New bridging tridentate bis-cyclopentadienyl ligands $[C_5Me_4(CH_2)_n]_2PPh$ (n = 1, 2) for organometallic synthesis

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Preparative procedures were developed for the synthesis of new transmethylated bis-cyclopentadienyl ligands with phosphine-containing bridging fragments. These ligands were isolated as the dilithium salts $Li_2[(C_5Me_4CH_2)_2PPh]$ (**1**) and $Li_2[(C_5Me_4CH_2CH_2)_2PPh]$ (**3**). Phosphorus-substituted 3-*ansa*-zirconocene dichloride $[(C_5Me_4CH_2)_2PPh]ZrCl_2$ was synthesized starting from **1**. The NMR spectroscopic data provide evidence for the absence of the Zr←P coordination interaction in solution. A straightforward approach to 5-*ansa*-zirconocene dichloride $[(C_5Me_4CH_2CH_2)_2PPh]ZrCl_2$ starting from lithium salt **3** and $ZrCl_4$ was shown to be impossible.

Key words: phosphanediyl-containing bis-cyclopentadienyl ligands, zirconium, NMR spectroscopy.

Among a vast number of heteroatom-functionalized cyclopentadienyl ligands widely used in organometallic chemistry, bis-cyclopentadienyl ligands containing a heteroatom in the bridging fragment have received little attention. However, their coordination ability toward transition metal atoms can radically differ from that of conventional bidentate chelating monocyclopentadienyls. This is associated with the possibility of the forced coordination at the rear of the heteroatomic functional group of the bridge to the metal atom in complexes with a particular geometry.

Oxygen-, nitrogen-, arsenic-, and phosphorus-containing derivatives are among the known tridentate bis-cyclopentadienyl ligands and metal complexes with these ligands. The lanthanide complexes $[O(CH_2CH_2C_5H_4)_2]LnCl$ (Ln = Y, Nd, Gd, Ho, Er, Yb, or Lu) were prepared.[1] The complexes of Ti,[2] Zr,[3–5] Cr,[6] U,[7] and lanthanides (Y, Pr, Nd, Sm, Dy, Er, Yb, and Lu)[8] with 2,6-pyridine-containing dicyclopentadiene $[2,6\text{-}C_5H_3N(CH_2C_5H_5)_2]$ were synthesized. The following derivatives of Group IV metals based on dicyclopentadienes with aliphatic amino groups were documented: $[H_3CN(CH_2CH_2C_5H_4)_2]ZrCl_2$,[3] $[Bu^nN(SiMe_2C_5H_4)_2]MCl_2$ (M = Ti, Zr, or Hf), and $[Bu^nN(SiMe_2C_9H_6)_2]ZrCl_2$ (C_9H_6 is 2-indenyl).[9] The arsenic-containing complexes $[PhAs(CH_2CH_2C_5H_4)_2]$-$TiCl_2$ (see Ref. 10) and $[PhAs(CH_2CH_2C_5H_4)_2]Fe$ (see Ref. 11) were prepared. The only dicyclopentadiene transalkylated at both rings, $[2,6\text{-}C_5H_3N(CH_2CH_2C_5Me_4H)_2]$, has been synthesized rather long ago;[12,13] however, no complexes with this ligand were prepared. Three examples of this type of phosphine ligands were reported: $[PhP(CH_2CH_2C_5H_5)_2]$ (Zr[14,15] and Fe[16] complexes were synthesized), $[MeP(CH_2CH_2C_5H_5)_2]$ (Y and Lu complexes were synthesized),[17] and $[RP(CMe_2C_5H_5)_2]$ (R = Ph or Cy; the corresponding ferrocenophanes were prepared).[18] To complete the picture, let us mention the $[PhP(C_{13}H_8)_2]MCl_2$ compounds (M = Zr or Hf; $C_{13}H_8$ is fluorenyl);[19] however, the phosphorus atom in these compounds in no case can be coordinated to the metal atom.

In the present study, we developed preparative procedures for the synthesis of new tridentate dicyclopentadienyl ligands, which were isolated as the dilithium salts $Li_2[(C_5Me_4CH_2)_2PPh]$ and $Li_2[(C_5Me_4CH_2CH_2)_2PPh]$, and *ansa*-zirconocene dichloride $[(C_5Me_4CH_2)_2PPh]ZrCl_2$.

Results and Discussion

Synthesis of dilithium salts of ligands

The synthesis of the dilithium salt $Li_2[(C_5Me_4CH_2)_2PPh]$ (**1**) was based on the nucleophilic addition of phosphides at position 6 of the fulvene molecule. Salt **1** was prepared by the successive addition of 1,2,3,4-tetramethylfulvene (**2**) (1 equiv.), Bu^nLi (1 equiv.), and **2** (1 equiv.) to a solution of PhPHLi in THF (Scheme 1). The target compound was isolated in good yield and characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

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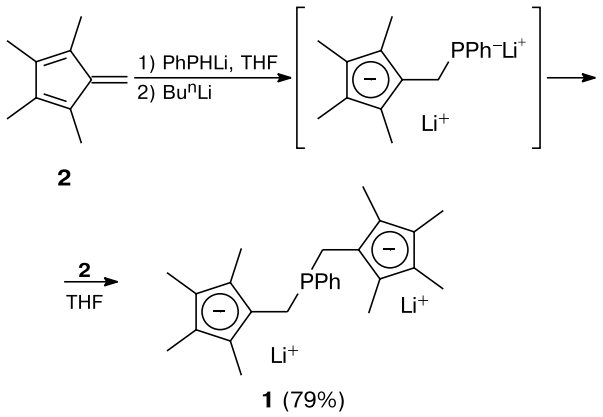
Scheme 1

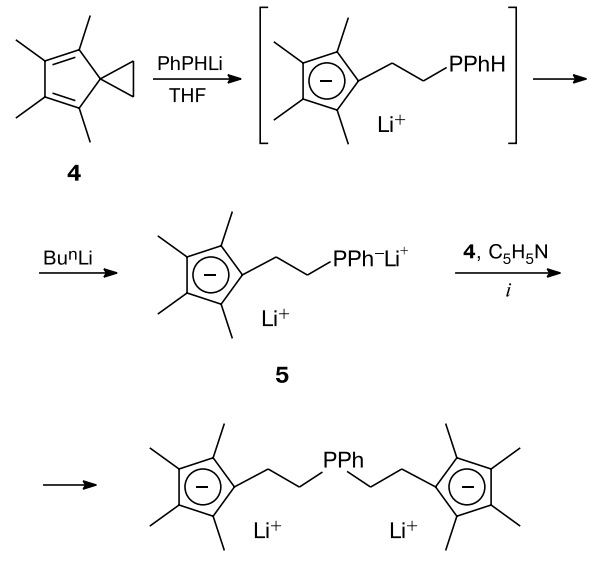


1 (79%)

The development of a preparative procedure for the synthesis of the dilithium salt $Li_2[(C_5Me_4CH_2CH_2)_2PPh]$ (**3**) with the aim of adapting the known one-pot synthesis of nonmethylated analog of **3**, $Li_2[(C_5H_4CH_2CH_2)_2PPh]$, was a more complex problem (Scheme 2). In the present study, the synthesis was performed in three successive steps: (1) cyclopropane ring opening in 4,5,6,7-tetramethylspiro[2.4]hepta-4,6-diene (**4**) with lithium phenylphosphide, (2) treatment of the resulting monolithium derivative with *n*-butyllithium in the cold, and (3) reaction of the dilithium salt $Li_2[C_5Me_4CH_2CH_2PPh]$ (**5**) with another equivalent of spirane **4**. The last step involving the opening of the second cyclopropane ring caused most problems. In this case, THF was of little use as the solvent because of very low solubility of dilithium salt **5**. The reaction requires drastic conditions (heating at 100 °C for 18 h), and the target compound is contaminated with cleavage products of the THF molecule. To exclude the cleavage of THF as the side reaction and provide milder reaction conditions, we performed the last reaction step in pyridine, in which salt **5** is much more readily soluble. Preliminary experiments showed that pyridine is resistant against PhPHLi (and, consequently, against **5**) at room temperature for 7 days. As a result, dilithium salt **3** was isolated in satisfactory yield and was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. It should be noted that **3** has very poor solubility in THF, which is insufficient even for the measurement of the ^1H NMR spectrum, but has very good solubility in pyridine.

In the synthesis of the zirconium complexes, we used, along with lithium salt **3**, the potassium derivative $K_2[(C_5Me_4CH_2CH_2)_2PPh]$ (**6**). The latter was prepared in good yield (79%) by the exchange reaction of salt **3** with Bu^{t}OK.

Scheme 2



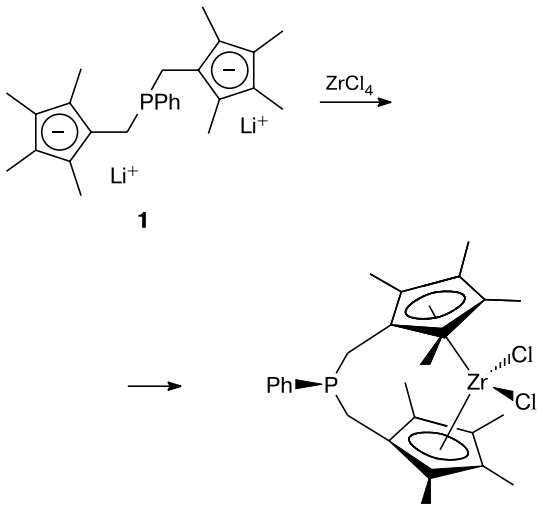
3 (43%)

Reaction conditions: *i*. 25 °C, 72 h.

Synthesis of zirconium ansa-complexes

The synthesis of Zr^{IV} *ansa*-complexes starting from dilithium salts **1** and **3** appeared to be a very laborious problem. Prolonged heating of lithium salt **1** with zirconium tetrachloride in toluene allowed us to prepare the sandwich complex $[(C_5Me_4CH_2)_2PPh]ZrCl_2$ (**7**) in low yield (Scheme 3). The target compound was isolated in the pure form and was characterized by mass spectrometry, ^1H, ^{13}C, and ^{31}P NMR spectroscopy, and elemental analysis.

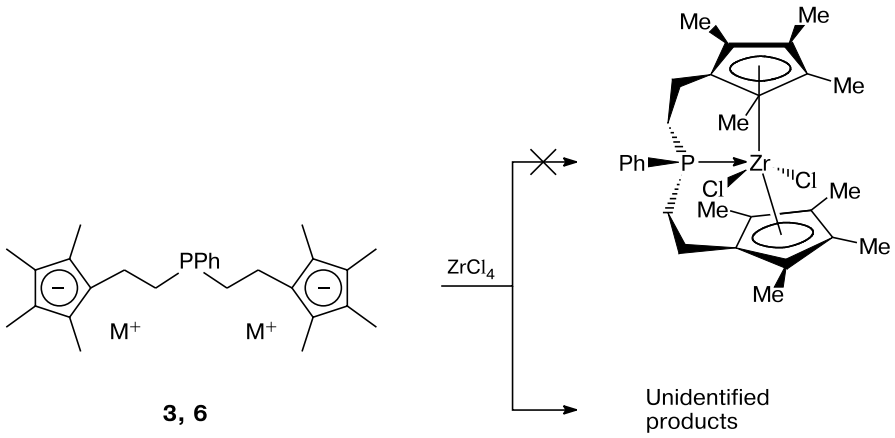
Scheme 3



7 (10%)

Reaction conditions: toluene.

Scheme 4



M = Li (**3**), K (**6**)

Reaction conditions: THF, DME, or toluene.

Due to the fact that the inversion of the pyramid at the phosphorus atom is hindered, molecule **7** has the symmetry group C_s (rather than C_{2v}), which is manifested in the nonequivalence of all Me groups in the rings as well as of the hydrogen atoms of the methylene bridge (AB spin system in the ^{1}H NMR spectrum). An interesting feature of the ^{13}C NMR spectrum is that the signal of one of four Me groups is split on the ^{31}P nucleus with $J_{C,P}$ = 15.1 Hz. This large four-bond spin-spin coupling constant is not typical of organophosphorus compounds. Apparently, the through-space interaction between the ^{31}P nucleus and the nearest Me group makes the main contribution to the spin-spin coupling constant.

In solution, the coordination of the phosphine substituent to the Zr atom in complex **7** should be, apparently, excluded. In three known examples of half-sandwich zirconium complexes with $C_5R_4CR^1R^2P(R^3)_2$- type ligands, this coordination is absent,[20] which is, apparently, associated with the insufficient length of the bridging fragment. The coordination of the phosphine group was observed only in the cationic sandwich complexes $\{[C_5R_4CR^1R^2P(R^3)_2]_2ZrX\}^+$.[21–23] The downfield shift (by ~14.5 ppm) of $\delta(^{31}P)$ in complex **7** (δ −20.1) compared to salt **1** (δ −34.5), which generally serves as a criterion of the coordination of the phosphine substituent to the metal atom, is accounted for by other factors. Most likely, this shift is associated with substantial changes in the nature of the substituent in the β position with respect to the phosphorus atom upon the coordination of the cyclopentadienyl ring to the Zr atom. For example, the change in $\delta(^{31}P)$ in the sandwich complexes $[C_5H_4CR^1R^2PPh_2]_2ZrCl_2$ (R^1, R^2 = Me; R^1 = H, R^2 = Me, R^2 = Bu^t; R^2 = Ph, R^2 = *p*-Tol) compared to the starting lithium salts varies from +12 ppm (R^1, R^2 = Me) to −15 ppm (R^1 = H, R^2 = *p*-Tol) depending on the nature of the substituent in the bridge.[24] At the same time, the $\delta(^{31}P)$ signal in the spectrum of the *ansa*-complex $[(C_5H_4CH_2CH_2)_2PPh]ZrCl_2$, for which the coordination of the phosphine group to the Zr atom was established, is shifted downfield with respect to that of the free ligand by 39.9 ppm.[15]

Noteworthy is high sensitivity of **7** to oxygen, which is characteristic of phosphine derivatives. This is manifested in the mass spectrum of this compound. Thus, upon the exposure of a solution of complex **7** to air, the most intense peak corresponds to the $[M - Cl + 16]^+$ ion belonging to the phosphine oxide complex.

We failed to synthesize the complex with the second bis-cyclopentadienyl ligand in spite of numerous attempts. Prolonged heating of the lithium (**3**) or potassium (**6**) salt with zirconium tetrachloride in nonsolvating (toluene) or solvating (THF or dimethoxyethane) solvents afforded a mixture of unidentified products, apparently, with a polymeric structure (Scheme 4) instead of the target *ansa*-complex.

In our opinion, this is associated with the difficulties of the *ansa*-ring closure in the intermediate half-sandwich complex due to the strong coordination of the phosphine substituent to the Zr atom. This is evidenced by the fact that the yield of even the nontransmethylated complex $[(C_5H_4CH_2CH_2)_2PPh]ZrCl_2$ is only 22%.[15] Apparently, a substantial increase in steric crowding of the cyclopentadienyl rings leads to a decrease in this rather low yield virtually to zero.

Experimental

All reactions and the preparation of samples for NMR spectroscopic studies were carried out in all-sealed evacuated Schlenk-type vessels. The solvents were purified according to

known procedures,[25] degassed *in vacuo* (residual pressure of noncondensable gases was 10^{-3} Torr), and introduced into reaction vessels by vacuum recondensation. Commercially available (Aldrich) phenylphosphine was dried over calcium hydride; $ZrCl_4$ was purified by sublimation in a dry hydrogen stream. 1,2,3,4-Tetramethylfulvene[26] and 4,5,6,7-tetramethylspiro[2,4]hepta-4,6-diene[27] were synthesized according to known procedures.

The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Varian VXR-400 and Bruker Avance-400 spectrometers operating at 400, 100, and 162 MHz, respectively. For the ^1H and ^{13}C NMR spectra, the chemical shifts of the deuterated solvents were used as the internal standard (7.19 and 123.5 ppm for C_5D_5N; 1.73 and 25.3 ppm for THF-d_8, respectively). For the ^{31}P NMR spectra, 85% H_3PO_4 was used as the external standard. The mass spectra were obtained on a Bruker Autoflex II instrument (MALDI, N_2 laser, 337 nm). The elemental analysis was carried out on an automated Carlo—Erba analyzer.

Lithium phenylphosphide. A solution of Bu^{n}Li in hexane (2.45 mol L^{-1}, 12.6 mL) was added to a solution of phenylphosphine (3.38 g, 30.7 mmol) in hexane (50 mL) at 0 °C, after which a yellow precipitate rapidly formed. The reaction mixture was stirred for 30 min and kept for 12 h. The precipitate was separated by decantation, washed with hexane, and dried in high vacuum. Lithium phenylphosphide was obtained as a yellow powder in a yield of 3.12 g (26.9 mmol, 88%). ^1H NMR (THF-d_8, 25 °C), δ: 2.09 (d, 1 H, PH, $^1J_{H,P}$ = 162 Hz); 6.23 (t, 1 H, *p*-CH, $^3J_{H,H}$ = 6.7 Hz); 6.52 (t, 2 H, *m*-CH, $^3J_{H,H}$ = 6.9 Hz); 7.05 (dd, 2 H, *o*-CH, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,P}$ = 5.1 Hz). $^{13}C—\{^1H\}$ NMR (THF-d_8), δ: 116.44 (s, *p*-CH); 126.75 (d, *m*-CH, $^3J_{C,P}$ = 4.7 Hz); 129.82 (d, *o*-CH, $^2J_{C,P}$ = 15.5 Hz); 161.69 (d, *ipso*-C, $^1J_{C,P}$ = 44.0 Hz). $^{31}P—\{^1H\}$ NMR (THF-d_8), δ: −111.2. ^1H NMR (C_5D_5N, 25 °C), δ: 3.28 (d, 1 H, PH, $^1J_{H,P}$ = 160 Hz); 6.60 (t, 1 H, *p*-CH, $^3J_{H,H}$ = 7.1 Hz); 6.90 (t, 2 H, *m*-CH, $^3J_{H,H}$ = 7.5 Hz); 7.70 (dd, 2 H, *o*-CH, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,P}$ = 5.2 Hz). $^{13}C—\{^1H\}$ NMR (C_5D_5N), δ: 116.17 (s, *p*-CH); 127.24 (d, *m*-CH, $^3J_{C,P}$ = 4.4 Hz); 129.64 (d, *o*-CH, $^2J_{C,P}$ = 15.3 Hz); 162.67 (d, *ipso*-C, $^1J_{C,P}$ = 45.6 Hz). $^{31}P—\{^1H\}$ NMR (C_5D_5N), δ: −99.0.

Dilithium 1,1′-[phenylphosphanediylbis(methyl)]bis(η^5-2,3,4,5-tetramethylcyclopenta-2,4-dieninde), {[C$_5$(CH$_3$)$_4$CH$_2$]$_2$PPh}Li$_2$ (1). A 0.66 *M* solution of 1,2,3,4-tetramethylfulvene (4.55 mmol) in toluene (6.9 mL) was added to a solution of PhPHLi (0.523 g, 4.51 mmol) in THF (50 mL) at 25 °C. The resulting yellow solution was stirred at 25 °C for 1 h. Then the solution was cooled to −20 °C, and a 2.45 *M* solution of Bu^{n}Li (4.53 mmol) in hexane (1.85 mL) was added. The solution rapidly turned orange, and a small amount of an orange precipitate was obtained. A 0.66 *M* solution of fulvene **2** (4.55 mmol) in toluene (6.9 mL) was added to the reaction mixture, and the mixture was stirred at 25 °C for 2 h. The solvents were removed, and the precipitate was washed with a 1 : 2 THF/Et_2O mixture and dried under high vacuum. Salt **1** was obtained as a white powdered substance in a yield of 1.40 g (3.58 mmol, 79%). ^1H NMR (C_5D_5N, 25 °C), δ: 2.19 and 2.47 (both s, 12 H, CCH_3); 3.38 (A part of an ABX system, 2 H, C$\underline{H}$HP, $^2J_{H,H}$ = 13.6 Hz, $^2J_{H,P}$ = 8.6 Hz); 3.64 (B part of an ABX system, CH$\underline{H}$P, 2 H, $^2J_{H,H}$ = 13.6 Hz, $^2J_{H,P}$ = 6.4 Hz); 7.26 (t, 1 H, *p*-CH, $^3J_{H,H}$ = 7.4 Hz); 7.38 (t, 2 H, *m*-CH, $^3J_{H,H}$ = 7.4 Hz); 7.90 (dd, 2 H, *o*-CH, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,P}$ = 5.6 Hz). $^{13}C—\{^1H\}$ NMR (C_5D_5N), δ: 11.19, 12.87 (C$\underline{C}$H$_3$); 29.06 (d, CH_2P, $^1J_{CP}$ = 19.0 Hz); 105.6 (br, $\underline{C}CH_2P$); 106.66, 107.51 ($\underline{C}CH_3$); 127.29 (*p*-CH); 128.33 (d, *m*-CH, $^3J_{C,P}$ = 4.8 Hz); 132.16 (d, *o*-CH, $^2J_{C,P}$ = 16.5 Hz); 146.4 (br.d, *ipso*-C, $^1J_{C,P}$ = 24 Hz). $^{31}P—\{^1H\}$ NMR (C_5D_5N), δ: −34.5.

Dilithium 1,1′-[2,2′-phenylphosphanediylbis(ethyl)]-bis(2,3,4,5-tetramethylcyclopenta-2,4-dienide), {[C$_5$(CH$_3$)$_4$CH$_2$CH$_2$]$_2$PPh}Li$_2$ (3). A solution of PhPHLi (0.485 g, 4.18 mmol) and spiroheptadiene **4** (0.65 g, 4.38 mmol) in THF (70 mL) was kept at 25 °C for 1 day and then heated at 50 °C for 4 h. The resulting orange solution was cooled to −20 °C, and then a 2.45 *M* solution of Bu^{n}Li in hexane (1.75 mL, 4.29 mmol) was added. The reaction mixture rapidly turned red. A yellow precipitate of **5** was formed within a few minutes. The precipitate was filtered off, washed with THF, dried, and treated with a solution of spirane **4** (0.52 g, 3.51 mmol) in pyridine (40 mL). The resulting black-red mixture was kept at 25 °C for three days and then heated at 60—70 °C for 3 h. The solvent was removed, and the oily residue was dissolved in THF. The precipitate that formed within a few minutes was separated from the intensely colored solution by decantation and washed with the solvent in the cold. Salt **3** was obtained as a greenish powder in a yield of 470 mg. An additional amount of the product (275 mg) was isolated from the mother liquor in THF remained after the isolation of **5**. The total yield was 745 mg (1.78 mmol, 43%). ^1H NMR (C_5D_5N, 25 °C), δ: 2.22 and 2.25 (both br, 28 H (a total), CCH_3, CH_2P); 2.98 (br, 4 H, C$\underline{H}_2$CH$_2$P); 7.27 (br.t, 1 H, *p*-CH); 7.39 (br, 2 H, *m*-CH); 7.78 (br, 2 H, *o*-CH). $^{13}C—\{^1H\}$ NMR (C_5D_5N), δ: 11.54 (C$\underline{C}$H$_3$); 23.4 (br, $\underline{C}H_2CH_2P$); 31.5 (br, CH_2P); 105.87, 106.53 ($\underline{C}CH_3$); 113.07 (d, $\underline{C}CH_2CH_2P$, $^3J_{C,P}$ = 12.0 Hz); 127.77 (*p*-CH); 128.40 (d, *m*-CH, $^3J_{C,P}$ = 5.6 Hz); 132.61 (d, *o*-CH, $^2J_{C,P}$ = 15.8 Hz); 142.4 (br, *ipso*-C). $^{31}P—\{^1H\}$ NMR (C_5D_5N), δ: −23.0.

Dipotassium 1,1′-[2,2′-phenylphosphanediylbis(ethyl)]-bis(2,3,4,5-tetramethylcyclopenta-2,4-dienide), {[C$_5$(CH$_3$)$_4$CH$_2$CH$_2$]$_2$PPh}K$_2$ (6). Salt **3** (0.74 mg, 1.77 mmol) was added with stirring to a solution of Bu^{t}OK (0.6 g, 5.35 mmol) in THF (40 mL). The lithium salt was completely dissolved, and a yellow substance precipitated from the solution within a few minutes. The precipitate was successively washed with THF and diethyl ether and then dried under high vacuum. Target compound **6** was obtained in a yield of 670 mg (1.39 mmol, 79%).

{1,1′-[Phenylphosphanediylbis(methyl)]bis(η^5-2,3,4,5-tetramethylcyclopenta-2,4-dienyl)}dichlorozirconium, {η^5-[C$_5$(CH$_3$)$_4$CH$_2$]$_2$PPh}ZrCl$_2$ (7). A suspension of lithium salt **1** (0.86 g, 2.20 mmol) and zirconium tetrachloride (0.53 g, 2.27 mmol) in toluene (60 mL) was stirred with heating on a boiling water bath for 20 h. The yellow solution was separated from the precipitate. The precipitate was extracted three times with toluene, the mother liquor and the extracts were combined, and the solvent was distilled off. The product was extracted three times from the oily residue with diethyl ether. The ethereal solution was concentrated. The precipitate that formed was separated from the solution by decantation and washed with cold diethyl ether. Complex **7** was obtained as a yellow powder in a yield of 119 mg (0.22 mmol, 10%). Found (%): C, 57.47; H, 6.08. $C_{26}H_{33}Cl_2PZr$. Calculated (%): C, 57.98; H, 6.18. ^1H NMR (THF-d_8, 27 °C), δ: 1.87, 1.95, 2.02, and 2.14 (all s, 6 H, CCH_3); 2.78 (A part of an ABX system, 2 H, C$\underline{H}$HP, $^2J_{H,H}$ = 14.0 Hz, $^2J_{H,P}$ = 7.2 Hz); 2.94 (B part of an ABX system, 2 H, CH$\underline{H}$P, $^2J_{H,H}$ = 14.0 Hz, $^2J_{H,P}$ = 5.7 Hz); 7.41 (m, 3 H, *m*-, *p*-CH); 7.72 (m, 2 H, *o*-CH). $^{13}C—\{^1H\}$ NMR (THF-d_8), δ:

12.04, 12.08, and 13.66 (all s, C$\underline{C}H_3$); 14.43 (d, C$\underline{C}H_3$, $J_{C,P}$ = 15.1 Hz); 26.02 (d, CH_2P, $^1J_{C,P}$ = 13.9 Hz); 117.86 (d, $\underline{C}CH_2$ or $\underline{C}CH_3$, $^2J_{C,P}$ or $^3J_{C,P}$ = 3.8 Hz); 118.42 (d, $\underline{C}CH_3$ or $\underline{C}CH_2$, $^3J_{C,P}$ or $^2J_{C,P}$ = 5.0 Hz); 127.12 and 127.19 (both s, $\underline{C}CH_3$); 129.43 (d, *m*-CH, $^3J_{C,P}$ = 6.2 Hz); 129.92 (s, *p*-CH); 132.29 (d, *o*-CH, $^2J_{C,P}$ = 18.5 Hz); 132.56 (d, $\underline{C}CH_3$, $^3J_{C,P}$ = 1.5 Hz); 139.97 (d, *ipso*-C, $^1J_{C,P}$ = 18.3 Hz). $^{31}P—\{^1H\}$ NMR (THF-d_8), δ: −20.1. ^1H NMR (C_5D_5N, 27 °C), δ: 1.82, 2.02, 2.15, and 2.26 (all s, 6 H, CCH_3); 2.87 (A part of an ABX system, 2 H, C$\underline{H}$HP, $^2J_{H,H}$ = 14.0 Hz, $^2J_{H,P}$ = 7.2 Hz); 3.01 (B part of an ABX system, 2 H, CH$\underline{H}$P, $^2J_{H,H}$ = 14.0 Hz, $^2J_{H,P}$ = 6.0 Hz); 7.49 (m, 3 H, *m*-, *p*-CH); 7.83 (m, 2 H, *o*-CH). $^{13}C—\{^1H\}$ NMR (C_5D_5N), δ: 11.92, 12.13, and 13.68 (all s, C$\underline{C}H_3$); 14.48 (d, C$\underline{C}H_3$, $J_{C,P}$ = 14.9 Hz); 25.45 (d, CH_2P, $^1J_{C,P}$ = 13.9 Hz); 117.84 (d, $\underline{C}CH_2$ or $\underline{C}CH_3$, $^2J_{C,P}$ or $^3J_{C,P}$ = 3.9 Hz); 118.12 (d, $\underline{C}CH_3$ or $\underline{C}CH_2$, $^3J_{C,P}$ or $^2J_{C,P}$ = 5.0 Hz); 126.75 and 127.12 (both s, $\underline{C}CH_3$); 129.25 (d, *m*-CH, $^3J_{C,P}$ = 6.1 Hz); 129.62 (s, *p*-CH); 131.89 (d, *o*-CH, $^2J_{C,P}$ = 17.8 Hz); 132.27 (d, $\underline{C}CH_3$, $^3J_{C,P}$ = 1.5 Hz); 139.35 (d, *ipso*-C, $^1J_{C,P}$ = 18.0 Hz). $^{31}P—\{^1H\}$ NMR (C_5D_5N), δ: −18.9. MS, *m/z* (I_{rel} (%)): 501 (5.2) $[M - Cl]^+$, 516 (100) $[M + O - Cl]^+$.

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