15 equiv.) at 25 °C for 2 days. The dark-brown solution was separated from the precipitate and quantitatively transferred into an NMR tube. The main signals in the $^1H$ and $^{13}C$ NMR spectra of the reaction mixtures are assigned to diphenylindenide anion **3**.

**X-ray diffraction study of complexes 1 and 2.** The X-ray diffraction data sets were collected on automated Enraf-Nonius CAD 4 (for **1**) and Bruker SMART APEX II (for **2**) diffractometers (MoKα radiation, λ = 0.71073 Å, graphite monochromator). The structures of **1** and **2** were solved by direct methods (SHELX-86).[12] All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method based on $F^2$

**Table 3.** Crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for compounds **1** and **2**

| Parameter | **1** | **2** |
|---|---|---|
| *M* | 696.78 | 564.67 |
| Crystal dimensions/mm | 0.40S0.20S0.03 | 0.25S0.20S0.15 |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | *Pbca* | $P2_1$ |
| *a*/Å | 13.098(5) | 8.922(4) |
| *b*/Å | 13.289(3) | 14.153(7) |
| *c*/Å | 37.290(14) | 10.940(5) |
| b/deg | 90 | 110.568(4) |
| $V$/Å$^3$ | 6491(4) | 1293.3(11) |
| *Z* | 8 | 2 |
| $d_{calc}$/g cm$^{-3}$ | 1.426 | 1.450 |
| μ/mm$^{-1}$ | 0.533 | 0.650 |
| *F*(000) | 2848 | 580 |
| *T*/°K | 293(2) | 303(2) |
| θ Scan range/deg | 2.25—25.48 | 2.83—28.00 |
| Number of measured reflections | 10016 | 11863 |
| Number of independent reflections ($R_{int}$) | 6018 (0.0701) | 6029 (0.0339) |
| Number of reflections with $I \geq 2\sigma(I)$ | 2239 | 5084 |
| Number of refined parameters | 406 | 288 |
| $R_1$ ($I \geq 2\sigma(I)$) | 0.0371 | 0.0474 |
| $wR_2$ (based on all reflections) | 0.0771 | 0.1138 |
| Goodness-of-fit on $F^2$ | 0.852 | 1.075 |
| Residual electron density (min/max) /e Å$^{-3}$ | 0.353/−0.511 | 0.610/−0.495 |

(SHELXL-97).[13] All hydrogen atoms were positioned geometrically and refined using a riding model. The structure of **2** is pseudosymmetric and can be solved in the centrosymmetric space group $P2_1/m$, but the refinement in this space group gave unsatisfactory results. In addition, the crystal of **2** was a racemic twin (the Flack parameter is 0.22(6)). The X-ray diffraction data collection and refinement statistics are given in Table 3.

## References

1. C. A. Bradley, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.*, 2003, **125**, 8110.
2. C. A. Bradley, I. Keresztes, E. Lobkovsky, V. G. Young, P. J. Chirik, *J. Am. Chem. Soc.*, 2004, **126**, 16937.
3. C. A. Bradley, E. Lobkovsky, I. Keresztes, P. J. Chirik, *J. Am. Chem. Soc.*, 2005, **127**, 10291.
4. C. A. Bradley, I. Keresztes, E. Lobkovsky, P. J. Chirik, *Organometallics*, 2006, **25**, 2080.
5. F. H. Allen, *Acta Cryst., Section B*, 2002, **58**, 380.
6. M. A. Schmid, H. G. Alt, W. Milius, *J. Organomet. Chem.*, 1996, **514**, 45.
7. R. Kravchenko, A. Masood, R. M. Waymouth, C. L. Myers, *J. Am. Chem. Soc.*, 1998, **120**, 2039.
8. W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, 4 ed., Oxford, 1996, 529.
9. D. P. Krut'ko, M. V. Borzov, L. G. Kuz'mina, A. V. Churakov, D. A. Lemenovskii, O. A. Reutov, *Inorg. Chim. Acta*, 1998, **280**, 257.
10. W. G. Miller, C. U. Pittman, *J. Org. Chem.*, 1974, **39**, 1955.
11. G. H. Llinas, M. Mena, F. Palacios, P. Royo, R. Serrano, *J. Organomet. Chem.*, 1988, **340**, 37.
12. G. M. Sheldrick, *Acta Cryst., Section A*, 1990, **A46**, 467.
13. G. M. Sheldrick, SHELXL-97. *Program for the Refinement of Crystal Structures*, (University of Göttingen, Germany), 1997.

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