# A Novel Route to the 5-[2-(Diphenylphosphanyl)ethyl]-1,2,3,4-tetramethylcyclopentadienyl Ligand – Synthesis and Crystal Structure of $[\eta^5:\eta^1\text{-}C_5(CH_3)_4CH_2CH_2PPh_2]ZrCl_3\cdot THF$

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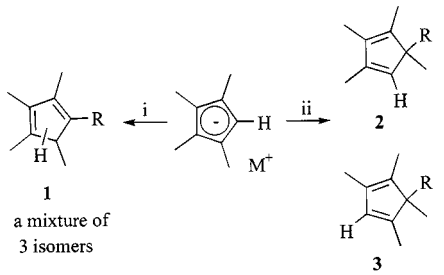
The five-step synthesis of the first transition metal complex with the $C_5(CH_3)_4CH_2CH_2PPh_2$ ligand $[\eta^5:\eta^1\text{-}C_5(CH_3)_4CH_2CH_2PPh_2]ZrCl_3\cdot THF$ (**11**), starting from the known compound [2-(dimethylamino)ethyl]tetramethylcyclopentadiene (**4**) via 4,5,6,7-tetramethylspiro[2,4]hepta-4,6-diene (**7**), is reported. Lithium cyclopentadienide $LiC_5(CH_3)_4CH_2CH_2PPh_2$ (**9**), silylated cyclopentadiene $(CH_3)_3SiC_5(CH_3)_4CH_2CH_2PPh_2$ (**10**) and cyclopentadiene $HC_5(CH_3)_4CH_2CH_2PPh_2$ (**12**) were isolated and characterised as pure substances. The crystal structure of the zirconium complex **11** was established by X-ray diffraction analysis.

## Introduction

Despite the attractiveness of [2-(diorganophosphanyl)ethyl]tetramethylcyclopentadienes as novel prospective ligands for organometallic synthesis, these side-chain-functionalized cyclopentadienes are relatively unavailable and complexes derived from them are still unknown. Direct alkylation of 1,2,3,4-tetramethylcyclopentadienides with alkyl halides or alkyl toluenesulfonates seems to be of little use in the preparation of 5-alkyl-1,2,3,4-tetramethylcyclopentadienes (**1**), and the question of the regioselectivity of this reaction remains unclear. Both the products of 5-alkylation (**1**)[1][2] and those of 1- and 2-alkylation (**2** and **3**, *gem*-dialkyl-subsituted cyclopentadienes)[3][4] were reported to dominate in the resultant mixtures of alkyltetramethylcyclopentadienes (see Scheme 1).

Nowadays, the synthesis of cyclopentadienes **1** is usually performed by treating 2,3,4,5-tetramethylcyclopenten-2-one with various Grignard or organolithium reagents, followed by dehydration.[5] Unfortunately, this approach is not applicable for the 2-heteroatom-functionalized ethyltetramethylcyclopentadienes **1** ($R = CH_2CH_2ER'_n$; $ER'_n = OR'$, $SR'$, $PR'_2$, $NR'_2$, etc.) due to the known instability of 2-heteroatom-functionalized alkylmagnesium or lithium compounds.[6] To overcome this difficulty, preparation procedures for $HC_5(CH_3)_4CH_2CH_2ER'_n$ involving double *sec*-butenylation of esters of 2-heteroatom-substituted propanoic acids $R''O(O)CCH_2CH_2ER'_n$ [$ER'_n = OCH_3$,[3][7] $N(CH_3)_2$,[3] $SCH_3$[8]], followed by dehydration and cyclization, were developed and shown to give good results. However, synthesis of tetramethyl(2-phosphanylethyl)cyclopentadienes by this latter method has not been reported.




route i dominates:

R-X = $ClCH_2CH_2$-OTs, $M^+ = Li^+$, THF, -10 - 0 °C (ref.[1])

R-X = $ClCH_2CH_2$-Br, $M^+ = K^+$, ether, r.t. (ref.[2])

route ii dominates:

R-X = $ClCH_2CH_2$-OTs, $M^+ = Li^+$, THF, -10 - 0 °C (refs.[3][4])

R-X = $(CH_3)_2NCH_2CH_2$-Cl, $M^+ = K^+$, THF, reflux (ref.[3])

Scheme 1. Direct alkylation of the tetramethylcyclopentadienide

Fortunately, the known cyclopropane ring cleavage reaction of spiro[2,4]hepta-4,6-diene with lithium dialkyl- or diarylphosphides[9] was recently shown for the novel 4,5,6,7-tetramethylspiro[2,4]hepta-4,6-diene (**7**),[2][4] and provided a straightforward route to $LiC_5(CH_3)_4CH_2CH_2PR_2$ (R = alkyl, aryl). In this way, the spiroheptadiene **7** could be, in principle, considered as a key compound in the synthesis of a variety of transition metal complexes derived from tetramethyl(2-phosphanylethyl)cyclopentadienes. However, the availability of the spirane **7** seemed to be rather doubtful. In this paper a convenient preparation procedure for **7**, and synthesis of the first example of a transition metal complex derived from the $C_5(CH_3)_4CH_2CH_2PPh_2$ ligand, are presented.

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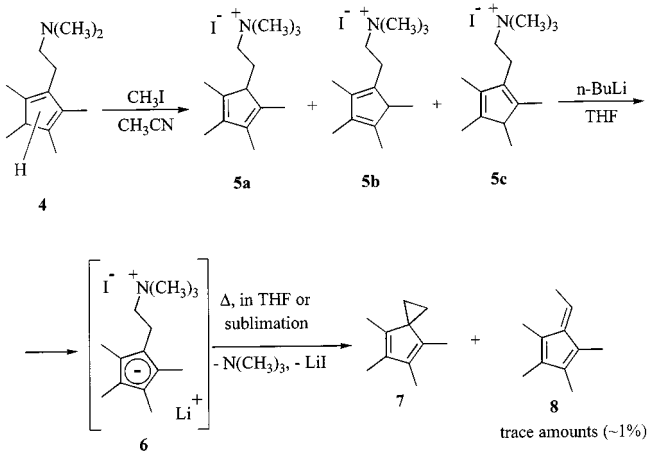
## Results and Discussion

### The Synthesis of Tetramethylspiroheptadiene 7

5-[2-(Dimethylamino)ethyl]-1,2,3,4-tetramethylcyclopentadiene (**4**) is a well-known and widely used ligand in organometallic chemistry.[10] However, it can also serve as a convenient synthetic precursor of the tetramethylspiroheptadiene **7**. Thus, quaternation of the amine **4** with iodomethane, followed by treatment of the ammonium salt **5** with *n*-butyllithium, leads to the spirane **7** in a good overall yield (see Scheme 2). The isolated product **7** is obtained as an orange/pale yellow liquid (m.p. −7°C). The coloration of **7** is caused by small amounts (ca. 1%) of 1,2,3,4,6-pentamethylfulvene (**8**),[11] which are detectable by $^1$H-NMR spectroscopy. Probably, the fulvene **8** is formed from the traces of tetramethyl(vinyl)cyclopentadiene which can be expected in the reaction mixture as the "normal" product of a destruction of the quaternary ammonium salt **5** with strong bases.




Scheme 2. Synthesis of the tetramethylspiroheptadiene **7**

The quaternary ammonium salt **5** was isolated as a white crystalline powder with > 95% purity (NMR-spectroscopy data). The dominant identifiable impurity is $CH_2$=$CHC(O)C(CH_3)$=$CH(CH_3)$. Supposedly, this admixture is formed from $(H_3C)_2NCH_2CH_2C(O)C(CH_3)$=$CH(CH_3)$ which is a typical pollutant of the starting aminoethylcyclopentadiene **4**. It is worth mentioning here that in contrast to the majority of quaternary ammonium iodides, the compound **5** is rather sensitive to air, especially when in a solution, and prolonged operations with it should be carried out either in a dry oxygen-free inert atmosphere or in vacuo.

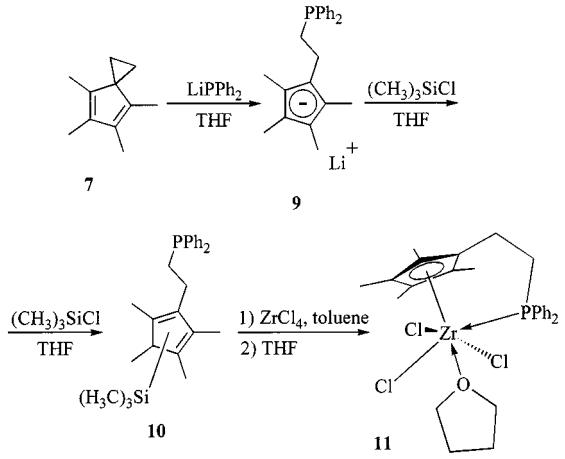
In general, ammonium salts are not typical synthetic precursors of cyclopropanes. In instances where examples of such quaternary salts producing cyclopropanes on treatement with strong bases are known,[12] there are hydrogen atoms at the γ-position to the ammonium group, which possess distinct C−H acidity. Following on from such work,[12] the formation of spiroheptadiene **7** from **5** might be supposed to proceed in at least two steps: deprotonation of cyclopentadiene **5** and the subsequent elimination of $N(CH_3)_3$ (see Scheme 2). In fact in practice, on adding *n*BuLi to a suspension of **5** in THF at −50°C and gradual warming the mixture up to −20°C, the consistency of the initial slurry changes and the precipitate becomes more voluminous. Vigorous evolution of $N(CH_3)_3$ begins only at temperatures exceeding 40−50°C, and to complete the reaction, which is indicated by the dissappearance of the solid phase and no further evolution of $N(CH_3)_3$, it is necessary to heat the reaction mixture under reflux for at least 30 min.

To clarify the reaction pathway, the stepwise conversion of the salt **5** into the spiroheptadiene **7** was attempted. It was found that the reaction of the ammonium salt **5** with *n*BuLi leads first to a solid product **6**, a snow-white powder which is extremely sensitive to air and moisture. Characterisation of the intermediate **6** by means of NMR spectroscopy proved impossible. When attempting to record the $^1$H-NMR spectrum only signals attributable to the spirane **7** and $N(CH_3)_3$ [NMR (30°C, [D$_8$]THF): $\delta_H$ = 2.11 (s), $\delta_C$ = 47.94 (s), molar ratio 1:1] were observed; indicative of the thermal instability of **6** in the solvating medium. Moreover, compound **6** is thermally unstable, not only in the presence of THF, but also when dry, and decomposes at a detectable rate when stored at −18°C (evacuated vessel). Thermolysis of dry **6** in vacuo ($1.3 \times 10^{-3}$ mbar) leads to the spirane **7**, $N(CH_3)_3$ (both trapped at −196°C) and LiI (residue) in a molar ratio 1:1:1. Despite the difficulties of characterising **6** by the usual techniques, the authors believe, however, that this deprotonation product possesses the structure suggested in Scheme 2.

### Preparation of $LiC_5(CH_3)_4CH_2CH_2PPh_2$ (9) and $[\eta^5{:}\eta^1\text{-}C_5(CH_3)_4CH_2CH_2PPh_2]ZrCl_3\cdot THF$ (11)

The complete synthesis of $[\eta^5{:}\eta^1\text{-}C_5(CH_3)_4CH_2CH_2PPh_2]ZrCl_3\cdot$THF (**11**) is presented in Scheme 3. The three-membered ring cleavage reaction for the spirane **7** with $LiPPh_2$ was performed as described previously,[4] but the excess of $LiPPh_2$ employed was decreased. In comparison with the considerably exothermic reaction of spiro[2,4]heptadiene-4,6 with $LiPPh_2$, which proceeds vigorously even at 10−15°C, in the case of **7** heating at 80−100°C for at least 8 h was required. It is suggested that this is a result of a lower thermodynamic preference for the formation of the pentaalkylcyclopentadienide anion compared to that of the monoalkylcyclopentadienide anion. The elevated temperature required also complicates the reaction due to the process of THF ring cleavage with phosphides,[13] and makes it necessary to apply a considerable excess of $LiPPh_2$.

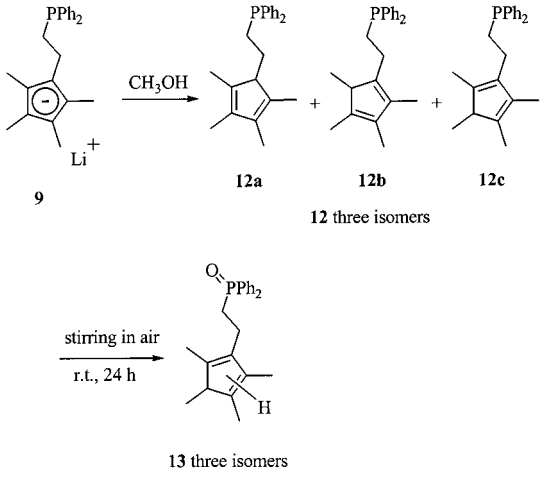
In its pure state the lithium salt **9** is a white crystalline powder, which is extremely sensitive to air and moisture. It is moderately soluble in THF at room or lower temperature. However, the solubility of **9** grows rapidly within the range 80−100°C (sealed vessel), and on cooling a stable supersaturated solution is formed. Previously, we observed that in contrast to the practically insoluble $LiC_5(CH_3)_5$ or $LiC_5(CH_3)_4H$, lithium cyclopentadienides $LiC_5(CH_3)_4CH_2CH_2ECH_3$ (E = O[7], S[8]) and $LiC_5H_4CH_2CH_2PPh_2$,[14]




Scheme 3. Synthesis of the halfsandwich complex **11**

with *n*-donor heteroatom functionalities in side chains, exhibit very good solublities in THF. Thus, from this viewpoint, the cyclopentadienide **9** presents an intermediate case. In the $^1$H-, $^{13}$C{$^1$H}- and $^{31}$P{$^1$H}-NMR spectra of **9** ([D$_8$]THF, 30°C) the signals are broadened, probably due to the inter- and/or intramolecular processes of coordination of $Li^+$ to $PPh_2$ groups. At the same time no signals due to [H$_8$]THF are present and, thus, one can conclude that the lithium salt **9** contains no solvated THF in the solid state. Taking all these facts into account, it is supposed that in the solid state **9** possesses a "multidecker polymer" structure, which is characteristic for $C_5H_5Li$,[15] while in a THF solution the cyclopentadienide **9** exists as mono-, or at least oligomeric, species with $PPh_2$ groups coordinated to $Li^+$.

As mentioned above, the preparation of $HC_5(CH_3)_4CH_2CH_2PPh_2$ (**12**) was reported previously by other workers.[1] In order to compare the present results with those given in this previous work dry cyclopentadienide **9** was quenched with methanol and the ligand of interest isolated in its C−H form, **12**, as a viscous pale yellow oil sensitive to air (see Scheme 4).




Scheme 4. Preparation and oxidation of the [2-diphenylphosphanyl)-ethylcyclopentadiene **12**

The assignment of the signals in the NMR spectra was performed on the basis of homo- and heteronuclear correlation spectroscopy experiments and coupled $^{13}$C spectra. The assignment of the signals to each of the isomers was additionally confirmed by homonuclear NOE experiments (difference spectra), with the relative intensities of the signals also taken into account. As was expected, it was found that **12** is a mixture of three (not two, as reported in ref.[1]) isomers, **12a−c**, in a molar ratio of 1:1.4:1.7, which is close to that observed previously for the three analogous isomers of $HC_5(CH_3)_4CH_2CH_2SCH_3$ (molar ratio ca. 3:4:5).[8] It must be noted here that, in general, the $^1$H-, $^{31}$P{$^1$H}-, and especially $^{13}$C{$^1$H}-NMR data for **12** in $C_6D_6$ solution presented in this work are in poor agreement with that reported by J. Szymoniak et al. for **12** in the same solvent.[1]

When a pentane solution of **12** is exposed to air, the precipitation of the corresponding phosphane oxides, **13a−c** (white amorphous powder), begins after several minutes. However, to complete the oxidation it is neccesary to stir the pentane solution for at least 24 h in air {NMR-spectroscopy monitoring of the reaction mixture; $\delta_P$ = 30.0 [s, (**13b**)], 30.1 [s, (**13c**)], 31.7 [s, (**13a**)]}.

In the $^1$H- and $^{13}$C-NMR spectra the isomers **12a−c**, **5a−c**[16] and the previously reported $HC_5(CH_3)_4CH_2CH_2SCH_3$[8] exhibit some significant common features which are worth mentioning here. In both these cases the side-chain protons H$^6$ and H$^7$ in the symmetric **a** isomers are markedly shielded (up to 0.5−0.6 ppm) with respect to the same protons in the **b** and **c** isomers. A similar high-field shift (up to 4−8 ppm) is also observed for the signals of C$^7$ in the **a** isomers. In contrast, the C$^6$ carbon atoms in the **a** isomers are deshielded (up to ca. 2 ppm) relative to the C$^6$ carbon atoms in the **b** and **c** isomers. These particularities of the $^1$H- and $^{13}$C{$^1$H}-NMR spectra also seem to be characteristic of a broad variety of 2-heteroatom-functionalized ethyltetramethylcyclopentadienes $HC_5(CH_3)_4CH_2CH_2X$ (X = O, S, N, P heteroatom functionality).

Lithium pentaalkylcyclopentadienides are the most usual and widely used direct precursors of the corresponding cyclpentadienyltrihalozirconium compounds. Undoubtedly, if treated with $ZrCl_4$ in either ether or toluene, the lithium salt **9** would give the desired half-sandwich **11**. However, in this work it was preferred to introduce an additional step and prepare the complex **11** via the intermediate trimethylsilyl-substituted cyclopentadiene **10**.

Cyclopentadienyltrimethylsilanes can be considered as one of the most convenient precursors of the monocyclopentadienyl trihalides of the Group IV metals $C_5H_5MCl_3$ (M = Ti, Zr and Hf).[17] Not long ago this method proved to be useful in the preparation of their ring-permethylated analogues, $C_5(CH_3)_5MCl_3$ (M = Ti, Zr and Hf).[18] In comparison with the route via lithium cyclopentadienides, application of silylated cyclopentadienes affords a number of advantages arising from the fact that the presence of LiCl as a co-product is initially excluded. It is known that LiCl can interact with the target half-sandwiches and form stable ionic products.[19] This complicates the isolation procedure,

and in some cases high-vacuum sublimation is necessary for the final purification of a metal complex.[7,8,20]

Treatment of **9** with $(CH_3)_3SiCl$ in THF followed by removal of the solvent and high-vacuum distillation gives the silane **10** as an air-sensitive pale yellow viscous oil, in an almost quantitative yield. It is an interesting fact that in contrast to the reaction between $(CH_3)_3SnCl$ and $C_5(CH_3)_5Li$ silylation of **9** does not proceed in ether, even at elevated temperatures (80−90°C, 7 h), and the initial cyclopentadienide **9** can be regenerated quantitatively. As expected, the broadened exchange signals in the $^1H$- and $^{31}P\{^1H\}$-NMR spectra of **10** indicate that it exists as an equilibrium mixture of three isomers [isomeric with respect to the position of the $(CH_3)_3Si$ group].

The zirconium complex **11** was obtained in a similar fashion to its ring nonmethylated analogue [$\eta^5$:$\eta^1$-$C_5H_4CH_2CH_2PPh_2$]$ZrCl_3$·THF (**14**),[14] and isolated as an adduct with one molecule of THF (well-formed pale yellow crystals moderately sensitive to air and moisture). The half-sandwich compound **11** was characterised by elemental analysis, mass spectrometry, $^1H$-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectroscopy and X-ray diffraction analysis (see below). In the NMR spectra, apart from the evident changes caused by replacement of $CH_3$ groups for hydrogen atoms, the parameters of **11** and **14** are rather similar. The $^{31}P$ shift of the $PPh_2$ group in $CD_2Cl_2$ for the compound **11** ($\delta_P$ = 5.8) indicates that in a solution this group remains coordinated to the metal centre [compare with $\delta_P$ = 6.1 for **14** (in $CD_2Cl_2$)[14] and $\delta_P \approx -14$ for non-coordinated $PPh_2$ groups of ($\eta^5$-$C_5H_4CH_2CH_2PPh_2$)($\eta^5$-$C_5H_5$)$ZrCl_2$[14] and compounds **9**, **10** and **12**].[21]

It is also notable that intramolecular coordination of the $PPh_2$ group to the Zr centre inverts the order of the absolute $^1J_{C-P}$ and $^2J_{C-P}$ values in the $Ph_2PCH_2CH_2$ fragment. Thus, both for **11** and **14** direct $|^1J_{C-P}|$ exceeds geminal $|^2J_{C-P}|$, while for all other previously studied compounds possessing the non-coordinated $Ph_2PCH_2CH_2$ moiety $|^1J_{C-P}| < |^2J_{C-P}|$.[14]

## X-ray Crystal Structure Analysis of the Complex 11

The crystal structure of **11** is shown in Figure 1. The central Zr atom possesses a distorted octahedral coordination, if one assumes that the cyclopentadienyl ligand occupies one coordination site. The cyclopentadienyl ring and the THF molecule lie in the apical positions while the phosphanyl group and three chlorine atoms occupy equatorial positions. The deviation of the Zr atom from the equatorial plane towards the cyclopentadienyl ligand is 0.53 Å. Analysis of the Cambridge Structural Database (Release: April 1998)[22] shows that the Zr−Cl distances [2.4619(10)−2.4921(8) Å] in **11** are within the range of normal values for terminal $Zr^{IV}$−Cl bonds in monocyclopentadienyl complexes (2.385−2.561 Å). The Zr−P bond [2.8906(11) Å] is significantly longer than was found for both crystalline modifications of the closely related complex **14** [2.8474(5)−2.8729(11) Å].[14] The latter fact can be explained by the influence of the electron-donating effect of four methyl groups at the cyclopentadienyl ring. The Zr−O(THF) bond [2.419(2) Å] in the structure of **11** is also much longer than was observed for the same apical bonds in $(C_5H_4R)ZrCl_3$·2THF [R = H, 2.393(3) Å; R = Me, 2.377(2) Å],[23] and in both modifications of **14** [2.350(3)−2.3613(12) Å].[14]

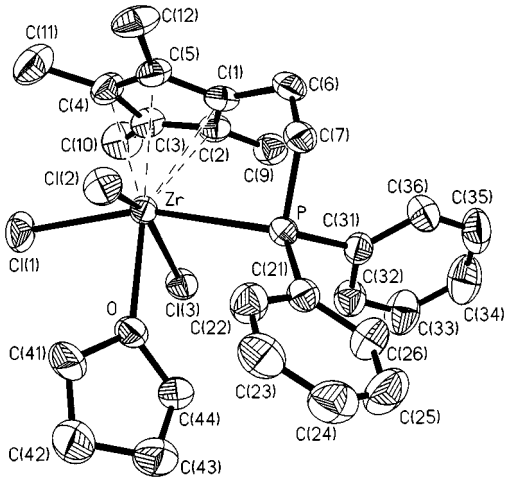



Figure 1. Molecular structure of complex **11**; displacement ellipsoids are shown at 50% probability level; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Zr−O 2.419(2), Zr−Cl(1) 2.4619(10), Zr−Cl(2) 2.4647(9), Zr−Cl(3) 2.4921(8), Zr−P 2.8906(11), Zr−PL, 2.256(1), P−C(31) 1.828(3), P−C(7) 1.829(3), P−C(21) 1.835(3); O−Zr−Cl(1) 81.72(5), O−Zr−Cl(2) 76.64(5), O−Zr−Cl(3) 76.76(5), Cl(1)−Zr−Cl(2) 89.69(3), Cl(1)−Zr−Cl(3) 90.06(3), Cl(2)−Zr−Cl(3) 153.15(3), O−Zr−P 77.30(5), Cl(1)−Zr−P 158.55(3), Cl(2)−Zr−P 81.23(3), Cl(3)−Zr−P 89.45(3), C(31)−P−C(7) 104.62(14), C(31)−P−C(21) 102.52(12), C(7)−P−C(21) 104.29(13), C(7)−P−Zr 98.59(11), C(21)−P−Zr 123.59(9), C(31)−P−Zr 120.43(9), C(1)−C(6)−C(7) 113.6(2), C(6)−C(7)−P 108.9(2); PL means the least-squares plane of the cyclopentadienyl ring

The cyclopentadienyl ring C(1) through C(5) is planar to within 0.009 Å. All four methyl substituents deviate slightly from the least-squares plane of the ring in the direction opposite to the Zr atom (0.111−0.241 Å). The maximum deviation was found for C(12), which is probably caused by the short intramolecular contact with the Cl(2) atom (3.116 Å).

The coordination environment of the phosphorus atom represents a distorted tetrahedron with approximately equal C−P−C angles [102.52(12)−104.62(14)°]. However, the exocyclic C(Ph)−P−Zr angles [120.43(9)° and 123.59(9)°] are much larger than the endocyclic C(7)−P−Zr angle [98.59(11)°]. Thus, the (Zr−)C(1)−C(6)−C(7)−P−Zr pseudo-metallacycle is significantly strained.

## Conclusion

It is evident, that the zirconium half-sandwich **11** may be considered as only the first "model" example of a transition metal complex derived from tetramethyl(2-phosphanylethyl)cyclopentadienyl ligands. Moreover, the authors are convinced that the availability of the key tetramethylspiroheptadiene **7** by the method reported herein opens a facile pathway to a broad variety of transition metal complexes,

not only with the $C_5(CH_3)_4CH_2CH_2PR_2$ ligands but also, probably, with their 2-arsanylethyl analogues.

## Experimental Section

**General Remarks:** All procedures were performed using either conventional glassware in dry oxygen-free argon or in sealed evacuated glass vessels. The solvents employed (and their perdeuterated analogues) were dried with, and distilled from, conventional agents {namely: diethyl ether and THF (sodium benzophenone ketyl); toluene, heptane and pentane (Na/K alloy); $CH_2Cl_2$ ($P_2O_5$ and then $CaH_2$); acetonitrile (a minimal amount of $P_2O_5$)]; $CD_3CN$ [stirred with and distilled from $CaH_2$ via a high-vacuum line ($1.3 \times 10^{-3}$ mbar) at 0−10°C]}. When performing procedures in evacuated vessels, the degassed solvents were stored in evacuated reservoirs over the corresponding drying agent, and then transferred via a high-vacuum line directly into reaction vessels by trapping with liq. $N_2$. Iodomethane (Fluka) was distilled from $CaH_2$; chlorotrimethylsilane (Fluka) was refluxed with and distilled from aluminium powder (high-vacuum line); diphenylphosphane and zirconium tetrachloride (Fluka) were used without additional purification. $(CH_3)_2NCH_2CH_2C_5(CH_3)_5H$ (**4**) was prepared according to the modified procedure.[3] Thus, for the dehydration and cyclization of $[(CH_3)_2NCH_2CH_2]C(OH)[(CH_3)CH{=}CH(CH_3)]_2$ anhydrous TsOH and DME were used instead of $TsOH{\cdot}H_2O$ and diethyl ether. Lithium diphenylphosphide was obtained by the reaction of $Ph_2PH$ with *n*-butyllithium in pentane, washed with the same solvent on a glass filter and dried in vacuo. − $^1H$, $^{13}C$, and $^{31}P\{^1H\}$ NMR: Varian VXR-400 spectrometer at 400, 100, and 162 MHz, respectively, internal reference standards $CD_3CN$ ($\delta_H$ = 1.93 and $\delta_C$ = 1.3), $CDCl_3$($\delta_H$ = 7.24 and $\delta_C$ = 77.0), $C_6D_6$ ($\delta_H$ = 7.15 and $\delta_C$ = 128.0), $CD_2Cl_2$ ($\delta_H$ = 5.32 and $\delta_C$ = 53.8), [$D_8$]THF ($\delta_H$ = 1.73 and $\delta_C$ = 25.3), external reference 85% $H_3PO_4$ ($^{31}P\{^1H\}$). − Elemental analyses: Carlo−Erba automated analyser. − Mass spectra: Kratos-MS-890 and Varian MAT CH7a Fa spectrometers.

**Ammonium Salt 5:** 25 mL (57.11 g, 402.4 mmol) of $CH_3I$ was added dropwise, at a rate sufficient to maintain gentle reflux, to a stirred solution of cyclopentadiene **4** (38.90 g, 201.2 mmol) in 100 mL of $CH_3CN$. The reaction mixture was stirred under reflux for an additional 1 h and left overnight at room temp. The crystalline precipitate was filtered off, washed on a glass filter with an ice-cold mixture of $CH_3CN/Et_2O$ (1:1, 2 × 20 mL) and with ether (3 × 20 mL) and dried in vacuo. The mother liquor and washings were combined, concentrated to ca. 50 mL and cooled to −18°C. The precipitated crystals were separated and washed as described above. The mother liquor and washings were worked up once more to give an additional portion of the product. The total amount of quaternary ammonium salt **5** was 47.30 g (70%). Decomposition at ca. 120°C without melting. − $^1H$ NMR (30°C, $CD_3CN$): δ = 0.98, 1.00 (each d, $^3J_{HH}$ = 7.6 Hz, $CHC\mathit{H}_3$), 1.69, 1.74, 1.75, 1.78, 1.80, 1.81, 1.86 (each br. s, $CCH_3$), 2.12 (m, $CHC\mathit{H}_2CH_2N$), 2.54 (m, $C\mathit{H}CH_3$, $CC\mathit{H}_2CH_2N$), 2.66 (m, $C\mathit{H}CH_3$, $CHCH_2C\mathit{H}_2N$), 2.80 (m, $C\mathit{H}CH_2CH_2N$, $CC\mathit{H}_2CH_2N$), 3.04, 3.17, 3.20 (each s, $NCH_3$), 3.25, 3.43 (each m, $CCH_2C\mathit{H}_2N$). − $^{13}C$ NMR (30°C, $CD_3CN$): δ = 10.96, 11.23, 11.56, 11.68, 11.81, 11.97 (each q, $^1J_{CH}$ = 125 Hz, $C\mathit{C}H_3$), 14.19, 14.34 (each q, $^1J_{CH}$ = 126 Hz, $CH\mathit{C}H_3$), 20.35, 20.79 (each t, $^1J_{CH}$ = 129 Hz, $C\mathit{C}H_2CH_2N$), 20.93 (t, $^1J_{CH}$ = 129 Hz, $CH\mathit{C}H_2CH_2N$), 50.17, 52.51 (each d, $^1J_{CH}$ = 123 Hz, $\mathit{C}HCH_3$), 53.51 (d, $^1J_{CH}$ = 123 Hz, $\mathit{C}HCH_2CH_2N$), 53.68 (br. q, $^1J_{CH}$ = 143 Hz, $NCH_3$), 62.84 (t, $^1J_{CH}$ = 144 Hz, $CHCH_2\mathit{C}H_2N$), 65.71, 66.20 (each t, $^1J_{CH}$ = 144 Hz, $CCH_2\mathit{C}H_2N$), 132.46, 132.96, 133.96, 134.69, 135.23, 138.10, 139.41, 140.02, 140.89, 143.55 (each s, $\mathit{C}CH_3$, $\mathit{C}CH_2CH_2N$). − EI MS (250°C, 70 eV); *m/z* (%): 149 (8) $[HC_5(CH_3)_4CH_2CH_2^+]$, 148 (55) $[HC_5(CH_3)_4CH{=}CH_2^+]$, 147 (8) $[C_7H_3(CH_3)_4^+]$, 142 (5) $[CH_3I^+]$, 134 (5) $[(CH_3)_4C_5{=}CH_2^+]$, 133 (100) $[C_7H_4(CH_3)_3^+]$, 128 (12) $[HI^+]$, 127 (10) $[I^+]$, 119 (21) $[C_7H_5(CH_3)_2^+]$, 105 (41) $[C_7H_6(CH_3)^+]$, 91 (42) $[C_7H_7^+]$, 59 (27) $[(CH_3)_3N^+]$, 58 (61) $[(CH_3)_2N{=}CH_2^+]$. − Compound **5** presents a material of > 95% purity ($^1H$-NMR data). The dominant admixture is $CH_2{=}CHC(O)C(CH_3){=}CH(CH_3)$. − $^1H$ NMR (30°C, $CD_3CN$): δ = 1.41 (dq, 3 H, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.6 Hz, $=CHC\mathit{H}_3$), 1.77 [quint, 3 H, $^4J_{HH}$ = $^5J_{HH}$ = 1.6 Hz, $=C(CH_3)-$], 5.21 (dd, 1 H, $^2J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 11.0 Hz, *cis*-$CH_2{=}$), 5.35 (dd, 1 H, $^2J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 17.1 Hz, *trans*-$CH_2{=}$), 5.43 (qq, 1 H, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.6 Hz, $=C\mathit{H}CH_3$), 6.87 (dd, 1 H, $^3J_{HH}$ = 17.1 Hz, $^3J_{HH}$ = 11.0 Hz, $C\mathit{H}{=}CH_2$).

**4,5,6,7-Tetramethylspiro[2,4]hepta-4,6-diene (7):** 57 mL of a 2.16 M hexane solution of *n*-butyllithium (124.0 mmol) was added to a stirred suspension of the ammonium salt **5** (41.53 g, 123.9 mmol) in 250 mL of THF at −60°C. The reaction mixture was allowed to warm gradually to room temp. under continued stirring. Scarlet coloration of the solution appeared and deepened while the white precipitate became more voluminous (ca. −20°C). The mixture was then heated for 30 min under reflux. Vigorous evolution of $N(CH_3)_3$ began at 40−50°C. The colour of the solution changed slowly from dark scarlet to pale orange and the precipitate dissolved. The resultant solution was cooled down to 0°C and poured into an approximately equal volume of ice-cold water. The organic layer was separated, the aqueous layer extracted with $Et_2O$ (3 × 50 mL) and the combined extracts dried with $MgSO_4$. On removing the solvents in a rotary evaporator the product was isolated by distillation as a yellow oil moderately sensitive to air, b.p. 47−48°C at 1.5 mbar. M.p. −7°C. Yield 15.57 g (85%). Compound **7** exhibited a pronounced tendency to undergo polymerisation and was stored at −18°C. − $^1H$ NMR (30°C, $CDCl_3$): δ = 1.23 (s, 4 H, $CH_2$), 1.64 (s, 6 H, $CH_3$), 1.94 (s, 6 H, $CH_3$). − $^{13}C$ NMR (30°C, $CDCl_3$): δ = 8.76 (q, $^1J_{CH}$ = 125 Hz, $CH_3$), 11.21 (t, $^1J_{CH}$ = 164 Hz, $CH_2$), 11.53 (q, $^1J_{CH}$ = 125 Hz, $CH_3$), 37.44 (s, C-3), 133.99, 134.39 (each s, $\mathit{C}CH_3$). − EI MS (25°C, 70 eV); *m/z* (%): 148 $[M]^+$ (3), 147 $[C_7H_3(CH_3)_4]^+$ (100), 133 $[C_7H_4(CH_3)_3]^+$ (33), 119 $[C_7H_5(CH_3)_2]^+$ (11), 105 $[C_7H_6(CH_3)]^+$ (10), 91 $[C_7H_7]^+$ (16), 28 $[C_2H_4]^+$ (15). − $C_{11}H_{16}$ (148.25): calcd. C 89.12, H 10.88; found C 88.73, H 11.11.

**Deprotonation Product 6:**[24] 0.33 mL of a 2.18 M solution of *n*BuLi in hexane (0.72 mmol) was added to a stirred suspension of **5** (0.23 g, 0.69 mmol) in 20 mL of THF at −60°C, and the reaction mixture allowed to warm up to ca. 0°C. The voluminous snow-white precipitate was separated by filtration, washed rapidly on a glass filter with THF (3 × 5 mL) and dried in vacuo to give 0.22 g of **6** as an extremely air- and moisture-sensitive powder. The product was not stable thermally and decomposed noticeably even when stored in an evacuated vessel at −18°C (and considerably faster when stored under THF).

**Thermolysis of Deprotonation Product 6:**[24] A small portion (41.5 mg, 0.12 mmol) of **6** was placed into a glass tube connected via a liq. $N_2$ cooled trap to a high-vacuum line. The tube was heated for 20 min at 80°C and then for 20 min at 120°C. The pale yellow liquid (24.0 mg) in the trap presented an equimolar mixture of $N(CH_3)_3$ (0.12 mmol) and spirane **7** (0.12 mmol) ($^1H$-NMR data). The pale yellow solid residue in the tube (16.5 mg) was found to be LiI (0.12 mmol).

**Lithium Cyclopentadienide (9):**[24] Solutions of spiroheptadiene **7** (2.46 g, 16.6 mmol) and lithium diphenylphosphide (4.00 g, 22.6 mmol) in THF (total volume 75 mL) were mixed at room

temp. and heated at 90−100°C for 10 h. The solvent was removed by distillation from a hot water bath and the residual brown/red oil allowed to cool down to room temp. In 1 d formation of a white precipitate began. After introducing 15 mL of THF and stirring at room temp. for 5 h, the precipitate was filtered off, washed with 10 mL of cold THF and then with 15 mL of ether. On drying in vacuo 4.50 g (80%) of **9** was obtained as a white powder which was extremely sensitive to air and moisture. − $^1$H NMR (30°C, [D$_8$]THF): δ = 1.70 (br., 12 H, $CH_3$), 1.99 (br., 2 H, $CH_2P$), 2.32 (br., 2 H, $CH_2CH_2P$), 7.26 (m, 6 H, *meta*-, *para*-$C_6H_5$), 7.41 (m, 4 H, *ortho*-$C_6H_5$). − $^{13}$C{$^1$H} NMR (30°C, [D$_8$]THF): δ = 11.1 (br. s, $CH_3$), 23.4 (br. d, $^2J_{CP}$ = 18 Hz, $CH_2CH_2P$), 32.2 (br. d, $^1J_{CP}$ = 14 Hz, $CH_2P$), 105.9, 106.7 (each br. s, $CCH_3$), 112.5 (br. d, $^3J_{CP}$ = 14 Hz, $CCH_2CH_2P$), 128.65 (s, *para*-$C_6H_5$), 128.82 (d, $^3J_{CP}$ = 6.0 Hz, *meta*-$C_6H_5$), 133.61 (d, $^2J_{CP}$ = 18.0 Hz, *ortho*-$C_6H_5$), 141.2 (br. d, $^1J_{CP}$ = 15 Hz, *ipso*-$C_6H_5$). − $^{31}$P{$^1$H} NMR (30°C [D$_8$]THF): δ = −14.6 (br.).

**(2-Diphenylphosphanylethyl)tetramethylcyclopentadiene (Mixture of Isomers) (12):**[24] 10 mL of dry degassed methanol [from over $Mg(OCH_3)_2$] was condensed via a high-vacuum line directly onto 0.67 g (1.97 mmol) of lithium cyclopentadienide **9** by trapping with liq. $N_2$ and the mixture allowed to warm up to room temp. On trapping methanol with liq. $N_2$ product **12** was isolated by distillation in vacuo as a pale yellow viscous oil (0.65 g, 99%). − $^1$H NMR (30°C, $C_6D_6$): δ = 0.90 [d, $^3J_{HH}$ = 7.6 Hz, $CHCH_3$ (**12c**)], 0.95 [d, $^3J_{HH}$ = 7.6 Hz, $CHCH_3$ (**12b**)], 1.65, 1.68, 1.71, 1.76, 1.78 (each br. s, $CCH_3$), 1.68 [obscured m, $CH_2P$ (**12a**)], 1.85 [m, $CH_2CH_2P$ (**12a**)], 2.06−2.19 [m, $CH_2P$ (**12b**, **12c**)], 2.37 [m, CH (**12b**)], 2.42 [m, $CH_2CH_2P$ (**12b**, **12c**)], 2.52 [m, CH (**12a**)], 2.57 [m, CH (**12c**)], 7.01−7.13 (m, *meta*-, *para*-$C_6H_5$), 7.40−7.50 (m, *ortho*-$C_6H_5$). − $^{13}$C NMR (30°C, $C_6D_6$): δ = 11.17, 11.20, 11.27, 11.31, 11.76, 11.80, 11.85 (each q, $^1J_{CH}$ = 126 Hz, $CCH_3$), 14.16 [q, $^1J_{CH}$ = 128 Hz, $CHCH_3$ (**12c**)], 14.25 [q, $^1J_{CH}$ = 128 Hz, $CHCH_3$ (**12b**)], 21.86 [dt, $^1J_{CH}$ = 128 Hz, $^1J_{CP}$ = 11.8 Hz, $CH_2P$ (**12a**)], 22.61 [dt, $^1J_{CH}$ = 128 Hz, $^2J_{CP}$ = 18.4 Hz, $CH_2CH_2P$ (**12b**)], 22.92 [dt, $^1J_{CH}$ = 128 Hz, $^2J_{CP}$ = 17.7 Hz, $CH_2CH_2P$ (**12c**)], 24.10 [dt, $^1J_{CH}$ = 128 Hz, $^2J_{CP}$ = 19.7 Hz, $CH_2CH_2P$ (**12a**)], 29.20 [dt, $^1J_{CH}$ = 128 Hz, $^1J_{CP}$ = 14.7 Hz, $CH_2P$ (**12b**)], 29.91 [dt, $^1J_{CH}$ = 128 Hz, $^1J_{CP}$ = 14.3 Hz, $CH_2P$ (**12c**)], 49.41 [d, $^1J_{CH}$ = 123 Hz, CH (**12c**)], 51.76 [d, $^1J_{CH}$ = 123 Hz, CH (**12b**)], 56.86 [dd, $^1J_{CH}$ = 123 Hz, $^3J_{CP}$ = 13.4 Hz, CH (**12a**)], 128.60 [dm, $^1J_{CH}$ = 158 Hz, *meta*-, *para*-$C_6H_5$], 133.17 [dm, $^1J_{CH}$ = 158 Hz, *ortho*-$C_6H_5$], 133.58, 134.22, 134.54, 135.02, 136.42, 138.21, 138.25, 138.26 (each s, $CCH_3$), 139.46 [d, $^3J_{CP}$ = 12.5 Hz, $CCH_2CH_2P$ (**12b**)], 139.79 [d, $^1J_{CP}$ = 14.6 Hz, *ipso*-$C_6H_5$], 139.83 [d, $^1J_{CP}$ = 14.0 Hz, *ipso*-$C_6H_5$], 139.94 (d, $^1J_{CP}$ = 14.7 Hz, *ipso*-$C_6H_5$), 142.46 [d, $^3J_{CP}$ = 12.3 Hz, $CCH_2CH_2P$ (**12c**)]. − $^{31}$P{$^1$H} NMR (30°C, $C_6D_6$): δ = −14.4 [s, (**12c**)], −13.9 [s, (**12b**)], −12.6 [s, (**12a**)]. − $^1$H NMR (30°C, $CD_2Cl_2$): δ = 1.00 [d, $^3J_{HH}$ = 7.6 Hz, $CHCH_3$ (**12c**)], 1.04 [d, $^3J_{HH}$ = 7.6 Hz, $CHCH_3$ (**12b**)], 1.56 [m, $CH_2P$ (**12a**)], 1.74, 1.78, 1.82, 1.84, 1.86, 1.87 (each br. s, $CCH_3$), 1.84 [obscured m, $CH_2CH_2P$ (**12a**)], 2.14−2.31 [m, $CH_2P$ (**12b**, **12c**)], 2.37 [m, $CH_2CH_2P$ (**12b**, **12c**)], 2.50 [m, CH (**12b**)], 2.71 [m, CH (**12a**, **12c**)], 7.34−7.45 (m, *meta*-, *para*-$C_6H_5$), 7.49−7.54 (m, *ortho*-$C_6H_5$). − EI MS (250°C, 70 eV); *m*/*z* (%): 334 (88) [M$^+$], 319 (85) [M$^+$ − $CH_3$], 306 (69) [M$^+$ − $CH_3$−$CH_3$], 291 (25) [M$^+$ − $CH_3$−$CH_3$−$CH_3$], 199 (100) [$(C_6H_5)_2PCH_2^+$], 121 (99) [M$^+$ − $(C_6H_5)_2PCH_2CH_2$]. − $C_{23}H_{27}P$ (334.45): calcd. C 82.60, H 8.14; found C 83.04, H 8.27.

**[2-(Diphenylphosphanyl)ethyl]tetramethyl(trimethylsilyl)cyclopentadiene (10):**[24] 1 mL (0.86 g, 7.92 mmol) of $(CH_3)_3SiCl$ was added at room temp. to a suspension of cyclopentadienide **9** (2.51 g, 7.37 mmol) in 20 mL of THF. The stirred reaction mixture was heated at 80°C for 30 min and the solvent removed into a trap cooled with liq. $N_2$. The product was isolated by distillation in vacuo as a viscous pale yellow oil sensitive to air. Yield 2.98 g (99%). − $^1$H NMR (30°C, $C_6D_6$): δ = −0.20 [br., $Si(CH_3)_3$], −0.10 [br., $Si(CH_3)_3$], 1.15 [br., $CH_3CSi(CH_3)_3$], 1.74, 1.79 (each br., $CCH_3$,), 2.19 (br., $CH_2P$), 2.49(br., $CH_2CH_2P$), 7.00−7.12 (br. m, *meta*-, *para*-$C_6H_5$), 7.42−7.52 (br. m, *ortho*-$C_6H_5$). − $^{31}$P{$^1$H} NMR (30°C, $C_6D_6$): δ = −13.8 (br.), −13.0 (br.). − EI MS (25°C, 70 eV); *m*/*z* (%): 406 (9) [M$^+$], 391 (8) [M$^+$ − $CH_3$], 334 (33) [M$^+$ − $CH_2Si(CH_3)_2$], 333 (85) [M$^+$ − $Si(CH_3)_3$], 221 (23) [M$^+$ − $(C_6H_5)_2P$], 220 (84) [M$^+$ − $(C_6H_5)_2PH$], 199 (46) [$(C_6H_5)_2PCH_2^+$], 185 (22) [$(C_6H_5)_2P^+$], 147 (62) [$C_7H_3(CH_3)_4^+$], 146 (87) [M$^+$ − $(C_6H_5)_2PH$−$HSi(CH_3)_3$], 134 (57) [$C_5(CH_3)_4$=$CH_2^+$], 133 (80) [$C_7H_4(CH_3)_3^+$], 119 (47) [$C_7H_5(CH_3)_2^+$], 105 (47) [$C_7H_6(CH_3)^+$], 91 (60) [$C_7H_7^+$], 73 (100) [$Si(CH_3)_3^+$]. − $C_{26}H_{35}PSi$ (406.63): calcd. C 76.80, H 8.68; found C 77.02, H 8.94.

**Zirconium Complex 11:**[24] A suspension of 1.28 g (5.49 mmol) of $ZrCl_4$ in 10 mL of toluene and a solution of 2.23 g (5.48 mmol) of silane **10** in 30 mL of the same solvent were mixed at room temp. and the reaction mixture heated at 90−100°C under vigorous stirring for 3 h. On cooling down to room temp., the reaction mixture consisted of a bright yellow solution and a small amount of a brown viscous oil. The solution was decanted and the oil extracted with hot toluene (2 × 5 mL). Removal of all of the volatile components from the combined extracts gave 2.54 g (87%) of crude THF-free **11** as a viscous lemon yellow oil. Addition of 10 mL of THF led to complete dissolution of crude **11**. In less than 1 min fast crystallization began. On removing approximately one-half of the initial amount of THF the mixture was kept overnight. The crystalline product **11** was filtered off, washed on a filter with ether (2 × 5 mL) and dried in vacuo. Yield 1.11 g (34%). The product decomposed at 143°C with foaming (elimination of THF). Single crystals suitable for X-ray analysis were obtained by crystallization from hot THF. − $^1$H NMR (30°C, $CD_2Cl_2$): δ = 1.75 (m, 4 H, $CH_2CH_2O$ in THF), 1.98, 2.18 (each s, 6 H, $CH_3$), 2.97 (dt, 2 H, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 21.0 Hz, $CH_2CH_2P$), 3.09 (q, 2 H, $^3J_{HH}$ = 7.0 Hz, $^2J_{HP}$ = 7.0 Hz, $CH_2P$), 3.77 (m, 4 H, $CH_2O$ in THF), 7.40 (m, 6 H, *meta*-, *para*-$C_6H_5$), 7.70 (m, 4 H, *ortho*-$C_6H_5$). − $^{13}$C NMR (30°C, $CD_2Cl_2$): δ = 13.24, 13.41 (each q, $^1J_{CH}$ = 127 Hz, $CH_3$), 21.18 (dt, $^1J_{CH}$ = 131 Hz, $^2J_{CP}$ = 11.0 Hz, $CH_2CH_2P$), 25.77 (t, $^1J_{CH}$ = 133 Hz, $CH_2CH_2O$ in THF), 29.84 (dt, $^1J_{CH}$ = 134 Hz, $^1J_{CP}$ = 21.4 Hz, $CH_2P$), 69.10 (t, $^1J_{CH}$ = 145 Hz, $CH_2O$ in THF), 128.32, 128.38 (each s, $CCH_3$), 129.53 (dd, $^1J_{CH}$ = 160 Hz, $^3J_{CP}$ = 8.4 Hz, *meta*-$C_6H_5$), 130.60 (d, $^1J_{CH}$ = 160 Hz, *para*-$C_6H_5$), 132.64 (d, $^1J_{CP}$ = 27.5 Hz, *ipso*-$C_6H_5$), 132.69 (dd, $^1J_{CH}$ = 160 Hz, $^2J_{CP}$ = 9.5 Hz, *ortho*-$C_6H_5$), 134.06 (d, $^3J_{CP}$ = 4.0 Hz, $CCH_2CH_2P$). − $^{31}$P{$^1$H} NMR (30°C, $CD_2Cl_2$): δ = 5.8 (s). − EI MS (250°C, 70 eV); *m*/*z* (%): 528 (13) [M$^+$ − THF], 513 (1) [M$^+$ − THF−$CH_3$], 493 (3) [M$^+$ − THF−Cl], 333 (23) [M$^+$ − THF−$ZrCl_3$], 308 (6) [M$^+$ −THF−$(C_6H_5)_2PCl$], 199 (100) [$(C_6H_5)_2PCH_2^+$], 185 (90) [$(C_6H_5)_2P^+$], 147 (14) [$C_7H_3(CH_3)_4^+$], 133 (24) [$C_7H_4(CH_3)_3^+$], 121 (48) [$C_9H_{13}^+$], 108 (59) [$C_8H_{12}^+$], 91 (21) [$C_7H_7^+$]. − $C_{27}H_{34}Cl_3OPZr$ (603.12): calcd. C 53.77, H 5.68; found C 53.27, H 5.75.

**X-ray Crystallographic Study of Complex 11:**[25] Crystal data: $C_{27}H_{34}Cl_3OPZr$, $M$ = 603.12, monoclinic, $a$ = 8.336(2), $b$ = 33.943(10), $c$ = 9.863(3) Å, β = 101.90(2)°, $V$ = 2730.8(13) Å$^3$, space group $P2_1/c$, $Z$ = 4, $D_c$ = 1.467 g/cm$^3$, $F$(000) = 1240, μ(Mo-$K_\alpha$) = 0.773 mm$^{-1}$. Data collection, structure solution and refinement. A crystal of approximate dimensions 0.4 × 0.3 × 0.3 was used for data collection. A total of 6093 reflections (4470 unique, $R_{int}$ = 0.0244) were measured with an Enraf−Nonius CAD4 diffractometer (graphite-monochromatized Mo-$K_\alpha$ radiation, λ =

0.71073 Å) at room temp. Data was collected in the range $2.19° < \theta < 24.99°$ ($-9 \le h \le 9$, $-40 \le k \le 40$, $0 \le l \le 11$) using the ω scan mode. The structure was solved by direct methods[26] and refined by full-matrix least squares on $F^2$[27] with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were placed in calculated positions. Both coordinates and isotropic thermal parameters for H atoms at side-chain carbon atoms C(6) and C(7) and at Ph groups were refined. All other hydrogen atoms were refined using a riding model ($U_{iso}$ were taken as $1.5 \times U_{eq}$ of parent C atoms). The methyl group at C(2) was found to be rotationally disordered over two positions with equal occupancies. The weighting scheme was $w^{-1} = \sigma^2(F^2) + (0.0483P)^2 + 0.5400P$, where $P = (2F_c^2 + F_o^2)/3$. The final residuals were: $R_1 = 0.0285$, $wR_2 = 0.0750$ for 3543 reflections with $I > 2\sigma(I)$ and 0.0463, 0.0802 for all data and 359 parameters. Goof: 1.086, maximum shift/e.s.d.: 0.001, maximum $\Delta\rho = 0.638$ e × Å$^{-3}$.

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