

Mono- and bis-[2-(*P,P*-dimethylphosphanyl)ethyl]tetramethylcyclopentadienyl zirconium(IV) complexes: Synthesis and structural studies in crystalline state and in solutions

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Abstract

Synthetic routines for a new ligand $C_5Me_4CH_2CH_2PMe_2$ (**2b**) in forms of its Li- (**2b-Li**), Na- (**2b-Na**) salts and in the CH-form (**2b-H**), as well as for silanes $Me_3Si-C_5H_4CH_2CH_2PMe_2$ (**3a**) and $Me_3Si-C_5Me_4CH_2CH_2PMe_2$ (**3b**) have been developed. On the basis of it, new half-sandwich $[\eta^5:\eta^1-\kappa P-C_5H_4CH_2CH_2PMe_2]ZrCl_3$ (**4a**), $[\eta^5:\eta^1-\kappa P-C_5Me_4CH_2CH_2PMe_2]ZrCl_3$ (**4b**) and sandwich $[\eta^5-C_5Me_4CH_2CH_2PMe_2]_2ZrCl_2$ (**5**), $[\eta^5-C_5Me_4CH_2CH_2PMe_2][\eta^5-C_5Me_5]ZrCl_3$ (**6**) complexes of Zr(IV) have been prepared and characterized. Along with them, the first example of X-ray structurally characterized dinuclear Zr(IV) complex incorporating both sandwich (**6**) and half-sandwich (**4b**) moieties linked one to another by means of $Zr \leftarrow P$ coordination bond **7**, has been described. Formation of an analogously organized trinuclear complex **8**, built from one sandwich fragment of **5** and two half-sandwich fragments of **4b** was proved by NMR spectroscopy methods. Molecular structures of half-sandwich complexes in their solvent-free dimeric forms (**4a** and **4b**) and as 1:1 adducts with THF (**4a-THF** and **4b-THF**) along with those of dinuclear complex **7** have been established by X-ray diffraction analyses. The dynamic behavior for di- and trinuclear complexes **7** and **8**, due to the intermolecular dissociation–coordination of the Me_2P -groups in THF-*d*₈ solutions has been studied by variable-temperature NMR spectroscopy. © 2005 Elsevier B.V. All rights reserved.

Keywords: Zirconium; Cyclopentadienyl ligands; Intramolecular coordination; P ligands; Dynamic behavior

1. Introduction

During the last two decades the chemistry of the organotransition metal complexes bearing pendant organophosphanyl groups has been developing rapidly [1]. Among these groups the dimethylphosphanyl functionality seems to be one of the most attractive due to its small size and high coordination capability.

Despite the compounds containing the dimethylphosphanyl moiety are somewhat synthetically “inconvenient” objects because of their extreme sensitivity to atmospheric oxygen, a representative series of side-chain Me_2P -functionalized cyclopentadienyl ligands and metal complexes derived from them has been prepared and characterized [1–10]. Here we report the preparation of a new ring-permethylated cyclopentadienyl ligand $C_5Me_4CH_2CH_2PMe_2$ along with half-sandwich and sandwich Zr(IV) complexes derived from it. For the structure and dynamic behavior comparison, a

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half-sandwich Zr(IV) complex derived from the known ring-non-permethylated $C_5H_4CH_2CH_2PMe_2$ ligand [2,8,11] was also prepared.

2. Results and discussion

2.1. Monocyclopentadienyl $Me_2PCH_2CH_2$ -functionalized complexes of Zr(IV)

2.1.1. Synthesis of (2-dimethylphosphanylethyl) substituted half sandwich Zr(IV) complexes **4a** and **4b**

The half-sandwich complexes $[\eta^5:\eta^1-\kappa P-C_5H_4CH_2CH_2PMe_2]ZrCl_3$ (**4a**) and $[\eta^5:\eta^1-\kappa P-C_5Me_4CH_2CH_2PMe_2]ZrCl_3$ (**4b**) were prepared via corresponding ring-silylated cyclopentadienes **3a** and **3b**. The silanes **3a** and **3b**, in their turn, were synthesized from alkali metal salts **2a** [2,11], **2b-Li** or **2b-Na** (prepared analogously to its Ph_2P -counterpart [12]) (see Scheme 1). Noteworthy, application of silanes **3a** and **3b** allows to completely avoid formation of the corresponding sandwich complexes and facilitates the synthetic procedure, especially in part concerning isolation of the target half-sandwiches.

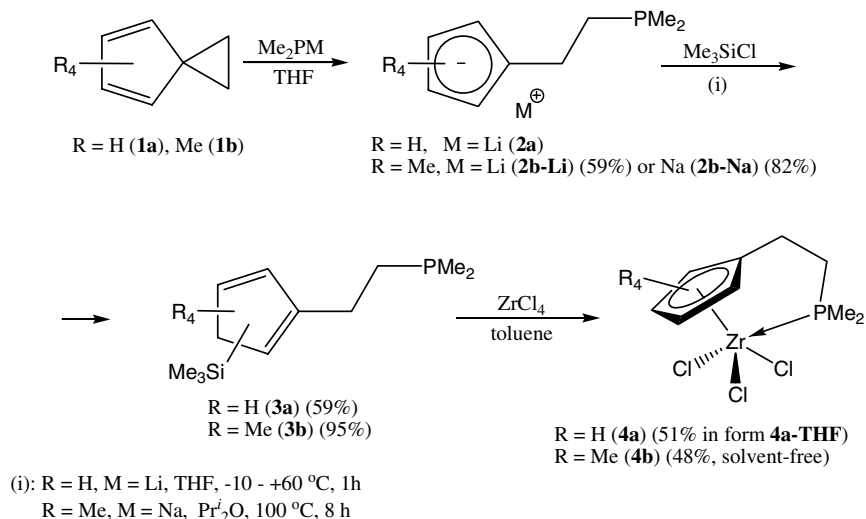
Ligand **2b** was also isolated and characterized in its CH-form $HC_5Me_4CH_2CH_2PMe_2$ **2b-H** by quenching the dry sodium salt **2b-Na** with MeOH. Exposure of the hexane solution of **2b-H** to air under stirring results in graduate oxidation of the dimethylphosphanyl group to the dimethylphosphanyl one $[HC_5Me_4CH_2CH_2P(=O)Me_2]$, three isomers in almost equimolar ratios; $\delta(^{31}P)$: 37.8, 37.9, 39.2 ppm], with the reaction completed after 8 h.

Previously we reported that silylation of ring-peralkylated lithium cyclopentadienides in THF is accompanied

by a parasite process of the solvent ring cleavage [13]. To avoid this misfortune, the silylation was performed in diisopropyl ether with more soluble and reactive sodium salt **2b-Na** at elevated temperature that gave excellent yield of silane **3b**.

It should be noted here, that while reaction of $ZrCl_4$ with the ring-non-permethylated silane **3a** proceeds relatively smoothly, formation of **4b** requires more strict conditions and was performed at 100 °C. This lower reactivity of the ring-permethylated silane, obviously, is due to its higher sterical hindrance.

As it was observed earlier for the Ph_2P - [12,14] and Me_2N - [13] analogues, complexes **4a** and **4b** form 1:1 adducts with THF **4a-THF** and **4b-THF**. However, the stability of these adducts in respect to the solvent-free complexes is markedly different. Thus, purification of compound **4a** requires its conversion into **4a-THF** (the same concerns $[\eta^5:\eta^1-\kappa P-C_5H_4CH_2CH_2PPh_2]ZrCl_3$ [14]). Despite the fact that crystals of the solvent-free **4a** (dimer $\{[\eta^5:\eta^1-\kappa P-C_5H_4CH_2CH_2PMe_2]ZrCl_2\}_2(\mu-Cl)_2$) suitable for X-ray diffraction analysis could be obtained by slow recrystallization of **4a-THF** from CH_2Cl_2 , complete removal of THF from this adduct not accompanied by the complex destruction seems to be, at least, difficult. Contrarily to it, ring-permethylated half-sandwich **4b** was initially isolated as a solvent-free dimer $\{[\eta^5:\eta^1-\kappa P-C_5Me_4CH_2CH_2PMe_2]ZrCl_2\}_2(\mu-Cl)_2$ (from THF (!); most likely, the solvent molecule is lost during drying the compound on a high-vacuum line even at room temperature). Single crystals of adduct **4b-THF** were prepared by a slow growth of its crystals from the saturated solution in THF. Noteworthy, that no monomeric forms of solvent-free **4a** or **4b** were observed (vide infra).



Scheme 1.

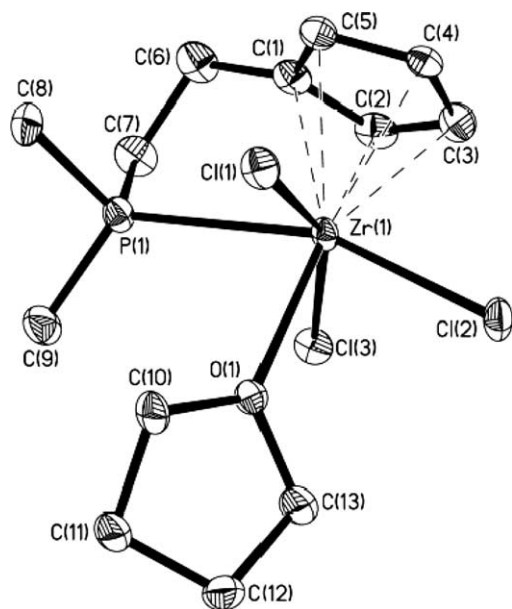


Fig. 1. Molecular structure of complex **4a**-THF. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 50% probability level.

2.1.2. X-ray structural investigation of half-sandwich complexes **4a**, **4b** and their 1:1 adducts with THF **4a-THF** and **4b-THF**

The molecular structure of complex **4a**-THF in its general features is very close to that of formerly reported for $[\eta^5:\eta^1-\kappa P-C_5H_4CH_2CH_2PPh_2]ZrCl_3 \cdot THF$ [14] (see Fig. 1). The selected bond lengths and angles for **4a**-THF are listed in Table 1. The coordination polyhedron of the Zr-atom represents a distorted octahedron (assuming that the Cp-ring occupies one coordination place), with chlorine atoms and phosphorous atom lying in the equatorial positions and the oxygen atom (THF) and the centroid of the Cp-ring (Cp_{cent}) placed at the apical ones. The principal structural parameters of **4a**-THF and $[\eta^5:\eta^1-\kappa P-C_5H_4CH_2CH_2PPh_2]ZrCl_3 \cdot THF$ are virtually close, except the considerably shorter distance of the Zr–P distance in **4a**-THF [compare 2.7702(9) Å in **4a**-THF vs. 2.8729(11), 2.8707(11), and 2.8474(5) Å in $[\eta^5:\eta^1-\kappa P-C_5H_4CH_2CH_2PPh_2]ZrCl_3 \cdot THF$ (two crystallographically independent units in modification 1 and modification 2, respectively)].

As it was mentioned above, in crystalline state the solvent-free **4a** molecule presents a centrosymmetric dimer $\{[\eta^5:\eta^1-\kappa P-C_5H_4CH_2CH_2PMe_2]ZrCl_2\}_2(\mu-Cl)_2$ in which two zirconium centers are connected with two bridging chlorine atoms Cl(1) and Cl(1a) (see Fig. 2). The selected bond lengths and angles for **4a** are listed in Table 2.

The coordination polyhedron of the metal center is a distorted octahedron (assuming that the Cp-ring occupies one coordination place), with the phosphorous atom and three chlorine atoms placed at the equatorial

Table 1
Selected bond lengths (Å) and angles (°) for complex **4a**-THF

| | |
|-------------------|------------|
| Zr(1)–O(1) | 2.370(2) |
| Zr(1)–C(4) | 2.475(4) |
| Zr(1)–Cl(2) | 2.4832(9) |
| Zr(1)–Cl(1) | 2.4896(9) |
| Zr(1)–C(3) | 2.493(3) |
| Zr(1)–Cl(3) | 2.4947(9) |
| Zr(1)–C(5) | 2.539(3) |
| Zr(1)–C(2) | 2.540(3) |
| Zr(1)–C(1) | 2.593(3) |
| Zr(1)–P(1) | 2.7702(9) |
| P(1)–C(7) | 1.820(4) |
| P(1)–C(9) | 1.825(4) |
| P(1)–C(8) | 1.830(4) |
| O(1)–C(10) | 1.460(4) |
| O(1)–C(13) | 1.470(5) |
| O(1)–Zr(1)–Cl(2) | 80.64(6) |
| O(1)–Zr(1)–Cl(1) | 77.45(6) |
| Cl(2)–Zr(1)–Cl(1) | 94.51(3) |
| O(1)–Zr(1)–Cl(3) | 77.12(6) |
| Cl(2)–Zr(1)–Cl(3) | 93.14(3) |
| Cl(1)–Zr(1)–Cl(3) | 151.83(3) |
| O(1)–Zr(1)–P(1) | 79.52(6) |
| Cl(2)–Zr(1)–P(1) | 159.67(3) |
| Cl(1)–Zr(1)–P(1) | 85.49(3) |
| Cl(3)–Zr(1)–P(1) | 78.16(3) |
| C(7)–P(1)–C(9) | 103.44(18) |
| C(7)–P(1)–C(8) | 104.1(2) |
| C(9)–P(1)–C(8) | 105.0(2) |
| C(7)–P(1)–Zr(1) | 103.40(14) |
| C(9)–P(1)–Zr(1) | 121.46(15) |
| C(8)–P(1)–Zr(1) | 117.18(12) |
| C(10)–O(1)–C(13) | 108.0(3) |
| C(10)–O(1)–Zr(1) | 127.1(2) |
| C(13)–O(1)–Zr(1) | 124.6(2) |

Distance Zr–PL is 2.223(2) Å. PL – the mean plane for atoms C(1)–C(5).

positions while the Cp-centroid and chlorine atom Cl(1a) (belongs to another subunit) situated at the apical places. Thus, each of the symmetrically equivalent chlorine atoms Cl(1) and Cl(1a) is in a *cis*-equatorial (in respect to P-atom) position towards its “own” Zr-atom and in an apical position towards another metal center. The cyclic fragment Zr(1)–Cl(1)–Zr(1a)–Cl(1a)–[Zr(1)] is a parallelogram, with the lengths of the “covalent” bonds Zr(1)–Cl(1) markedly shorter than those of “coordination” ones Zr(1)–Cl(1a) (2.5576(3) vs. 2.7893(3) Å, respectively). This structural motif is typical for $MeOCH_2CH_2-$ [15], $MeSCH_2CH_2-$ [16], and even for bulkier 8-quinolinylyl substituted monocyclopentadienyl [17] complexes of Zr(IV). Of interest, this type of spatial organization was not observed for solvent-free $[\eta^5:\eta^1-\kappa N-C_5H_4CH_2CH_2NMe_2]ZrCl_3$ (monomeric) [13] and $[\eta^5:\eta^1-\kappa P-C_5H_4CH_2CH_2PPh_2]ZrCl_3$ (only complicated solvent-free ionic product corresponding to formula $\{[\eta^5:\eta^1-\kappa P-C_5H_4CH_2CH_2PPh_2]ZrCl_2(\mu-Cl)_3\}_2^+[(ZrCl_3)_2(\mu-Cl)_2]^{2-}$ was crystallographically characterized [14]). The Zr–P distances in

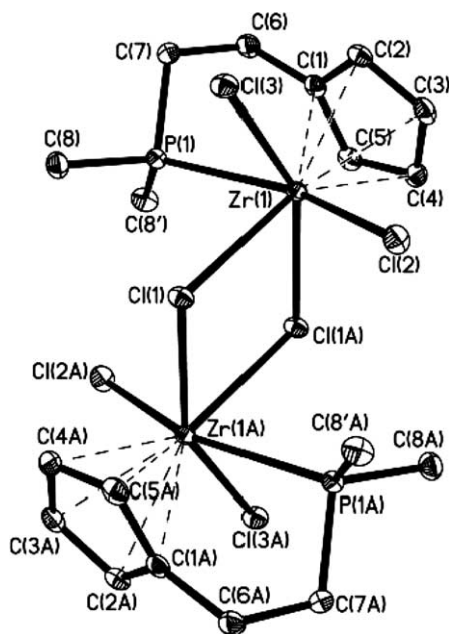


Fig. 2. Molecular structure of complex **4a**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 50% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for complex **4a**

| | |
|--------------------|-------------|
| Zr(1)–Cl(3) | 2.4721(3) |
| Zr(1)–Cl(2) | 2.4758(3) |
| Zr(1)–C(4) | 2.4864(13) |
| Zr(1)–C(3) | 2.5090(13) |
| Zr(1)–C(5) | 2.5292(13) |
| Zr(1)–C(2) | 2.5473(13) |
| Zr(1)–Cl(1A) | 2.5576(3) |
| Zr(1)–C(1) | 2.5854(13) |
| Zr(1)–P(1) | 2.7733(4) |
| Zr(1)–Cl(1) | 2.7893(3) |
| P(1)–C(8) | 1.8144(14) |
| P(1)–C(8') | 1.8207(14) |
| P(1)–C(7) | 1.8321(13) |
| Cl(1)–Zr(1A) | 2.5576(3) |
| Cl(3)–Zr(1)–Cl(2) | 90.496(12) |
| Cl(3)–Zr(1)–Cl(1A) | 148.692(11) |
| Cl(2)–Zr(1)–Cl(1A) | 93.099(11) |
| Cl(3)–Zr(1)–P(1) | 78.873(11) |
| Cl(2)–Zr(1)–P(1) | 160.175(11) |
| Cl(1A)–Zr(1)–P(1) | 87.732(10) |
| Cl(3)–Zr(1)–Cl(1) | 78.450(10) |
| Cl(2)–Zr(1)–Cl(1) | 81.633(10) |
| Cl(1A)–Zr(1)–Cl(1) | 71.357(11) |
| P(1)–Zr(1)–Cl(1) | 79.876(10) |
| C(8)–P(1)–C(8') | 105.51(7) |
| C(8)–P(1)–C(7) | 105.00(7) |
| C(8')–P(1)–C(7) | 101.60(7) |
| C(8)–P(1)–Zr(1) | 118.15(5) |
| C(8')–P(1)–Zr(1) | 121.54(5) |
| C(7)–P(1)–Zr(1) | 102.39(4) |
| Zr(1A)–Cl(1)–Zr(1) | 108.643(11) |

Symmetry transformations used to generate equivalent atoms: $-x + 1, -y, -z + 1$. Distance Zr–PL is 2.2238(6); Å. PL – the mean plane for atoms C(1)–C(5).

solvent-free complex **4a** (2.7733(4) Å) are nearly the same as in **4a**-THF.

The molecular structures of ring-permethylated complexes **4b**-THF and **4b** (see Figs. 3 and 4, Tables 3 and 4, respectively) in their general features are similar to those of **4a**-THF and **4a**. Permethylation of the cyclopentadienyl ring only slightly affects the Zr–P distances and practically does not affect the Zr–O(THF) bond lengths. The coordination environments of the P-atoms in all of the half-sandwiches of question are distorted tetrahedrons, with the angles C–P–C lying within a rather narrow range (101.60(7)–105.51(7)°). At the same time, the

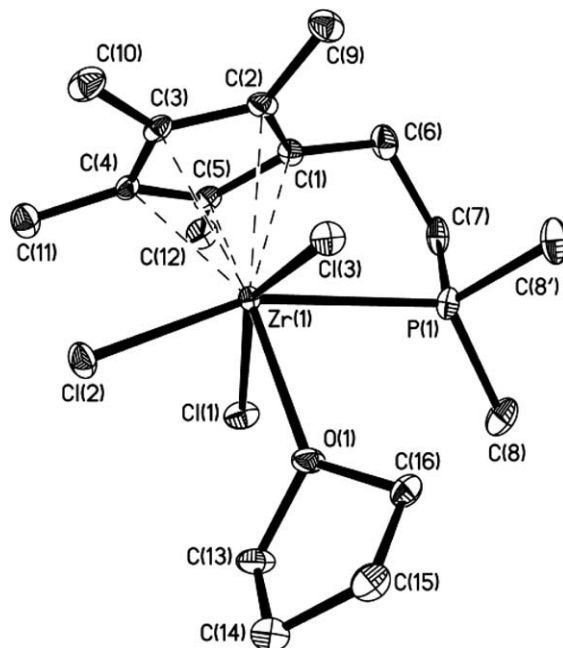


Fig. 3. Molecular structure of complex **4b**-THF. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 50% probability level.

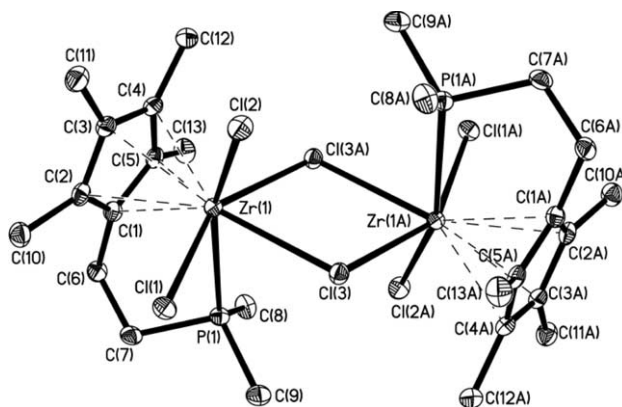


Fig. 4. Molecular structure of complex **4b**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 50% probability level.

Table 3
Selected bond lengths (Å) and angles (°) for complex **4b**-THF

| | |
|-------------------|------------|
| Zr(1)–O(1) | 2.374(2) |
| Zr(1)–Cl(2) | 2.4652(7) |
| Zr(1)–Cl(1) | 2.4819(7) |
| Zr(1)–Cl(3) | 2.4953(7) |
| Zr(1)–C(3) | 2.515(3) |
| Zr(1)–C(4) | 2.526(3) |
| Zr(1)–C(2) | 2.561(3) |
| Zr(1)–C(1) | 2.570(3) |
| Zr(1)–C(5) | 2.581(3) |
| Zr(1)–P(1) | 2.7850(8) |
| P(1)–C(8) | 1.814(3) |
| P(1)–C(8') | 1.818(3) |
| P(1)–C(7) | 1.821(3) |
| O(1)–Zr(1)–Cl(2) | 79.40(5) |
| O(1)–Zr(1)–Cl(1) | 76.20(5) |
| Cl(2)–Zr(1)–Cl(1) | 94.74(3) |
| O(1)–Zr(1)–Cl(3) | 76.72(5) |
| Cl(2)–Zr(1)–Cl(3) | 91.48(3) |
| Cl(1)–Zr(1)–Cl(3) | 150.54(3) |
| O(1)–Zr(1)–P(1) | 78.83(5) |
| Cl(2)–Zr(1)–P(1) | 158.18(3) |
| Cl(1)–Zr(1)–P(1) | 78.74(3) |
| Cl(3)–Zr(1)–P(1) | 84.86(2) |
| C(8)–P(1)–C(8') | 103.25(18) |
| C(8)–P(1)–C(7) | 102.21(16) |
| C(8')–P(1)–C(7) | 103.54(17) |
| C(8)–P(1)–Zr(1) | 121.02(12) |
| C(8')–P(1)–Zr(1) | 120.15(12) |
| C(7)–P(1)–Zr(1) | 103.91(11) |
| C(16)–O(1)–C(13) | 104.2(2) |
| C(16)–O(1)–Zr(1) | 131.22(17) |
| C(13)–O(1)–Zr(1) | 124.38(18) |

Distance Zr–PL is 2.249(1) Å. PL – the mean plane for atoms C(1)–C(5).

“exocyclic” angles C(Me)–P–Zr (117.18(12)–124.24(9)°) are distinctly greater than the “endocyclic” angles C(7)–P–Zr (102.39(4)°). However, taking into account the known great s-character of the lone pair at the phosphorous atom one could not conclude this to be indicative of some considerable constriction of the Zr(1)–C(1)–C(6)–C(7)–P(1)–(Zr(1)) pseudo-metallacycle.

2.1.3. The variable-temperature NMR studies of half-sandwich complexes **4a** and **4b** in solutions

For complexes **4a** and **4b**, the variable-temperature NMR spectroscopy data unambiguously indicate the retention of the P → Zr coordination both in solvating (THF-*d*₈) and non-solvating (CD₂Cl₂) media. Within the temperature range –90 to +55 °C no particular changes are observed in their ³¹P NMR spectra, with the variations of δ(³¹P) not exceeding 3 ppm. Of interest, with the decrease of temperature in the ¹H NMR spectrum of **4a**-THF in CD₂Cl₂ the signals of free (non-coordinated) THF appear. At the same time, the molar ratio of the coordinated THF and the complex remains equal to 1:1. This liberation of THF is due to crystallization of dimeric complex **4a** from the solution.

Table 4
Selected bond lengths (Å) and angles for complex **4b**

| | |
|--------------------|-------------|
| Zr(1)–Cl(2) | 2.4612(6) |
| Zr(1)–Cl(1) | 2.4676(6) |
| Zr(1)–C(4) | 2.505(2) |
| Zr(1)–C(3) | 2.535(2) |
| Zr(1)–C(5) | 2.541(2) |
| Zr(1)–Cl(3A) | 2.5426(6) |
| Zr(1)–C(1) | 2.546(2) |
| Zr(1)–C(2) | 2.551(2) |
| Zr(1)–P(1) | 2.7890(7) |
| Zr(1)–Cl(3) | 2.7997(6) |
| P(1)–C(9) | 1.812(3) |
| P(1)–C(8) | 1.823(3) |
| P(1)–C(7) | 1.831(3) |
| Cl(2)–Zr(1)–Cl(1) | 92.09(2) |
| Cl(2)–Zr(1)–Cl(3A) | 91.21(2) |
| Cl(1)–Zr(1)–Cl(3A) | 147.49(2) |
| Cl(2)–Zr(1)–P(1) | 158.74(2) |
| Cl(1)–Zr(1)–P(1) | 77.650(19) |
| Cl(3A)–Zr(1)–P(1) | 87.934(18) |
| Cl(2)–Zr(1)–Cl(3) | 79.213(19) |
| Cl(1)–Zr(1)–Cl(3) | 76.835(19) |
| Cl(3A)–Zr(1)–Cl(3) | 72.056(19) |
| P(1)–Zr(1)–Cl(3) | 80.327(18) |
| Zr(1A)–Cl(3)–Zr(1) | 107.944(19) |
| C(9)–P(1)–C(8) | 103.20(13) |
| C(9)–P(1)–C(7) | 105.45(12) |
| C(8)–P(1)–C(7) | 102.17(12) |
| C(9)–P(1)–Zr(1) | 118.35(9) |
| C(8)–P(1)–Zr(1) | 124.24(9) |
| C(7)–P(1)–Zr(1) | 100.72(9) |

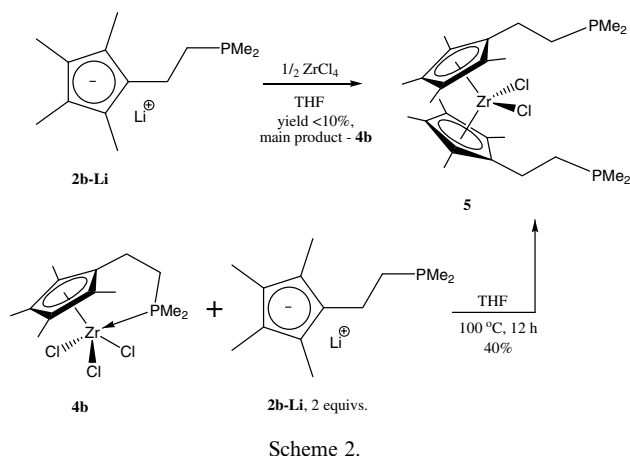
Symmetry transformations used to generate equivalent atoms: –*x* + 2, –*y*, –*z*. Distance Zr(1)–PL is 2.229(1) Å. PL – the mean plane for atoms C(1)–C(5).

Thus, the coordination-dissociation lability of the phosphanyl group seems not to be attributive for the Zr(IV) ← P compounds of the question and was observed in few cases only [14,18,19].

2.2. Biscyclopentadienyl Me₂PCH₂CH₂-functionalized complexes of Zr(IV)

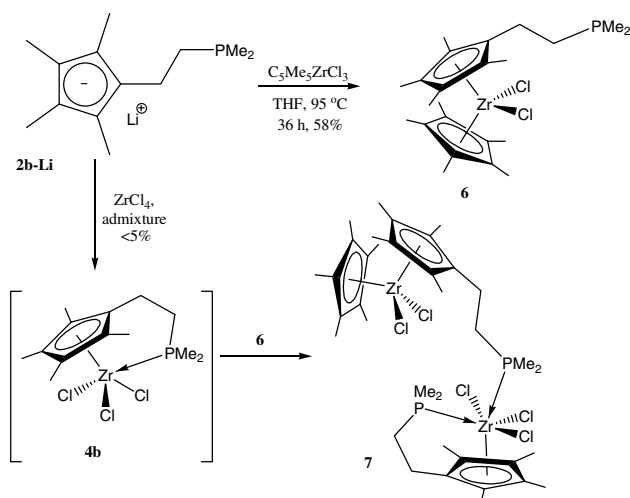
Nowadays among the organometallic chemists there is a steady opinion that preparation of biscyclopentadienyl complexes of Zr(IV), especially symmetrically ligated ones, is a routine and trivial procedure of too little interest to be paid a particular attention. This section demonstrates how far away from the real matter of things this viewpoint may be.

Thus, it turned out that the evident approach to symmetrically ligated biscyclopentadienyl complex [η⁵-C₅Me₄CH₂CH₂PMe₂]₂ZrCl₂ (**5**) starting from 2 equivalents of lithium salt **2b**-Li and ZrCl₄ is not a good one and among the products both the desired sandwich complex **5** and half-sandwich complex **4b** are present, with the **4b** dominating in the reaction mixture. Further workup of the product mixture with excess of **2b**-Li allowed to isolate the target compound **5** in only 10% yield (see Scheme 2).



Consequently, an attempt to obtain complex **5** starting from half-sandwich **4b** and a two-fold excess of salt **2b-Li** was undertaken. The NMR spectroscopy monitoring of this reaction mixture revealed that after 12h of heating at 100 °C only ~67% of initial **4b** converted into **5**. Further prolongation of the reaction time gives no result and even after 120 h heating at 100 °C the composition of the mixture remained nearly the same. The target product **5** was isolated, finally, from this reaction mixture in an acceptable yield by multiple fractional low-temperature crystallizations from hexane.

Preparation of the ring-peralkylated unsymmetrically ligated complex $[\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{PMe}_2][\eta^5\text{-C}_5\text{Me}_5]\text{-ZrCl}_2$ (**6**) met less problems and it was synthesized accordingly to Scheme 3 and purified by crystallization from hexane. However, the insoluble in aliphatic hydrocarbons residue remaining after crystallization (formed in small amounts) possessed abnormally high melting point (234–236 °C). Recrystallization of the latter from THF provided single crystals suitable for X-ray diffraction analysis. Thus, the residue was assigned the struc-



ture of a dinuclear zirconium complex **7** (see Fig. 5; the selected bond lengths and angles are listed in Table 5). Formation of complex **7** can be explained by presence of small (<5%) amounts of ZrCl_4 as an admixture in initial $[\eta^5\text{-C}_5\text{Me}_5]\text{ZrCl}_3$.

Analysis of the Cambridge Structural Database [20] reveals that complex **7** is the first example of a structurally characterized zirconium compound that incorporates both sandwich and half-sandwich Zr(IV) fragments linked one to another by the non-transition element $\rightarrow\text{Zr(IV)}$ coordination bond. In case of complex **7**, The bridging $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{PMe}_2$ ligand coordinates in the η^5 -fashion to one of the Zr atoms and in η^1 - κP -fashion to another metal center. The bicyclopentadienyl part of the complex presents a bent sandwich with the $\text{Cp}_{\text{cent}}\text{-Zr(2)-Cp}_{\text{cent}}$ angle 135.9° what is within the typical range and close to the corresponding value for the similarly substituted decaalkylzirconocene dichloride $[\eta^5\text{-C}_5\text{Me}_4\text{C}_2\text{H}_5]_2\text{ZrCl}_2$ [21]. In the monocyclopentadienyl fragment of **7**, the coordination polyhedron of the Zr(1) atom is a distorted octahedron (assuming that the Cp-ring takes one coordination place). However, in this case the apical position opposite to the Cp-ring is occupied not by the bridging chlorine atom, as in **4a** and **4b**, or by oxygen atom, as in **4a-THF** and **4b-THF**, but by the phosphorous atom related to the sandwich moiety. In the half-sandwich subpart of **7**, like it was observed for **4a** and **4b** and their O- [15], S- [16], and N- [13] counterparts the apical bond is considerably longer than the corresponding equatorial bond [compare Zr(1)-P(2) 2.8468(9) Å vs. Zr(1)-P(1) 2.7873(9) Å].

^1H and ^{31}P NMR spectra of **7** in $\text{THF-}d_8$ present nearly a superposition of those for **4b** and **6** in an equimolar ratio. In $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, there are two signals at $\delta(^{31}\text{P})$ -8.5 and -39 ppm (integral ratio 1:1, P(1) and P(2), respectively; for numbering see Fig. 5). However, at room temperature the signal related to the P(2) atom is broad what could be assigned to the apical Me_2P -group coordination-dissociation equilibrium. At -70 °C, this equilibrium “freezes” and in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum two doublets at $\delta(^{31}\text{P})$ -6.9 and -26.2 ppm ($^2J_{\text{PP}} = 10$ Hz, equatorial and axial phosphanyl groups, respectively) are observed. So, the low temperature spectrum of **7** is in an excellent agreement with the X-ray structural data.

These results on observation of dinuclear complex **7** enforced us to re-examine the reaction between **4b** and **2b-Li** more attentively and study the insoluble in hexane fraction left after purification of complex **5b**. NMR-spectroscopy data indicate, that in ~80% this residue presents the analogous to **7** trinuclear complex **8** (see Scheme 4), comprising a sandwich moiety of **5** linked by its two pendant dimethylphosphanyl groups to two half-sandwich moieties of **4b** in the manner like in dinuclear complex **7**. Indeed, the ^1H and $^{13}\text{P}\{^1\text{H}\}$ NMR

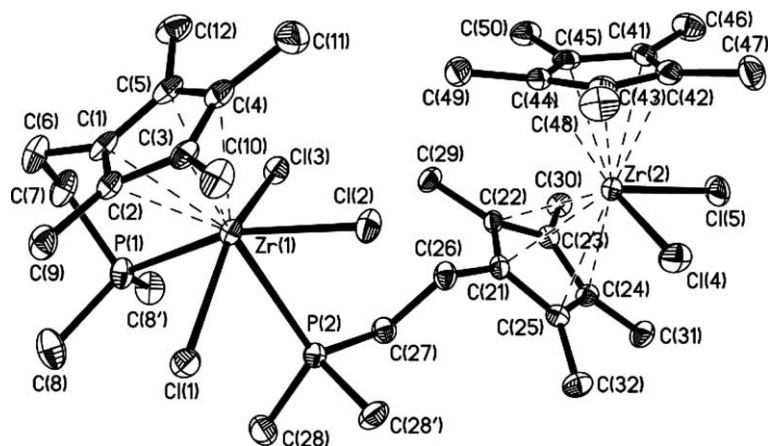


Fig. 5. Molecular structure of complex 7. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 50% probability level.

spectra of **8** in THF are, practically, a superposition of those of **4b** and **5** in 2:1 molar ratio. In the $^{13}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** there are two signals at $\delta(^{31}\text{P})$ -8.6 (sharp singlet) and -39 ppm (broad signal) of the integral ratio 1:1. The decrease of temperature down to -70 °C causes changes nearly identical to the ones in case of compound **7** and two doublets at $\delta(^{31}\text{P})$ -7.1 and -25.6 ppm ($^2J_{\text{PP}} = 10$ Hz, equatorial and axial phosphanyl groups, respectively; integral ratio 1:1) are observed.

We consider that the very difficulties conjugated with preparation of complex **5** are due to the great affinity of the Me_2P -group towards the Zr(IV) electron-deficient center, on one hand, and sterical hindrances, on the other. In the course of the reaction between **4b** and **2b-Li**, each molecule of newly formed sandwich **5** can “block” up to two molecules of initial **4b** into a sterically hindered and coordinatively saturated complex **8**, that dramatically decreases the rate of the reaction and, practically, stops it far away from completion. Possible to say, that this reaction relates to auto-inhibitory ones.

3. Experimental

3.1. General remarks

All procedures were performed in sealed-off evacuated glass vessels. The employed solvents (and their perdeuterated analogues) were dried with and distilled from conventional agents (namely: diethyl ether and THF – with sodium benzophenone ketyl; toluene, alifatic hydrocarbons – with Na–K alloy; CH_2Cl_2 – with P_2O_5 and then with CaH_2). Methanol was refluxed with metal Mg (MgOMe) under argon, degassed and kept over MgOMe. When performing procedures in evacuated vessels, the degassed solvents were stored in evacuated reservoirs over corresponding drying agent and transferred on a high vacuum line directly into reaction

vessels by trapping them with liq. N_2 . Trimethylchlorosilane (Fluka) was refluxed with and distilled from aluminium powder (high vacuum line). $[\eta^5\text{-C}_5(\text{CH}_3)_5\text{-ZrCl}_3$ [22,23], solutions of Me_2PLi and Me_2PNa in THF [24], 4,5,6,7-tetramethylspiro[2,4]heptadiene-4,6 [12], and lithium salt **2a** [2,11] were prepared accordingly to the reported procedures. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded on a Varian VXR-400 spectrometer at 400, 100 and 162 MHz, respectively. For ^1H and ^{13}C spectra, the solvent resonances [$\delta_{\text{H}} = 7.15$ and $\delta_{\text{C}} = 128.0$ (C_6D_6), $\delta_{\text{H}} = 5.32$ and $\delta_{\text{C}} = 53.8$ (CD_2Cl_2), $\delta_{\text{H}} = 1.73$ and $\delta_{\text{C}} = 25.3$ ($\text{THF-}d_8$)] were used as internal reference standards. For $^{31}\text{P}\{^1\text{H}\}$ spectra, 85% H_3PO_4 was employed as an external reference. For temperature calibration, the standard methanol and ethyleneglycol sample was used. Mass spectra were measured on Kratos-MS-890 and Varian MAT CH7a Fa spectrometers. The elemental analyses were performed on the Carlo-Erba automated analyzer.

3.2. Synthetic procedures

3.2.1. Trimethylsilyl-(2-P,P-dimethylphosphanylethyl)-cyclopentadiene **3a**

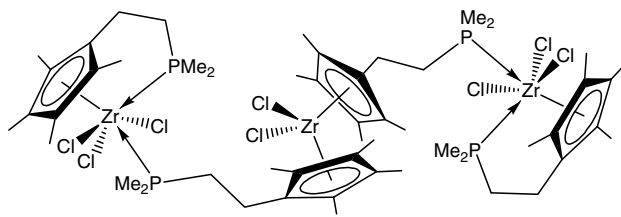
To a solution of the lithium salt **2a** (1.55 g, 9.73 mmol) in THF (40 mL), a solution of Me_3SiCl (1.3 mL, 1.10 g, 10.10 mmol) was added at vigorous stirring and cooling at -10 °C. The mixture was allowed to warm up to room temperature and the stirring was continued for additional 20 min. The solvent and unreacted Me_3SiCl were removed under high vacuum from a bath maintained at 60 °C. The residue was subjected to high-vacuum molecular distillation that gave 1.30 g of colorless oil. Yield 59.0%. ^1H NMR (listed for allylic isomers) (25 °C, C_6D_6): δ -0.07 (s, 9H, SiMe_3), 0.84 (d, 6H, $^2J_{\text{HP}} = 2.8$ Hz, PMe_2), 1.54 (m, 2 H, CH_2P), 2.56 (q, 2H, $^3J_{\text{HH}} = 8.4$ Hz, $^3J_{\text{HP}} = 8.4$ Hz, $\text{CH}_2\text{CH}_2\text{P}$), 3.17 [br s, 1H, $\text{CH}(\text{SiMe}_3)$], 6.11 (br s, 1H, $=\text{CH}-$), 6.43 (br s, 1H, $=\text{CH}-$), 6.54 (br s, 1H, $=\text{CH}-$). $^{13}\text{C}\{^1\text{H}\}$ NMR

Table 5
Selected bond lengths (Å) and angles (°) for complex 7

| | |
|-------------------|------------|
| Zr(1)–Cl(3) | 2.4813(8) |
| Zr(1)–Cl(1) | 2.4855(9) |
| Zr(1)–Cl(2) | 2.4877(8) |
| Zr(1)–C(3) | 2.522(3) |
| Zr(1)–C(1) | 2.547(3) |
| Zr(1)–C(2) | 2.547(3) |
| Zr(1)–C(4) | 2.548(3) |
| Zr(1)–C(5) | 2.590(3) |
| Zr(1)–P(1) | 2.7873(9) |
| Zr(1)–P(2) | 2.8468(9) |
| Zr(2)–Cl(4) | 2.4441(9) |
| Zr(2)–Cl(5) | 2.4455(9) |
| Zr(2)–C(21) | 2.509(3) |
| Zr(2)–C(23) | 2.528(3) |
| Zr(2)–C(41) | 2.538(3) |
| Zr(2)–C(45) | 2.538(3) |
| Zr(2)–C(42) | 2.539(3) |
| Zr(2)–C(22) | 2.550(3) |
| Zr(2)–C(25) | 2.553(3) |
| Zr(2)–C(24) | 2.554(3) |
| Zr(2)–C(43) | 2.559(3) |
| Zr(2)–C(44) | 2.575(3) |
| P(1)–C(8) | 1.815(4) |
| P(1)–C(8') | 1.816(4) |
| P(1)–C(7) | 1.822(4) |
| P(2)–C(28') | 1.820(4) |
| P(2)–C(27) | 1.831(3) |
| P(2)–C(28) | 1.835(4) |
| Cl(3)–Zr(1)–Cl(1) | 146.60(3) |
| Cl(3)–Zr(1)–Cl(2) | 93.41(3) |
| Cl(1)–Zr(1)–Cl(2) | 96.20(3) |
| Cl(3)–Zr(1)–P(1) | 76.60(3) |
| Cl(1)–Zr(1)–P(1) | 82.62(3) |
| Cl(2)–Zr(1)–P(1) | 157.62(3) |
| Cl(3)–Zr(1)–P(2) | 79.53(3) |
| Cl(1)–Zr(1)–P(2) | 72.01(3) |
| Cl(2)–Zr(1)–P(2) | 75.90(3) |
| P(1)–Zr(1)–P(2) | 82.54(3) |
| Cl(4)–Zr(2)–Cl(5) | 93.74(3) |
| C(8)–P(1)–C(8') | 104.1(2) |
| C(8)–P(1)–C(7) | 103.8(2) |
| C(8')–P(1)–C(7) | 101.0(2) |
| C(8)–P(1)–Zr(1) | 118.94(14) |
| C(8')–P(1)–Zr(1) | 122.57(14) |
| C(7)–P(1)–Zr(1) | 103.38(13) |
| C(28')–P(2)–C(27) | 101.6(2) |
| C(28')–P(2)–C(28) | 99.9(2) |
| C(27)–P(2)–C(28) | 100.7(2) |
| C(28')–P(2)–Zr(1) | 111.29(13) |
| C(27)–P(2)–Zr(1) | 119.57(11) |
| C(28)–P(2)–Zr(1) | 120.53(13) |

Distances Zr(1)–PL(1), Zr(2)–PL(2) and Zr(2)–PL(3) are 2.247(1), 2.233(1) and 2.245(1) Å, respectively. PL(1), PL(2) and PL(3) – mean planes for atom groups C(1)–C(5), C(21)–C(25) C(41)–C(45), respectively.

(25 °C, C₆D₆): δ –1.99 (s, SiMe₃), 14.15 (d, ¹J_{CP} = 14.8 Hz, PMe₂), 26.48 (d, ²J_{CP} = 14.8 Hz, CH₂CH₂P), 32.94 (d, ¹J_{CP} = 11.8 Hz, CH₂P), 50.98 [(s, CH(SiMe₃)], 127.08 (s, =CH–), 132.42 (s, =CH–), 134.10 (s, =CH–), 146.43 (d, ³J_{CP} = 11.0 Hz, =CCH₂CH₂P). ³¹P{¹H} NMR (25 °C, C₆D₆): δ –50.4 (s). EI MS



8

Scheme 4.

(70 eV) *m/z* (%): 226 (0.1) [M]⁺, 164 (7.8) [M – HPMe₂]⁺, 153 (14.8) [M – SiMe₃]⁺, 151 (35.6) [M – CH₂PMe₂]⁺, 92 (100) [M – SiMe₃ – PMe₂]⁺, 91 (59.6) [C₇H₇]⁺, 78 (93.4) [C₅H₄=CH₂]⁺, 75 (35.7) [CH₂PMe₂]⁺, 73 (45.4) [SiMe₃]⁺, 61 (8.1) [PMe₂]⁺, 47 (23.5) [HPMe]⁺, 40 (26.2) [C₃H₄]⁺.

3.2.2. Lithium (2-*P,P*-dimethylphosphanylethyl)tetramethylcyclopentadienide **2b-Li**

To a solution of Me₂PLi prepared from tetramethyldiphosphane (1.80 g, 14.7 mmol) and excess of Li sand (0.5 g) in THF (50 mL), a solution of tetramethylspiroheptadiene **1** (4.29 g, 28.9 mmol) in THF (10 mL) was added at room temperature and the reaction mixture was stirred overnight. The solution was then heated at 60 °C for 30 min and then concentrated under high vacuum and gentle heating down to ca. 10 mL and ether (80 mL) was entered. The white voluminous precipitate was filtered off from the orange-red mother liquor, washed three times with the same composition of solvents and dried on the high-vacuum line. White voluminous powder. Yield 3.70 g (59.0%, based on **1**). ¹H NMR (25 °C, THF-*d*₈): δ 0.95 [s, 6H, P(CH₃)₂], 1.27 (br m, 2H, CH₂P), 1.71, 1.72 [each s, 6H, C₅(CH₃)₄], 2.21 (br m, 2H, CH₂CH₂P). ¹³C NMR (25 °C, THF-*d*₈): δ 10.80, 10.90 [each q, ¹J_{CH} = 123 Hz, C₅(CH₃)₄], 14.42 [qd, ¹J_{CH} = 126 Hz, ¹J_{CP} = 14.8 Hz, P(CH₃)₂], 22.65 (td, ¹J_{CH} = 125 Hz, ²J_{CP} = 14.3 Hz, CH₂CH₂P), 35.97 (td, ¹J_{CH} = 128 Hz, ¹J_{CP} = 10.0 Hz, CH₂P), 105.85, 106.78 (each s, CCH₃), 112.89 (d, ³J_{CP} = 13.3 Hz, CCH₂CH₂P). ³¹P{¹H} NMR (25 °C, THF-*d*₈): δ –51.6 (s).

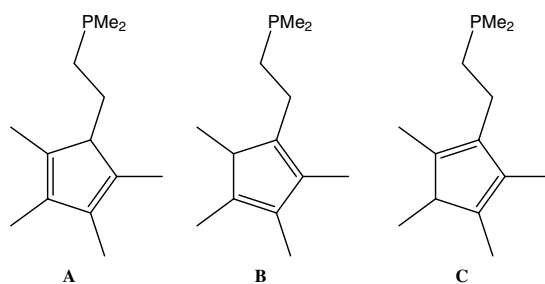
3.2.3. Sodium (2-*P,P*-dimethylphosphanylethyl)tetramethylcyclopentadienide **2b-Na**

To a solution of Me₂PNa [prepared from tetramethyldiphosphane (3.90 g, 32.0 mmol) and excess of Na sand (1.0 g) by cleavage in octane] in THF (50 mL), a solution of tetramethylspiroheptadiene **1** (4.29 g, 28.9 mmol) in THF (80 mL) was added at –10 °C. The reaction mixture was stirred at this temperature during 30 min and then allowed to warm gradually up to room temperature and left to stay overnight. The mixture was diluted with THF (400 mL) and the solution decanted from the precipitate. The solvent was returned back and the extraction repeated. The THF extract was concentrated

nearly till dryness, diethyl ether entered (100 mL), the precipitated crude product washed by decantations three times and dried on the high-vacuum line. White crystalline powder. Yield 11.12 g (82.0% based on **1**). ^1H NMR (25 °C, THF- d_8): δ 0.94 [d, 6H, $^2J_{\text{HP}} = 1.6$ Hz, $\text{P}(\text{CH}_3)_2$], 1.51 (dt, 2H, $^2J_{\text{HP}} = 1.2$ Hz, $^3J_{\text{HH}} = 7.4$ Hz, CH_2P), 1.98, 1.99 [each s, 6H, $\text{C}_5(\text{CH}_3)_4$], 2.57 (dt, 2H, $^3J_{\text{HP}} = 11.2$ Hz, $^3J_{\text{HH}} = 7.4$ Hz, $\text{CH}_2\text{CH}_2\text{P}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C, THF- d_8): δ 11.89, 12.08 [each s, $\text{C}_5(\text{CH}_3)_4$], 14.13 [d, $^1J_{\text{CP}} = 12.1$ Hz, $\text{P}(\text{CH}_3)_2$], 23.45 (d, $^2J_{\text{CP}} = 11.5$ Hz, $\text{CH}_2\text{CH}_2\text{P}$), 37.56 (d, $^1J_{\text{CP}} = 4.2$ Hz, CH_2P), 104.81, 105.62 (each s, CCH_3), 111.74 (d, $^3J_{\text{CP}} = 9.1$ Hz, $\text{CCH}_2\text{CH}_2\text{P}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, THF- d_8): δ -55.2 (s).

3.2.4. (2-*P,P*-dimethylphosphanylethyl)tetramethylcyclopentadiene **2b-H**

Onto a dry sample of sodium salt **2b-Na** (0.58 g, 2.50 mmol), MeOH (10 mL) was transferred on the high-vacuum line by trapping with liq. N_2 . The mixture was allowed to warm up to room temperature under stirring. The solvent was removed by trapping it into a liq. N_2 cooled trap and the residue subjected to molecular distillation under high vacuum, that gave 0.49 g of colorless viscous oil. Yield 93%. ^1H NMR (25 °C, C_6D_6): δ 0.79, 0.86, 0.87 [each d, $^2J_{\text{HP}} = 2.8$ Hz, $\text{P}(\text{CH}_3)_2$], 0.84 [partially obscured m, CH_2P (A)], 0.98 [d, $^3J_{\text{HH}} = 7.6$ Hz, CHCH_3 (B, C)], 1.27–1.42 [m, CH_2P (B, C)], 1.72, 1.75, 1.76, 1.77, 1.79, 1.81 (each s, $=\text{CCH}_3$), 1.72 [obscured m, $\text{CH}_2\text{CH}_2\text{P}$ (A)], 2.23–2.66 [overlapped mm, CHCH_3 (B, C), $\text{CHCH}_2\text{CH}_2\text{P}$ (A), $\text{CH}_2\text{CH}_2\text{P}$ (B, C)]. $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C, C_6D_6): δ 11.19, 11.26, 11.31, 11.79, 11.84, 11.92 (each s, $=\text{CCH}_3$), 14.15–14.46 [overlapped signals, $\text{P}(\text{CH}_3)_2$, CHCH_3 (B, C)], 22.53, 22.87 [each d, $^2J_{\text{CP}} = 15.3$ Hz, $\text{CH}_2\text{CH}_2\text{P}$ (B, C)], 23.91 [d, $^2J_{\text{CP}} = 17.0$ Hz, $\text{CH}_2\text{CH}_2\text{P}$ (A)], 25.54 [d, $^1J_{\text{CP}} = 9.9$ Hz, CH_2P (A)], 33.24, 33.93 [each d, $^1J_{\text{CP}} = 12.4$ Hz, CH_2P (B, C)], 49.57, 51.79 [each s, CHCH_3 (B, C)], 56.92 [d, $^3J_{\text{CP}} = 11.8$ Hz, $\text{CHCH}_2\text{CH}_2\text{P}$ (A)], 133.64, 134.29, 134.56, 134.60, 136.28, 137.73, 137.93, 138.18 (each s, $=\text{CCH}_3$), 139.69, 142.78 [each d, $^3J_{\text{CP}} = 10.7$ Hz, $=\text{CCH}_2\text{CH}_2\text{P}$ (B, C)]. $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, C_6D_6): δ -50.2, -50.0, -49.9 (each s) (Scheme 5).¹ GC/MS EI (70 eV) m/z (%): 210 (99.5) $[\text{M}]^+$, 195 (100) $[\text{M} - \text{CH}_3]^+$, 182 (11.7) $[\text{M} - \text{C}_2\text{H}_4]^+$, 181 (12.5) $[\text{M} - \text{CH}_3 - \text{CH}_2]^+$, 167 (38.2) $[\text{M} - \text{CH}_3 - \text{C}_2\text{H}_4]^+$, 135 (16.1) $[\text{C}_5(\text{CH}_3)_5]^+$, 134 (13.5) $[\text{C}_5(\text{CH}_3)_4=\text{CH}_2]^+$, 133 (21.4) $[\text{C}_7\text{H}_4(\text{CH}_3)_3]^+$, 119 (17.8) $[\text{C}_7\text{H}_5(\text{CH}_3)_2]^+$, 105 (24.3) $[\text{C}_7\text{H}_6(\text{CH}_3)]^+$, 91 (20.2) $[\text{C}_7\text{H}_7]^+$, 77 (11.7) $[\text{HPMe}_3]^+$, 76 (77.3) $[\text{CH}_2\text{P}(\text{HMe})_2]^+$, 75 (12.1) $[\text{CH}_2\text{P}(\text{Me})_2]^+$, 62 (6.8) $[\text{HPMe}_2]^+$, 61 (10.7) $[\text{PMe}_2]^+$. $\text{C}_{13}\text{H}_{23}\text{P}$ (210.29): calc. C 74.25, H 11.02; found C 73.77, H 10.04.



Scheme 5.

3.2.5. Trimethylsilyl-(2-*P,P*-dimethylphosphanylethyl)-tetramethylcyclopentadiene **3b**

To a solution of Me_3SiCl (1.70 g, 15.6 mmol) in diisopropyl ether (50 mL), sodium salt **2b-Na** (3.00 g, 12.9 mmol) was added. The mixture was heated at 100 °C for 8 h. The resulting slurry was filtered through a tight glass wool tampon and the solid residue was extracted one time with Pr_2O . The solution and extract were combined and concentrated under high vacuum and the residue was subjected to molecular distillation distilled on the high-vacuum line. Yield 3.48 g (95%). ^1H NMR (25 °C, C_6D_6): δ -0.11 (br s, SiMe_3), 0.75–0.90 (br m, PMe_2 , CH_2P), 1.18 [br, $\text{CH}_3\text{C}(\text{SiMe}_3)$], 1.41 (br, CH_2P), 1.80 (br s, $=\text{CCH}_3$), 2.02 (br, $\text{CH}_2\text{CH}_2\text{P}$), 2.41 (br, $\text{CH}_2\text{CH}_2\text{P}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C, C_6D_6): δ 2.56 (s, SiMe_3), 11.25, 12.57 (each s, $=\text{CCH}_3$), 13.88 [br, $\text{CH}_3\text{C}(\text{SiMe}_3)$], 14.26 [d, $^1J_{\text{CP}} = 14.5$ Hz, $\text{P}(\text{CH}_3)_2$], 22.52 (d, $^2J_{\text{CP}} = 14.0$ Hz, $\text{CH}_2\text{CH}_2\text{P}$), 24.46 (d, $^2J_{\text{CP}} = 15.2$ Hz, $\text{CH}_2\text{CH}_2\text{P}$), 28.10 (br s, CH_2P), 33.22 (br s, CH_2P), 53.7, 56.9, 60.0 (each br, $\text{C}(\text{SiMe}_3)$), 133.8, 134.6, 135.4, 136.4, 138.3, 138.9, 140.2, 142.8 (each br, $=\text{C}-$). $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, C_6D_6): δ -50.4, -50.2 (each br s). EI MS (70 eV) m/z (%): 282 (3.9) $[\text{M}]^+$, 267 (4.9) $[\text{M} - \text{CH}_3]^+$, 220 (9.0) $[\text{M} - \text{HPMe}_2]^+$, 209 (40.8) $[\text{M} - \text{SiMe}_3]^+$, 148 (34.4) $[\text{M} - \text{SiMe}_3 - \text{PMe}_2]^+$, 147 (31.4) $[\text{C}_7\text{H}_3(\text{CH}_3)_4]^+$, 134 (25.8) $[\text{C}_5(\text{CH}_3)_4=\text{CH}_2]^+$, 133 (47.9) $[\text{C}_7\text{H}_4(\text{CH}_3)_3]^+$, 119 (33.0) $[\text{C}_7\text{H}_5(\text{CH}_3)_2]^+$, 105 (24.0) $[\text{C}_7\text{H}_6(\text{CH}_3)]^+$, 91 (29.7) $[\text{C}_7\text{H}_7]^+$, 75 (38.1) $[\text{CH}_2\text{P}(\text{Me})_2]^+$, 73 (100) $[\text{SiMe}_3]^+$, 62 (4.2) $[\text{HPMe}_2]^+$, 61 (6.5) $[\text{PMe}_2]^+$. $\text{C}_{16}\text{H}_{31}\text{PSi}$ (282.48): calc. C 68.03, H 11.06; found C 67.65, H 9.86.

3.2.6. $\eta^5:\eta^1\text{-}\kappa\text{P}$ -(2-*P,P*-dimethylphosphanylethyl)cyclopentadienyltrichlorozirconium(IV), adduct with THF 1:1 **4a-THF**

To a suspension of ZrCl_4 (1.16 g, 4.97 mmol) in toluene (15 mL), a solution of silane **3a** (1.25 g, 5.52 mmol) in the same solvent (45 mL) was added at -20 °C under vigorous stirring. The mixture was allowed to warm up to room temperature (ZrCl_4 dissolves completely) and then heated at 60 °C. In 15 min formation of white voluminous precipitate started. The reaction slurry was heated at 80 °C under stirring for additional 20 min

¹ Naming of the isomers is given in Scheme 5.

and left to stay overnight. The slurry was concentrated down to ca. 40 mL, the solution was decanted from the precipitate, a portion of fresh toluene (40 mL) was added and the decantation repeated. The rests of the solvent were removed in high vacuum and the solid residue recrystallized from the minimal volume of hot THF. The mother liquor was decanted, the well-formed crystals of the product were washed two times with portions of ice-cold THF (3–5 mL), two times with diethyl ether (20 mL) and dried on the high-vacuum line that gave 0.79 g of white crystalline solid. Analogous workup of the mother liquor gave additional 0.28 g of the adduct **4a**-THF. Total yield 1.07 g (51% based on ZrCl₄). Single crystals of **4a** free of THF were prepared by dissolving of the adduct in CH₂Cl₂ followed by slow crystallization. ¹H NMR (for **4a**-THF) (25 °C, THF-*d*₈): δ 1.34 [d, 6H, ²J_{HP} = 8.4 Hz, P(CH₃)₂], 2.34 (dt, 2H, ²J_{HP} = 7.4 Hz, ³J_{HH} = 7.0 Hz, CH₂P), 2.88 (dt, 2H, ³J_{HP} = 21.6 Hz, ³J_{HH} = 7.0 Hz, CH₂CH₂P), 6.28, 6.40 (each virt t, 2H, ³⁺⁴J_{HH} = 4.8, C₅H₄). ¹³C{¹H} NMR (for **4a**-THF) (25 °C, THF-*d*₈): δ 11.92 [d, ¹J_{CP} = 16.6 Hz, P(CH₃)₂], 24.64 (d, ²J_{CP} = 9.6 Hz, C H₂CH₂P), 35.13 (d, ¹J_{CP} = 22.6 Hz, CH₂P), 115.34, 123.05 (each s, C₅H₄), 133.74 (d, ³J_{CP} = 5.7 Hz, CCH₂CH₂P). ³¹P{¹H} NMR (for **4a**-THF) (25 °C, THF-*d*₈): δ -9.3 (s). ¹H NMR (for **4a**) (25 °C, CD₂Cl₂): δ 1.40 [d, 6H, ²J_{HP} = 8.8 Hz, P(CH₃)₂], 1.87 (m, 4H, CH₂CH₂O in THF), 2.38 (dt, 2H, ²J_{HP} = 8.4 Hz, ³J_{HH} = 7.0 Hz, CH₂P), 2.91 (dt, 2H, ³J_{HP} = 22.0 Hz, ³J_{HH} = 7.0 Hz, CH₂CH₂P), 4.03 (m, 4H, CH₂O in THF), 6.44 (m, 4H, C₅H₄). ¹³C NMR (for **4a**) (25 °C, CD₂Cl₂): δ 12.01 [qd, ¹J_{CH} = 131 Hz, ¹J_{CP} = 18.4 Hz, P(CH₃)₂], 24.37 (td, ¹J_{CH} = 130 Hz, ²J_{CP} = 9.1 Hz, CH₂CH₂P), 25.70 (t, ¹J_{CH} = 133 Hz, C H₂CH₂O in THF), 35.25 (td, ¹J_{CH} = 135 Hz, ¹J_{CP} = 23.7 Hz, CH₂P), 70.97 (t, ¹J_{CH} = 147 Hz, CH₂O in THF), 115.72, 121.07 (each d, ¹J_{CH} = 176 Hz, CH), 135.95 (d, ³J_{CP} = 4.6 Hz, C CH₂CH₂P). ³¹P{¹H} NMR (for **4a**) (25 °C, CD₂Cl₂): δ -4.7 (s). EI MS (70 eV) *m/z* (%): 348 (6.4) [M - THF]⁺, 195 (3.9) [ZrCl₃]⁺, 153 (100) [C₅H₄CH₂CH₂PMe₂]⁺, 91 (22.2) [C₇H₇]⁺, 75 (35.9) [CH₂PMe₂]⁺, 62 (25.4) [HPMe₂]⁺, 47 (3.0) [HPMe]⁺. C₁₃H₂₂Cl₃OPZr (422.86): calc. C 36.92, H 5.24; found C 36.10, H 5.13.

3.2.7. η⁵:η^{1-κ} *P*-(2-*P*,*P*-dimethylphosphanylethyl)tetramethylcyclopentadienyl]trichlorozirconium(IV) **4b**

To a suspension of ZrCl₄ (2.73 g, 11.60 mmol) in toluene (80 mL), silane **3b** (3.45 g, 12.2 mmol) was added under vigorous stirring and cooling down to -20 °C. The reaction mixture was allowed to warm up to room temperature (nearly complete dissolving of ZrCl₄ was observed) heated for 2 h at 100 °C and left to stay overnight. On removal of toluene from the resultant yellow solution, the residual was recrystallized from THF, that gave yellowish crystals of the product. The well-formed

crystals were washed two times with the minimal possible amount of ice-cold THF, two times with diethyl ether (2 × 50 mL) and dried on the high-vacuum line, that gave 1.41 g of lemon-yellow crystalline solid. The THF mother liquor was concentrated down to ca. 20 mL and diethyl ether was added (80 mL). The precipitated solid was separated by decantation, washed with the same mixture of THF and Et₂O (80 mL) and processed as described above that gave additional amount of the product (0.85 g). Total yield 2.26 g (48%). ¹H NMR spectroscopy data reveal that the product contains no THF. Single crystal of **4b** suitable for X-ray diffraction analysis was obtained by its slow crystallization from CH₂Cl₂. Single crystals of **4b**-THF, suitable for X-ray diffraction analysis were grown up by slow crystallization from THF. ¹H NMR (for **4b**-THF) (25 °C, THF-*d*₈): δ 1.27 [d, 6H, ²J_{HP} = 7.6 Hz, P(CH₃)₂], 2.04, 2.01 [each s, 6H, C₅(CH₃)₄], 2.21 (dt, 2H, ²J_{HP} = 8.8 Hz, ³J_{HH} = 7.0 Hz, CH₂P), 2.65 (dt, 2H, ³J_{HP} = 20.8 Hz, ³J_{HH} = 7.0 Hz, CH₂CH₂P). ¹³C{¹H} NMR (for **4b**-THF) (25 °C, THF-*d*₈): δ 11.94 [d, ¹J_{CP} = 14.8 Hz, P(CH₃)₂], 13.08, 14.20 [each s, C₅(CH₃)₄], 21.05 (d, ²J_{CP} = 11.1 Hz, CH₂CH₂P), 36.16 (d, ¹J_{CP} = 23.4 Hz, CH₂P), 124.31, 129.27 (each s, CCH₃), 131.59 (d, ³J_{CP} = 6.1 Hz, CCH₂CH₂P). ³¹P{¹H} NMR (for **4b**-THF) (25 °C, THF-*d*₈): δ -6.7 (s). ¹H NMR (for **4b**) (25 °C, CD₂Cl₂): δ 1.41 [d, 6H, ²J_{HP} = 8.8 Hz, P(CH₃)₂], 2.180, 2.184 [each s, 6H, C₅(CH₃)₄], 2.37 (dt, 2H, ²J_{HP} = 8.8 Hz, ³J_{HH} = 7.0 Hz, CH₂P), 2.81 (dt, 2H, ³J_{HP} = 21.6 Hz, ³J_{HH} = 7.0 Hz, CH₂CH₂P). ¹³C NMR (for **4b**) (25 °C, CD₂Cl₂): δ 12.56 [qd, ¹J_{CH} = 132 Hz, ¹J_{CP} = 18.6 Hz, P(CH₃)₂], 13.28, 13.37 [each q, ¹J_{CH} = 128 Hz, C₅(CH₃)₄], 21.36 (td, ¹J_{CH} = 130 Hz, ²J_{CP} = 10.1 Hz, CH₂CH₂P), 35.97 (td, ¹J_{CH} = 132 Hz, ¹J_{CP} = 22.9 Hz, CH₂P), 127.29, 127.41 (each s, CCH₃), 137.62 (d, ³J_{CP} = 5.9 Hz, CCH₂CH₂P). ³¹P{¹H} NMR (for **4b**) (25 °C, CD₂Cl₂): = 1.0 (s). EI MS (70 eV) *m/z* (%): 404 (4.9) [M]⁺, 369 (12.0) [M - Cl]⁺, 334 (0.9) [M - 2Cl]⁺, 294 (2.1) [(C₅(CH₃)₄=CH₂)ZrCl₂]⁺, 259 (3.3) [(C₅(CH₃)₄=CH₂)ZrCl]⁺, 209 (78.7) [C₅(CH₃)₄CH₂CH₂PMe₂]⁺, 195 (14.9) [ZrCl₃]⁺, 147 (80.8) [C₇H₃(CH₃)₄]⁺, 134 (31.8) [C₅(CH₃)₄=CH₂]⁺, 133 (68.7) [C₇H₄(CH₃)₃]⁺, 119 (60.6) [C₇H₅(CH₃)₂]⁺, 105 (33.9) [C₇H₆(CH₃)⁺, 91 (54.0) [C₇H₇]⁺, 75 (100) [CH₂PMe₂]⁺, 62 (44.0) [HPMe₂]⁺. C₁₃H₂₂Cl₃PZr (406.87): calc. C 38.38, H 5.45; found C 38.21, H 5.54.

3.2.8. Bis[η⁵-(2-*P*,*P*-dimethylphosphanylethyl)tetramethylcyclopentadienyl]dichlorozirconium(IV) **5**

To a solution of complex **4b** (0.44 g, 1.08 mmol) in THF (5 mL), a solution of the lithium salt **2b**-Li (0.51 g, 2.36 mmol) in THF (10 mL) was added at -10 °C under stirring. The reaction mixture was allowed to warm up to room temperature and then was heated in a boiling water bath for 12 h. The solvent was removed by trapping it into a vessel cooled with liq. N₂. The

residue was taken with hexane (15 ml), the precipitate filtered off and extracted 5 times with hexane (15 mL portions). The combined extracts were concentrated down to ca. 10 mL. Fractional crystallizations of from hexane gave, in total, 250 mg of target complex **5**. Yield 40% (based on $ZrCl_4$). 1H NMR (25 °C, THF- d_8): δ 0.97 [d, 12H, $^2J_{HP} = 2.4$ Hz, $P(CH_3)_2$], 1.33 (m, 4H, CH_2P), 1.98, 2.00 [each s, 12H, $C_5(CH_3)_4$], 2.55 (m, 4H, CH_2CH_2P). ^{13}C NMR (25 °C, THF- d_8): δ 12.24, 12.28 [each q, $^1J_{CH} = 127$ Hz, $C_5(CH_3)_4$], 14.28 [qd, $^1J_{CH} = 128$ Hz, $^1J_{CP} = 14.8$ Hz, $P(CH_3)_2$], 24.07 (td, $^1J_{CH} = 130$ Hz, $^2J_{CP} = 16.2$ Hz, CH_2CH_2P), 33.25 (td, $^1J_{CH} = 130$ Hz, $^1J_{CP} = 13.3$ Hz, CH_2P), 122.83, 124.68 (each s, CCH_3), 128.74 (d, $^3J_{CP} = 12.5$ Hz, CCH_2CH_2P). $^{31}P\{^1H\}$ NMR (25 °C, THF- d_8): δ -49.5 (s). EI MS (70 eV) m/z (%): 578 (0.2) $[M]^+$, 563 (0.1) $[M - CH_3]^+$, 543 (0.7) $[M - Cl]^+$, 369 (53.8) $[M - C_5(CH_3)_4CH_2CH_2PMe_2]^+$, 353 (47.2) $[M - C_5(CH_3)_4CH_2CH_2PMe_2 - CH_4]^+$, 209 (62.6) $[C_5(CH_3)_4CH_2CH_2PMe_2]^+$, 147 (33.1) $[C_7H_3(CH_3)_4]^+$, 134 (30.9) $[C_5(CH_3)_4=CH_2]^+$, 133 (43.4) $[C_7H_4(CH_3)_3]^+$, 119 (55.2) $[C_7H_5(CH_3)_2]^+$, 105 (22.4) $[C_7H_6(CH_3)]^+$, 91 (40.5) $[C_7H_7]^+$, 75 (100) $[CH_2PMe_2]^+$, 62 (20.6) $[HPMe_2]^+$. $C_{26}H_{44}Cl_2P_2Zr$ (580.70): calc. C 53.78, H 7.64; found C 53.51, H 7.46.

3.2.9. Trinuclear adduct of **4b** and **5** (2:1) (**8**, crude product)

The lower-soluble in hexane fraction from the preceding procedure was washed with hexane and dried under high vacuum that gave 210 mg of pale-yellow solid. The estimated purity (NMR spectroscopy data) is ca. 80%. 1H NMR (25 °C, THF- d_8): δ 1.21 [d, 12H, $^2J_{HP} = 2.4$ Hz, $P^2(CH_3)_2$], 1.27 [d, 12H, $^2J_{HP} = 8.0$ Hz, $P^1(CH_3)_2$], 1.56 (m, 4H, CH_2P^2), 1.97, 1.99 [each s, 12H, $C_5(CH_3)_4$ in sandwich], 2.01, 2.11 [each s, 12H, $C_5(CH_3)_4$ in half-sandwich], 2.23 (dt, 4H, $^2J_{HP} = 8.8$ Hz, $^3J_{HH} = 7.1$ Hz, CH_2P^1), 2.62 (dt, 4H, $^3J_{HP} = 21.0$ Hz, $^3J_{HH} = 7.1$ Hz, $CH_2CH_2P^1$), 2.68 (m, 4H, $CH_2CH_2P^2$). $^{13}C\{^1H\}$ NMR (25 °C, THF- d_8): δ 12.24, 12.70 [each s, $C_5(CH_3)_4$ in sandwich], 12.37 [s, $P^2(CH_3)_2$], 12.56 [d, $^1J_{CP} = 15.2$ Hz, $P^1(CH_3)_2$], 13.21, 13.75 [each s, $C_5(CH_3)_4$ in half-sandwich], 20.97 (d, $^2J_{CP} = 10.8$ Hz, $CH_2CH_2P^1$), 22.89 (d, $^2J_{CP} = 6.0$ Hz, $CH_2CH_2P^2$), 31.21 (s, CH_2P^2), 38.06 (d, $^1J_{CP} = 22.8$ Hz, CH_2P^1), 122.68, 124.74 (each s, CCH_3 in sandwich), 125.58, 129.63 (each s, CCH_3 in half-sandwich), 127.93 (d, $^3J_{CP} = 12.6$ Hz, $CCH_2CH_2P^2$), 131.92 (d, $^3J_{CP} = 5.9$ Hz, $CCH_2CH_2P^1$). $^{31}P\{^1H\}$ NMR (25 °C, THF- d_8): δ -36 (br, P^2), -8.6 (s, P^1).

3.2.10. η^5 -(2-*P,P*-dimethylphosphanylethyl)tetramethylcyclopentadienyl][η^5 -pentamethylcyclopentadienyl] dichlorozirconium(IV) **6**

To a solution of [η^5 - C_5Me_5]- $ZrCl_3$ (0.68 g, 2.04 mmol) in THF (50 mL), lithium salt **2b**-THF (0.46 g,

2.10 mmol) was added at -30 °C and vigorous stirring. Initially yellow THF solution turned red. The mixture was allowed to warm up to room temperature (red coloration gradually discharges) and the heated in a water bath (95 °C) for 36 h. On removal of the solvent from the pale-orange solution, the residue was taken in toluene (30 mL), the formed precipitate filtered off and washed with additional portion of toluene (30 mL). The combined toluene solutions were concentrated till nearly dryness and hexane (30 mL) was entered. The precipitate was collected, washed on a filter with cold hexane (2 \times 20 mL) and dried on a high-vacuum line that gave 0.60 g (58%) of pale-yellow crystalline **6**. 1H NMR (25 °C, THF- d_8): δ 0.96 [d, 6H, $^2J_{HP} = 2.8$ Hz, $P(CH_3)_2$], 1.33 (m, 2H, CH_2P), 1.97 [s, 15H, $C_5(CH_3)_5$], 1.98, 1.99 [each s, 6H, $C_5(CH_3)_4$], 2.54 (m, 2H, CH_2CH_2P). ^{13}C NMR (25 °C, THF- d_8): δ 12.16, 12.22 [each q, $^1J_{CH} = 126$ Hz, $C_5(CH_3)_4$], 12.24 [q, $^1J_{CH} = 126$ Hz, $C_5(CH_3)_5$], 14.30 [qd, $^1J_{CH} = 127$ Hz, $^1J_{CP} = 15.0$ Hz, $P(CH_3)_2$], 24.02 (td, $^1J_{CH} = 129$ Hz, $^2J_{CP} = 16.3$ Hz, CH_2CH_2P), 33.29 (td, $^1J_{CH} = 129$ Hz, $^1J_{CP} = 13.3$ Hz, CH_2P), 122.73, 124.44 (each s, CCH_3), 124.11 [s, $C_5(CH_3)_5$], 128.77 (d, $^3J_{CP} = 12.5$ Hz, CCH_2CH_2P). $^{31}P\{^1H\}$ NMR (25 °C, THF- d_8): δ -49.7 (s). EI MS (70 eV) m/z (%): 369 (25.8) $[M - C_5(CH_3)_5]^+$, 353 (7.2) $[M - C_5(CH_3)_5 - CH_4]^+$, 295 (10.3) $[(C_5(CH_3)_5)ZrCl_2]^+$, 259 (5.5) $[(C_5(CH_3)_4=CH_2)ZrCl]^+$, 209 (55.6) $[C_5(CH_3)_4CH_2CH_2 - PMe_2]^+$, 147 (17.8) $[C_7H_3(CH_3)_4]^+$, 135 (16.3) $[C_5(CH_3)_5]^+$, 134 (16.2) $[C_5(CH_3)_4=CH_2]^+$, 133 (23.5) $[C_7H_4(CH_3)_3]^+$, 119 (49.1) $[C_7H_5(CH_3)_2]^+$, 105 (30.8) $[C_7H_6(CH_3)]^+$, 91 (34.6) $[C_7H_7]^+$, 75 (100) $[CH_2PMe_2]^+$, 62 (19.2) $[HPMe_2]^+$. $C_{23}H_{37}Cl_2PZr$ (506.64): calc. C 54.53, H 7.36; found C 54.22, H 7.18.

3.2.11. Dinuclear adduct of **4b** and **6** (1:1) (**7**)

Concentrating of the hexane mother liquor from the preceding procedure resulted in formation of a small amount of precipitate. On collecting the precipitate and washing it on a filter with the minimal amount of cold hexane, the yellowish-white crystalline solid was dried on the high-vacuum line. Total amount 34 mg. Single crystals of **7** suitable for X-ray diffraction analysis were prepared by crystallization from THF. 1H NMR (25 °C, THF- d_8): δ 1.14 [br s, 6H, $P^2(CH_3)_2$], 1.27 [d, 6H, $^2J_{HP} = 8.0$ Hz, $P^1(CH_3)_2$], 1.48 (m, 2H, CH_2P^2), 1.97 [s, 21H, $C_5(CH_3)_5$, $C_5(CH_3)_4$ in sandwich], 1.98 [s, 6H, $C_5(CH_3)_4$ in sandwich], 2.02, 2.11 [each s, 6H, $C_5(CH_3)_4$ in half-sandwich], 2.24 (dt, 2H, $^2J_{HP} = 8.9$ Hz, $^3J_{HH} = 7.2$ Hz, CH_2P^1), 2.63 (dt, 2H, $^3J_{HP} = 21.3$ Hz, $^3J_{HH} = 7.2$ Hz, $CH_2CH_2P^1$), 2.69 (m, 2H, $CH_2CH_2P^2$). $^{31}P\{^1H\}$ NMR (25 °C, $[D_8]THF$): -39 (br, P^2), -8.5 (s, P^1). EI MS (70 eV) m/z (%): presents a superposition of the MS spectra of **4b** and **6**.

3.3. X-ray crystallographic study of complexes **4a**, **4b**, **4a-THF**, **4b-THF**, and **5**

The X-ray diffraction data were collected on a Bruker SMART CCD diffractometer (graphite-monochromatized Mo K α radiation, 0.71073 Å) using ω scan mode. Experimental intensities were corrected for Lorentz and polarization effects [25]. Semi-empirical absorption corrections based on the measurements of equivalent reflections were applied [26,27]. All of the structures were solved by direct methods [28] and refined by full matrix least-squares on F^2 [29] with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms, except H(30A), H(30B), and H(30C) in the structure **5**, were found from difference Fourier synthesis and refined with isotropic thermal parameters. Hydrogen

atoms H(30A), H(30B), and H(30C) in complex **5** were placed in calculated positions and refined using a riding model. Details of X-ray structural investigations are listed in Table 6.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center CCDC No. 266114 for compound **4a**, CCDC No. 266111 for compound **4b**, CCDC No. 266112 for compound **4a-THF**, CCDC No. 266113 for compound **4b-THF**, and No. 266115 for compound **5**. Copies of this information can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK, fax: (int code)

Table 6
Details of X-ray crystallographic study for complexes **4a**, **4b**, **4a-THF**, **4b-THF**, and **5**

| Empirical formula | C ₁₈ H ₂₈ Cl ₆ P ₂ Zr ₂ (4a) | C ₁₃ H ₂₂ Cl ₃ OPZr (4a-THF) | C ₂₆ H ₄₄ Cl ₆ P ₂ Zr ₂ (4b) | C ₁₇ H ₃₀ Cl ₃ OPZr (4b-THF) | C ₃₆ H ₅₉ Cl ₅ P ₂ Zr ₂ (5) |
|--|--|--|--|--|---|
| Formula weight | 701.48 | 422.85 | 813.69 | 478.95 | 913.46 |
| Color, habit | Colorless block | Colorless block | Colorless block | Colorless parallelepiped | Colorless block |
| Crystal size (mm) | 0.4 × 0.2 × 0.2 | 0.4 × 0.3 × 0.2 | 0.3 × 0.2 × 0.1 | 0.24 × 0.14 × 0.10 | 0.5 × 0.3 × 0.1 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Orthorhombic. | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> <i>bca</i> | <i>P</i> 2 ₁ / <i>n</i> |
| Unit cell dimensions | | | | | |
| <i>a</i> (Å) | 7.8308(1) | 14.6364(17) | 9.6791(4) | 9.6552(6) | 16.3743(8) |
| <i>b</i> (Å) | 14.8061(3) | 8.1463(9) | 13.0343(6) | 15.2586(9) | 14.8062(8) |
| <i>c</i> (Å) | 11.0988(2) | 14.8564(16) | 12.7468(6) | 27.3531(16) | 17.4403(9) |
| β (°) | 101.420(1) | 108.726(2) | 96.179(1) | 90 | 104.734(1) |
| Volume (Å ³) | 1261.36(4) | 1677.6(3) | 1598.8(1) | 4029.8(4) | 4089.2(4) |
| <i>Z</i> | 2 | 4 | 2 | 8 | 4 |
| Density (calc.) (g cm ⁻³) | 1.847 | 1.674 | 1.690 | 1.579 | 1.484 |
| Absorption coefficient (mm ⁻¹) | 1.594 | 1.218 | 1.270 | 1.025 | 0.939 |
| <i>F</i> (000) | 696 | 856 | 824 | 1968 | 1880 |
| Temperature (K) | 120(2) | 115(2) | 115(2) | 120(2) | 120.0(2) |
| θ Range (°) | 2.32 < θ < 28.00 | 1.47 < θ < 28.00 | 2.24 < θ < 27.00 | 1.49 < θ < 28.00 | 1.52 < θ < 27.00 |
| Index ranges | -7 ≤ <i>h</i> ≤ 10 -18 ≤ <i>k</i> ≤ 19 -14 ≤ <i>l</i> ≤ 14 | -19 ≤ <i>h</i> ≤ 19 -10 ≤ <i>k</i> ≤ 9 -19 ≤ <i>l</i> ≤ 15 | -12 ≤ <i>h</i> ≤ 11 -16 ≤ <i>k</i> ≤ 9 -15 ≤ <i>l</i> ≤ 16 | -9 ≤ <i>h</i> ≤ 12 -20 ≤ <i>k</i> ≤ 19 -36 ≤ <i>l</i> ≤ 16 | -22 ≤ <i>h</i> ≤ 18 -20 ≤ <i>k</i> ≤ 18 -20 ≤ <i>l</i> ≤ 24 |
| Reflections collected | 9114 | 10,283 | 9110 | 21,554 | 28,364 |
| Independent reflections [<i>R</i> _{int}] | 3044 [0.0179] | 3868 [0.1638] | 3458 [0.0188] | 4867 [0.0514] | 8922 [0.0429] |
| Reflections with <i>I</i> > 2 σ (<i>I</i>) | 2859 | 3459 | 3075 | 4067 | 7093 |
| Min/max transmissions | 0.5681/0.7411 | 0.6414/0.7927 | 0.7018/0.8835 | 0.7911/0.9045 | 0.5554/0.9281 |
| Data/restraints/parameters | 3044/0/184 | 3868/0/261 | 3458/0/251 | 4867/0/328 | 8498/0/630 |
| Goodness of fit on F^2 | 1.049 | 1.148 | 1.133 | 1.122 | 1.120 |
| Final <i>R</i> indices <i>I</i> > 2 σ (<i>I</i>) | 0.0150, 0.0379 | 0.0545, 0.1558 | 0.0315, 0.0797 | 0.0430, 0.0815 | 0.0480, 0.1186 |
| <i>R</i> ₁ , <i>wR</i> ₂ | | | | | |
| <i>R</i> -indices (all data) <i>R</i> ₁ , <i>wR</i> ₂ | 0.0168, 0.0384 | 0.0686, 0.1863 | 0.0356, 0.0819 | 0.0563, 0.0857 | 0.0584, 0.1256 |
| Extinction coefficient | 0.0018(2) | 0.0053(18) | – | – | – |
| Largest differential peak and hole (e Å ⁻³) | 0.408 and -0.308 | 1.041 and -2.662 | 1.826 and -0.376 | 0.663 and -0.905 | 3.117 and -0.657 |

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or www:<http://www.ccdc.cam.ac.uk>.

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