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General route for the synthesis of terminal phosphanylphosphido complexes of Zr(IV) and Hf(IV): Structural investigations of the first zirconium complex with a phosphanylphosphido ligand

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Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 70th birthday

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A B S T R A C T

Reactions of $R_2P–P(SiMe_3)Li$ with $[Cp_2MCl_2]$ (M = Zr, Hf) in hydrocarbons yield the related terminal phosphanylphosphido complexes $[Cp_2M(Cl)\{(Me_3Si)P–PR_2\text{-}\kappa P^1\}]$ (R = ^{i}Pr and ^{t}Bu). The solid state structures of $[Cp_2M(Cl)\{P(SiMe_3)–P^iPr_2\text{-}\kappa P^1\}]$ (M = Zr, Hf) were established by single crystal X-ray diffraction studies. The phosphido-P atoms adopt almost planar geometries and the phosphanyl P atoms adopt pyramidal geometries. The reaction of a mixture of $(Me_3Si)_2PLi$ and $Ph_2P–P(SiMe_3)Li$ with $[CpZrCl_3]$ in toluene yields the dinuclear complex $[Cp_2Zr_2Cl_5(Ph_2PPPSiMe_3)(Li\ THF\ DME)]$.

1. Introduction

Group(IV) metallocenes with organylphosphido ligands have been a subject of thorough studies [1]. An important entrance to this class of compounds are reactions of related metallocene dichlorides $[Cp_2MCl_2]$ (M = Zr, Hf; Cp = cyclopentadienyl or substituted cyclopentadienyl) with lithium derivatives of primary and secondary phosphanes of medium or large steric effects leading to the formations of disubstituted [2–10] and monosubstituted [2,10–16] compounds, which were in part structurally characterized. Low temperature and dropwise addition of reagents suppress the formation of diphosphanes and cyclic dinuclear M(III) complexes [3,17]. In the course of our work upon the reactivity of lithiated diphosphanes $R_2P–P(SiMe_3)Li$ (R = ^{t}Bu, Et_2N, $^iPr_2N$) towards group(IV) dichlorometallocenes we have established that these compounds can act as precursors for two types of new organophosphorus ligands: phosphanylphosphidene $R_2P–P$ ligands [18] and terminal phosphanylphosphido ligands $R_2P–P(SiMe_3)$ [19]. Scheme 1 shows the structures of phosphanylphosphido complexes compared to the well-known “classical” phosphido complexes.

Now we present the results of our studies on the reactivity of $R_2P–P(SiMe_3)Li$ (R = ^{i}Pr, ^{t}Bu, Ph) towards $[Cp_2ZrCl_2]$, $[CpZrCl_3]$ and $[Cp_2HfCl_2]$. This work was presented in a preliminary form at the 18th International Conference on Phosphorus Chemistry [20].

2. Experimental

Toluene and THF were dried over Na/benzophenone and distilled under nitrogen. Pentane was dried over Na/benzophenone/diglyme and distilled under nitrogen. All manipulations were performed in flame-dried Schlenk type glassware on a vacuum line. ^{31}P and ^{1}H NMR spectra were recorded on Bruker AC250, Bruker AMX300 and Bruker AV400 MHz spectrometers (external standard 85% H_3PO_4) at ambient temperature. The simulation and iteration of spectra was made using Bruker software [21]. For the numbering of atoms see Schemes 1 and 3, Figs. 1–3. $[Cp_2ZrCl_2]$ was purchased from Aldrich. Literature methods were used to prepare $[Cp_2HfCl_2]$ [22], $^tBu_2P–P(SiMe_3)Li$ [23], $^iPr_2P–P(SiMe_3)Li$, $Ph_2P–P(SiMe_3)Li$ [24] and $[CpZrCl_3]$ [25]. $Ph_2P–P(SiMe_3)Li$ could not be obtained in pure form because during the lithiation of $Ph_2P–P(SiMe_3)_2$ the P–P bond was split [24]. So we used a mixture consisting of $Ph_2P–P(SiMe_3)Li$, $(Me_3Si)_2PLi$ and $Ph_2P–PPh_2$.

2.1. Reaction of $^tBu_2P–P(SiMe_3)Li$ with $[Cp_2ZrCl_2]$

A suspension of $^tBu_2P–P(SiMe_3)Li·2THF$ (0.351 g, 0.878 mmol) in pentane (2 mL) was slowly added to a suspension of $[Cp_2ZrCl_2]$ (0.232 g, 0.795 mmol) in pentane (3 mL) which was placed in a cooling bath at −40 °C. The temperature of the reaction was maintained at −40 °C to −30 °C. The reaction mixture turned immediately violet. The resulting solution was stirred for 2 h at room temperature, LiCl was filtered off and the solvent removed under

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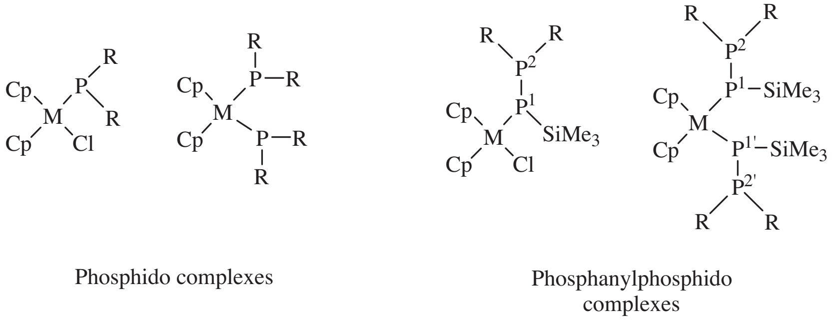
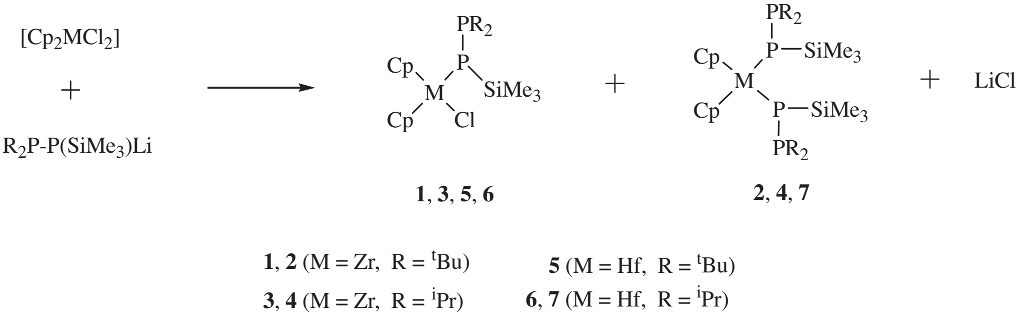
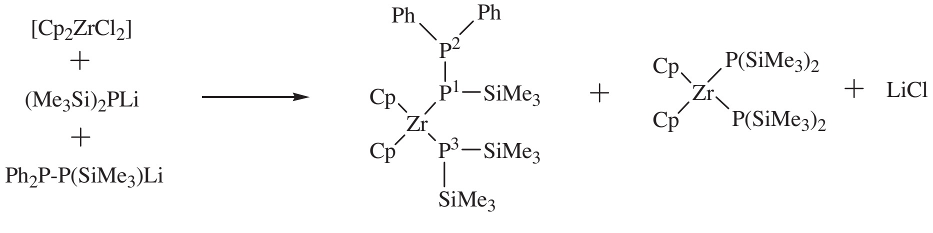


Scheme 1.



Scheme 2.



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Scheme 3.

vacuum. The resulted $[Cp_2ZrCl\{P^1(SiMe_3)–P^2(^tBu)_2\text{-}\kappa P^1\}]$ (**1**) is very well soluble in hydrocarbons. After evaporation of pentane we obtained a deep red oil. Attempts to obtain any crystals of **1** were unsuccessful.

^{31}P NMR (evacuated reaction solution, in toluene-d_8): (**1**) 68.5 ppm (d, P^2), −3.9 ppm (d, P^1) $^1J_{P1-P2} = -520.3$ Hz; $^tBu_2P–P(SiMe_3)H$ [25], $^tBu_2PH$, and a small amount of $P_4(P^tBu_2)_4$ [26]. In some runs small resonances probably of $[Cp_2Zr\{P^{1,1'}(SiMe_3)–P^{2,2'}{}^tBu_2\}_2]$ (**2**) were visible: 66.3 ppm (d, $P^{2,2'}$); −110.8 ppm (d, $P^{1,1'}$), $^1J_{P1-P2} = -517.7$ Hz. The signals display no features of an AA′XX′ spin pattern, however.^1H NMR (evacuated reaction solution, in toluene-d_8): (**1**) 6.05 ppm (br.s, 11.1 H, C_5H_5) the expected two signals are not resolved; 1.34 ppm (d, $^3J_{PH}$ 11.96 Hz, 19.3 H, $C(CH_3)_3$); 0.56 ppm (br. d, $^3J_{PH}$ 4.15 Hz, 9H, $Si(CH_3)_3$).

2.1.1. *Reaction of $^iPr_2P–P(SiMe_3)Li$ with $[Cp_2ZrCl_2]$, synthesis of $[Cp_2Zr(Cl)\{P(SiMe_3)\text{-}P^iPr_2\text{-}\kappa P^1\}]$ (**3**)*

A solution of $^iPr_2P–P(SiMe_3)Li{\cdot}2.7THF$ (0.159 g, 0.377 mmol) in toluene (2 mL) was slowly added to a suspension of $[Cp_2ZrCl_2]$ (0.109 g, 0.373 mmol) in toluene (2 mL) which was placed in a cooling bath at −40 °C to −30 °C. The reaction mixture turned immediately bright red. Then the resulting solution was stirred for 2 h at room temperature, LiCl was filtered off and the solvent was removed under vacuum. The residue was dissolved in pentane (1.5 mL) and after 1 week at room temperature small red needles of **3** were deposited (0.050 g, yield 28%).

$^{31}P\{1H\}$ NMR (reaction solution in toluene, C_6D_6, ambient temperature): (**3**) 35.1 ppm (d, P^2), 2.9 ppm (d, P^1), $^1J_{P1-P2} = -427.5$ Hz. Additionally: probably $[Cp_2Zr\{P^{1,1'}(SiMe_3)–P^{2,2'}{}^iPr_2\}_2]$ (**4**) 31.9 ppm (d, $P^{2,2'}$); −94.9 ppm (d, P^1,$P^{1'}$), $^1J_{P1-P2} = -409.2$ Hz, no features of an AA′XX′ pattern were visible; $^iPr_2P^2–P^1(SiMe_3)H$ −8.6 ppm (d, P^2), −201.6 ppm (d, P^1), $^1J_{P-P} = -188.2$ Hz, $^1J_{P-H} \approx 190$ Hz; $^iPr_2P–P(SiMe_3)_2$ [23]; $^iPr_2PH$ −15.4 (s, $^1J_{P-H} \approx 191$ Hz) and $^tPr_2P^2–P^1H–P^iPr_2$: −2.6 ppm (d, P^2), −140.0 ppm (t, P^1), $^1J_{P-P} = -199.0$ Hz, $^1J_{P-H} \approx 190$ Hz.

$^{31}P\{1H\}$ NMR (C_6D_6, ambient temperature): (**3**) 35.1 ppm (d, P^2), 2.9 ppm (d, P^1), $^1J_{P1-P2} = -427.5$ Hz.

^1H NMR (C_6D_6, ambient temperature): (**3**) 6.061 ppm (s, 4.5H, C_5H_5), 6.058 ppm (s, 4.6H, C_5H_5), 2.18 ppm (quart, quart, d, d, $^2J_{HH}$ 6.96 Hz, $^2J_{HH}$ 6.83 Hz, $^2J_{PH}$ 6.30 Hz, $^3J_{PH}$ 4.23 Hz, 2.0H, $(CH_3)_2CH$), 1.36 ppm (dd, $^2J_{HH}$ 6.96 Hz, $^3J_{PH}$ 13.54 Hz, 11.7H (broad signal under the multiplet), $(CH_3)_2CH$), 1.25 ppm (ddd, $^2J_{HH}$ 6.83 Hz, $^3J_{PH}$ 15.89 Hz, $^4J_{PH}$ 0.8 Hz, 7.0H, $(CH_3)_2CH$), 0.54 ppm (d, $^3J_{PH}$ 4.26 Hz, 9H, $(CH_3)_3Si$).

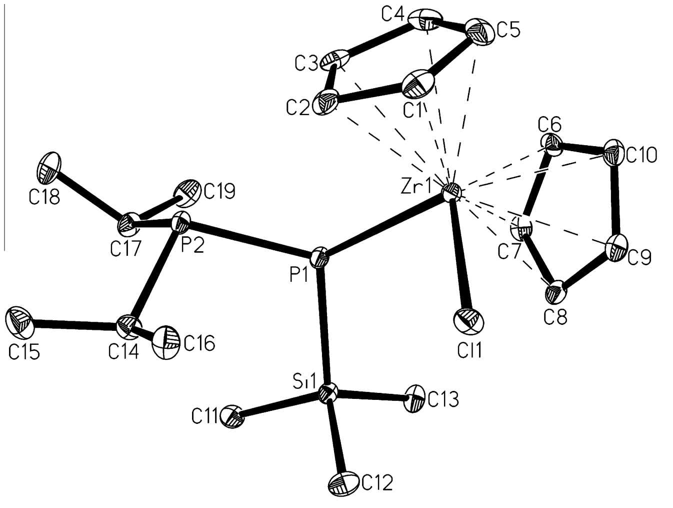


Fig. 1. Molecular structure of **3** showing the atom-numbering scheme (30% probability displacement ellipsoids), important bond lengths (pm) and bond angles (°). H atoms have been omitted. Zr1–Cl1 247.4(1), Zr1–P1 258.3(1), P1–P2 218.7(2), P1–Si1 225.4(2), P1–Zr1–Cl1 100.56(4), Zr1–P1–P2 117.56(5).

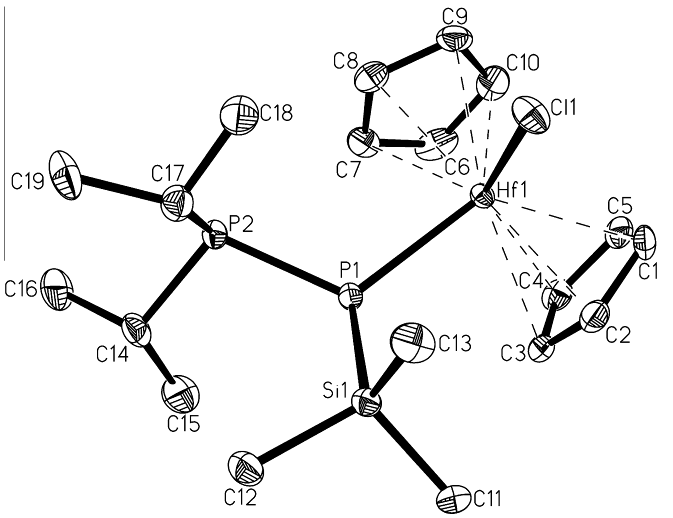


Fig. 2. Molecular structure of **6** showing the atom-numbering scheme (30% probability displacement ellipsoids), important bond lengths (pm) and bond angles (°). H atoms have been omitted. Hf1–Cl1 244.83(9), Hf1–P1 256.81(9), P1–P2 218.5(1), P1–Si1 225.2(1), P1–Hf1–Cl1 100.30(3), Hf1–P1–P2 117.16(4).

^{13}C{1H} NMR (C$_6$D$_6$, ambient temperature): (**3**) 112.45 ppm (s, C$_5$H$_5$), 112.41 ppm (s, C$_5$H$_5$), 29.0 ppm (dd, 3.5 Hz, 21.9 Hz (CH$_3$)$_2$CH), 24.3 ppm (dd, 5.3 Hz, 12.5 Hz (*C*H$_3$)$_2$CH), 24.1 ppm (dd, 5.8 Hz, 22.5 Hz (*C*H$_3$)$_2$CH)), 6.70 ppm (d, 8.6 Hz (*C*H$_3$)$_3$Si).

Elemental analysis of (**3**): *Anal.* Calc. for C$_{19}$H$_{33}$P$_2$ZrSiCl: C, 47.72; H, 6.96. Found: C, 47.74; H, 6.40%.

2.1.2. Reaction of ^{t}Bu$_2$P–P(SiMe$_3$)Li with [Cp$_2$HfCl$_2$]

A suspension of [Cp$_2$HfCl$_2$] (0.123 g, 0.313 mmol) in toluene (2 mL) was slowly added to a solution of ^{t}Bu$_2$P–P(SiMe$_3$)Li·2THF (0.148 g, 0.314 mmol) in toluene (2 mL) which was placed in a cooling bath at −40 °C to −30 °C. The reaction mixture turned slowly orange. After adding the suspension of [Cp$_2$HfCl$_2$] the resulting slurry was stirred overnight at room temperature and turned dark red. After that the solvent was removed under vacuum, the residue was dissolved in pentane (4 mL) and LiCl was filtered off. The resulted [Cp$_2$HfCl{P(SiMe$_3$)–P^{t}Bu$_2$-κ*P*^{1}}] (**5**) is very well soluble in hydrocarbons and thus the attempts to obtain any crystals of **5** were unsuccessful. After evaporation of pentane we obtained a red-violet oil.

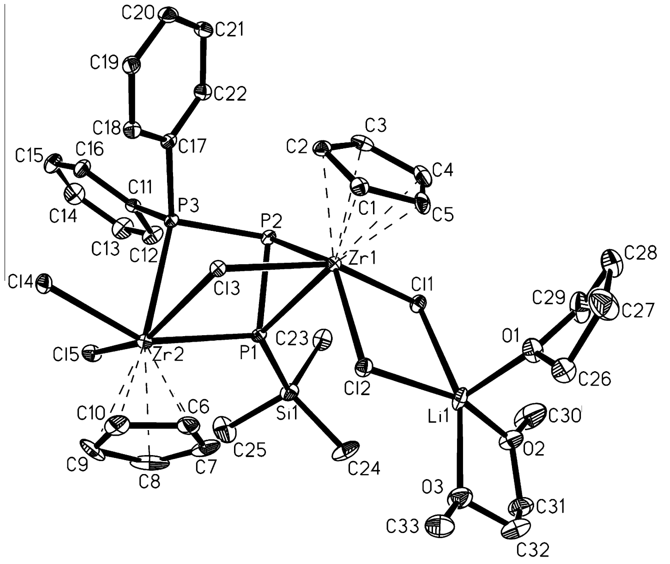


Fig. 3. Molecular structure of **9** showing the atom-numbering scheme (30% probability displacement ellipsoids), important bond lengths (pm) and bond angles (°). H atoms have been omitted. C11–P3 183.8(4); C17–P3 188.5(5); Cl1–Zr1 252.3(1); Cl1–Li1 259.7(8); Cl2–Li1 250,1(8); Cl2–Zr1 252.7(1); Cl3–Zr1 263.6(1); Cl3–Zr2 264.0(1); Cl4–Zr2 248,8(1); Cl5–Zr2 244.8(1); Li1–O1 195.5(9); Li1–O2 203.3(9); Li1–O3 206.7(10); P1–P2 218.6(2); P1–Si 225,5(2); P1–Zr2 267.9(1); P1–Zr1 267.8(1); P2–P3 218.1(2); P2–Zr1 266.3(1); C17–P3–C11 101.8(2); C17–P3–P2 106.5(1); C11–P3–P2 105.1(1); P1–P2–P3 88.70(6); P3–P2–Zr1 104.65(6); Zr2–P1–Zr1 102.67(4); P2–P1–Si1 108.59(7); Zr1–Cl3–Zr2 104.87(4).

^{31}P NMR (reaction solution, toluene, C$_6$D$_6$): (**5**) 67.5 ppm (d, P^2), −44.5 ppm (d, P^1), $^1J_{P1-P2}$ = −511.5 Hz; additionally ^{t}Bu$_2$P–P(SiMe$_3$)H, ^{t}Bu$_2$P–P(SiMe$_3$)$_2$ and a small amount of two unidentified compounds.

^{1}H NMR (reaction solution, toluene, C$_6$D$_6$): (**5**) 6.03 ppm (br. s, 10.3H, C$_5$*H*$_5$) the expected two signals are not resolved; 1.39 ppm (d, $^3J_{PH}$ 12.1 Hz, 20.2H, C(C*H*$_3$)$_3$); 0.60 ppm (br. d, $^3J_{PH}$ 3.74 Hz, 9H, Si(C*H*$_3$)$_3$).

2.1.3. Reaction of ^{i}Pr$_2$P–P(SiMe$_3$)Li with [Cp$_2$HfCl$_2$], synthesis of [Cp$_2$Hf(Cl){P(SiMe$_3$)-P^{i}Pr$_2$-κ*P*^{1}}] (**6**)

A suspension of [Cp$_2$HfCl$_2$] (0.124 g, 0.327 mmol) in toluene (2 mL) was slowly added to a solution of ^{i}Pr$_2$P–P(SiMe$_3$)Li·3THF (0.145 g, 0.327 mmol) in toluene (2 mL) which was placed in a cooling bath at −40 °C. The temperature of the reaction was maintained at −40 °C to −30 °C. The reaction mixture turned slowly yellow. The resulting solution was stirred overnight at room temperature and turned orange. Then the solvent was removed under vacuum, the residue was dissolved in pentane (4 mL), LiCl was filtered off and the solution was concentrated to 1 mL. After 3 days at −35 °C yellow crystals of **6** were deposited (0.055 g, yield 30.2%).

^{31}P{1H} NMR (reaction solution, toluene, C$_6$D$_6$): (**6**) 35.8 ppm (d, P^2), −26.0 ppm (d, P^1), $^1J_{P1-P2}$ = −423.2 Hz; probably [Cp$_2$Hf{P$^{1,1'}$(SiMe$_3$)–P$^{2,2'i}$Pr$_2$}$_2$] (**7**) (small amount), 31.1 ppm (d, P$^{2,2'}$), −114.8 ppm (d, P$^{1,1'}$), $^1J_{P1-P2}$ = −410.5 Hz; ^{i}Pr$_2$P–P(SiMe$_3$)H, ^{i}Pr$_2$P–P(SiMe$_3$)$_2$ [24], ^{i}Pr$_2$PH and ^{t}Pr$_2$P–PH–P^{i}Pr$_2$.

^{1}H NMR (reaction solution, toluene, C$_6$D$_6$): (**6**) 5.985 ppm (s, 4.8H, C$_5$*H*$_5$), 5.980 ppm (s, 4.7H, C$_5$*H*$_5$), 2.19 ppm (quart, quart, d, d, $^2J_{HH}$ 6.98 Hz, $^2J_{HH}$ 6.83 Hz, $^2J_{PH}$ 6.90 Hz, $^3J_{PH}$ 4.23 Hz, (CH$_3$)$_2$C*H*, partly hidden by solvent peak), 1.37 ppm (dd, $^2J_{HH}$ 6.98 Hz, $^3J_{PH}$ 13.54 Hz, 6.9H, (C*H*$_3$)$_2$CH)), 1.27 ppm (ddd, $^2J_{HH}$ 6.83, $^3J_{PH}$ 15.89 Hz, $^4J_{PH}$ 0.95 Hz, 7.7H, (C*H*$_3$)$_2$CH)), 0.56 ppm (d, $^3J_{PH}$ 4.20 Hz, 9H, (C*H*$_3$)$_3$Si).

2.1.4. Reaction of $Ph_2P–P(SiMe_3)Li$ and $(Me_3Si)_2PLi·3THF$ with $[Cp_2ZrCl_2]$

A suspension of 0.441 g of a mixture consisting of $Ph_2P–P(SiMe_3)Li·3THF$ (0.172 g, 0.336 mmol), $(Me_3Si)_2PLi·3THF$ (0.225 g, 0.563 mmol) and $Ph_2P–PPh_2$ (0.044 g, 0.118 mmol) in pentane (3 mL) was slowly added to a suspension of $[Cp_2ZrCl_2]$ (0.180 g, 0.617 mmol) in pentane (3 mL) which was placed in a cooling bath at −40 °C to −30 °C. The reaction mixture turned immediately violet. The resulting solution was stirred for 2 h at room temperature, LiCl was filtered off and the solvent was partially removed under vacuum. The concentrated solution was stored for two days at −70 °C and an amorphous solid of unknown composition deposited (the ^{31}P NMR examination excluded **8**).

^{31}P NMR (reaction solution, pentane, C_6D_6): (**8**) 1.6 ppm (dd, P^2), −42.1 ppm (dd, P^3), −46.2 ppm (dd, P^1), $^1J_{P1–P2} = -376.0$ Hz, $^2J_{P1–P3} = 13.1$ Hz, $^3J_{P2–P3} = 8.7$ Hz; additionally $[Cp_2Zr\{P(SiMe_3)_2\}_2]$ (strong signal), −72.0 ppm (s) [27]; small amounts of Ph_2PSiMe_3 −56.6 ppm (s) [28]; $Ph_2P–PPh_2$ −16.0 ppm (s) [28]; Ph_2PH −40.3 ppm (s) [29].

*2.1.5. Reaction of $Ph_2P–P(SiMe_3)Li$ and $(Me_3Si)_2PLi$ with $[CpZrCl_3]$, synthesis of $[Cp_2Zr_2Cl_5(Ph_2PPPSiMe_3)(Li·THF·DME)]$ (**9**)*

A suspension of 0.249 g of a mixture consisting of $Ph_2P–P(SiMe_3)Li·3THF$ (0.097 g, 0.190 mmol), $(Me_3Si)_2PLi·3THF$ (0.127 g, 0.317 mmol) and $Ph_2P–PPh_2$ (0.025 g, 0.067 mmol) in toluene (2 mL) was slowly added to a suspension of $[CpZrCl_3·DME]$ (0.178 g, 0.505 mmol) in toluene (2 mL) which was placed in a cooling bath at −40 °C to −30 °C. The reaction mixture turned immediately deep red. The resulting solution was warmed to room temperature and filtered. The filtrate was reduced to its half volume and stored at ambient temperature. After several days a small amount of red crystals of **9** deposited.

^{31}P NMR (reaction solution, toluene, C_6D_6): (**9**) −15.0 ppm (dd, P^3), −77.7 ppm (dd, P^2); −118.0 ppm (dd, P^1), $^1J_{P2–P3} = -228.5$ Hz, $^1J_{P1–P2} = -197.8$ Hz, $^2J_{P1–P3} = 19.1$ Hz; additionally $Ph_2P–PPh_2$; Ph_2PSiMe_3; $P(SiMe_3)_3$; $P(SiMe_3)_2H$; $Ph_2P–P(SiMe_3)_2$ [24].

2.1.6. X-ray diffraction

Experimental diffraction data were collected on a KM4CCD kappa-geometry diffractometer, equipped with a Sapphire2 CCD detector. An enhanced X-ray Mo Kα radiation source with a graphite monochromator was used. Determination of the unit cells and data collection were carried out at 150 and 120 K. Data reduction, absorption correction, space group determination, solution and refinement were made using the CRYSALIS software package (Oxford Diffraction, 2008) [30].

Structures of **3**, **6** and **9** were solved by direct methods and all non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least squares procedures based on F^2. All hydrogen atoms were refined using an isotropic model with $U_{iso}(H)$ values fixed to be 1.5 times U_{eq} of C atoms for CH_3 or 1.2 times U_{eq} for CH_2 and CH groups. Solutions and refinements were carried out using the SHELX-97 program package [31].

3. Results and discussion

3.1. Reactivity

The addition of 1 equiv. of $R_2P–P(SiMe_3)Li$ (R = ^{i}Pr or ^{t}Bu) to zirconocene dichloride or to hafnocene dichloride, respectively, in toluene or pentane leads to coloured solutions containing presumably the monosubstituted derivatives $[Cp_2M(Cl)\{P(SiMe_3)–PR_2\text{-}\kappa P^1\}]$ (M = Zr or Hf) (compounds **1**, **3**, **5**, **6**) and small amounts of the disubstituted derivatives $[Cp_2M\{P(SiMe_3)–PR_2\text{-}\kappa P^1\}_2]$ (compounds **2**, **4**, **7**) (Scheme 2).

The reactivity of zirconocene dichloride towards $R_2P–P(SiMe_3)Li$ is much higher compared to hafnocene dichloride. The sterical effects of cyclopentadienyl rings are important, $R_2P–P(SiMe_3)Li$ does not react at ambient temperature with $[Cp^*{}_2MCl_2]$ ($Cp^* = C_5Me_5$, M = Zr, Hf).

The reactions involving $Ph_2P–P(SiMe_3)Li$ are considerably more complex because of a significant amount of $(Me_3Si)_2PLi$ in the reagent which we have used [24] and because the P–P bond in $Ph_2P–P(SiMe_3)Li$ is prone to fission reactions. The outcomes of a reaction of $[Cp_2ZrCl_2]$ with a mixture of $Ph_2P–P(SiMe_3)Li$ and $(Me_3Si)_2PLi$ are shown in Scheme 3.

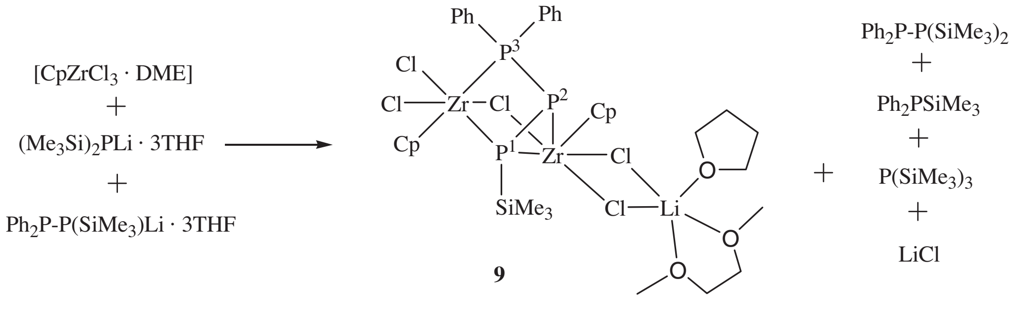
All these compounds are very well soluble in hydrocarbons. We were able to isolate only compounds **3** and **6**. Additionally, the contents of compounds **2**, **4** and **7** in the reaction solutions are low. These compounds are very sensitive to moisture and oxygen. Compound **3** is relatively stable and can be observed for several days in the reaction solutions in sealed NMR tubes at ambient temperature but attempts to dissolve **6** in C_6D_6 or in pentane lead to its almost complete decomposition and to formation of white polymeric materials.

The isolation of compound **9** with the new triphosphorus ligand $Ph_2P–P–P(SiMe_3)$ in a reaction of $Ph_2P–P(SiMe_3)Li·3THF$ and $(Me_3Si)_2PLi·3THF$ with a suspension of $[CpZrCl_3·DME]$ indicates the formation of a new P–P bond in the coordination sphere of a Zr(IV) atom (Scheme 4).

The mechanism of the formation of **9** is not clear. We exclude an intermediate with a $Ph_2P–PLi$- group on the Zr atom because the lithiation of a $P–SiMe_3$ moiety is only possible in donor solvents [19]. $Ph_2P–P(SiMe_3)Li$ is not stable, but we have found no traces of a triphosphane formation in a sample containing $Ph_2P–P(Li)–SiMe_3$ and $(Me_3Si)_2PLi$ in C_6D_6 at ambient temperature.

*3.2. X-ray crystallographic studies of **3**, **6** and **9***

The crystal data and details of the data collection and refinement for **3**, **6** and **9** are given in Table 1.



Scheme 4.

Table 1
Crystallographic data and structure refinement details for **3**, **6** and **9**.

Compound	(**3**)	(**6**)	(**9**)
Empirical formula	$C_{19}H_{33}ClZrP_2Si$	$C_{19}H_{33}ClHfP_2Si$	$C_{33}H_{47}Cl_5LiO_3Zr_2P_3Si$
M_r (g mol^{-1})	478.15	565.42	478.15
Temperature (K)	120(2)	120(2)	120(2)
Wavelength (Å)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	7.5665(10)	7.58010(10)	13.5652(6)
b (Å)	17.518(3)	17.4850(3)	21.4372(10)
c (Å)	18.170(4)	18.1108(4)	21.9544(14)
α (°)	90.0	90.0	90.568(4)
β (°)	109.267(14)	109.142(2)	91.132(5)
γ (°)	90.0	90.0	99.627(4)
V (Å^3)	2273.5(7)	2267.65(7)	6292.6(6)
Z	4	4	6
D_{calc} (mg m^{-3})	1.397	1.656	1.551
F(0 0 0)	992	1120	2976
Absorption coefficient (mm^{-1})	0.795	4.912	0.990
Crystal size (mm)	0.28 × 0.14 × 0.08	0.37 × 0.12 × 0.07	0.22 × 0.18 × 0.12
θ Range (°)	2.61–26.0	2.38–25.50	2.43–25.50
Limiting indices	$-9 \leqslant h \leqslant 9$ $-21 \leqslant k \leqslant 20$ $-22 \leqslant l \leqslant 22$	$-7 \leqslant h \leqslant 9$ $-20 \leqslant k \leqslant 21$ $-21 \leqslant l \leqslant 18$	$-16 \leqslant h \leqslant 16$ $-25 \leqslant k \leqslant 25$ $-26 \leqslant l \leqslant 20$
Reflections collected/unique	15435/4480 [R_{int} = 0.0553]	16001/4215 [R_{int} = 0.0246]	44649/23354 [R_{int} = 0.0453]
Completeness to θ_{max} (%)	100.0	100.0	99.7
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4480/0/224	4215/0/224	23354/0/1312
Goodness-of-fit on F^2	1.167	1.223	1.083
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0525, wR_2 = 0.1163	R_1 = 0.0221, wR_2 = 0.0597	R_1 = 0.0563, wR_2 = 0.1257
R indices (all data)	R_1 = 0.0597 wR_2 = 0.1213	R_1 = 0.0258 wR_2 = 0.0683	R_1 = 0.0597 wR_2 = 0.1342
Largest difference in peak and hole (e Å^{-3})	0.845 and −0.458	1.816 and −0.952	1.236 and −0.522

Fig. 1 shows the molecular structure with thermal ellipsoids for **3**, Fig. 2 shows the molecular structure with thermal ellipsoids for **6**. The complexes **3** and **6** are isostructural and isotypic. Both **3** and **6** contain the metal atoms in highly distorted pseudotetrahedral geometries. The angle between Zr, the centre of Cp1 and the centre of Cp2 is 130.11°. Similarly the angle between Hf, the centre of Cp1 and the centre of Cp2 is 130.06°. The angle P1–Zr1–Cl1 is 100.56(4)° and the angle Cl1–Hf1–P1 is 100.30(3)°. The distances Zr1–P1 of 258.3(1) pm and Hf1–P1 of 256.81(9) pm indicate the partial double bond character of the Zr1–P1 and Hf–P1 bonds. The angle Zr1–P1–P2 is 117.56(5)° and Hf1–P1–P2 is 117.16(4).

The relatively short P1–P2 distances (218.7(2) pm in **3** and 218.5(1) pm in **6**) suggest a partial double bond character of this bonds. In both compounds the geometries around P1 indicate a high degree of planarity (the sum of angles around P1 is 348.57° in **3** and 347.33° in **6**) which is consistent with the short M–P1 distances. In spite of short P1–P2 distances the geometries around P2 are pyramidal (the sum of angles around P2 is 313.11° in **3** and 317.04° in **6**).

The distances M–P1 in **3** and **6** are slightly longer than reported for classical phosphido complexes of Zr(IV) and Hf(IV) with almost planar geometry around the P atom, see [12–14]. For classical phosphido complexes showing a more pyramidal geometry, longer M–P distances than in **3** and **6** were reported [10,15,16]. The known X-ray structure of $[Cp_2Hf(Cl)\{P(SiMe_3)–P(NEt_2)_2\text{-}\kappa P^1\}]$[19] enables us to discuss a significant impact of the substituents bearing nitrogen atoms in the phosphanyl group on the geometries of the phosphanylphosphido complexes of hafnium(IV). The presence of NEt_2 groups increases the distance Hf–P1 from 256.81(9) pm in **6** to 264.8(4) pm in $[Cp_2Hf(Cl)\{P(SiMe_3)–P(NEt_2)_2\text{-}\kappa P^1\}]$, increases the distance P1–P2 from 218.5(1) pm in **6** to 224.0(5) pm in $[Cp_2Hf(Cl)\{P(SiMe_3)–P(NEt_2)_2\text{-}\kappa P^1\}]$ and decreases the planarity around P1. The sum of angles around P1 in **6** is 347.33° compared to 322.71° in $[Cp_2Hf(Cl)\{P(SiMe_3)–P(NEt_2)_2\text{-}\kappa P^1\}]$. Thus the presence of amino groups in the phosphanyl part of the $R_2P–P(SiMe_3)$ ligand eliminates the π-bonding participation in the bonds of the Hf–P1–P2 chain.

Complex **9** (Fig. 3) includes three metal centres: two zirconium atoms and one lithium atom. Both zirconium atoms possess distorted octahedral geometry, each of them is bonded to a cyclopentadienyl group, to three chloride atoms, and two phosphorus atoms of the $Ph_2P3–P2–P1SiMe_3$ unit. In this ligand, the P1 atom coordinates to both zirconium atoms, P2 coordinates only to Zr1, and P3 only to Zr2. The P–P distances in this ligand are very similar (average value 218.5 Å). This value suggests a partial double bond character of the P–P bonds in this moiety. The lithium atom is surrounded by three oxygen atoms (one from a THF molecule and two from a DME molecule) and two chloride atoms.

4. Conclusions

We introduce here the method for the synthesis of a new class of transition metal complexes with diphosphorus ligands. In reactions of Cp_2MCl_2 (M = Zr, Hf) with $R_2P–P(SiMe_3)Li$ (R = ^{t}Bu, ^{i}Pr) in toluene or pentane, the main products are phosphanylphosphido complexes $[Cp_2M(Cl)\{P(SiMe_3)–PR_2\text{-}\kappa P^1\}]$. Disubstituted phosphanylphosphido complexes $[Cp_2M\{P(SiMe_3)–PR_2\text{-}\kappa P^1\}_2]$ were present in the reactions mixtures only in small amounts. In the case of isopropyl derivatives, the solid state structures were investigated by X-ray diffraction. In a reaction of $[CpZrCl_3{\cdot}DME]$ with a mixture of $Ph_2P–P(SiMe_3)Li{\cdot}3THF$ and $(Me_3Si)_2PLi{\cdot}3THF$ in toluene, we observed the formation of a new P–P bond in the coordination sphere of zirconium resulting in the triphosphorus ligand $Ph_2P–P–PSiMe_3$ as part of a dinuclear Zr complex.

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Appendix A. Supplementary data

CCDC 797324, 787649, and 797323 contains the supplementary crystallographic data for the structures of **3**, **6** and **9**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] E. Hey-Hawkins, Chem. Rev. 94 (1994) 1661.
[2] S.R. Wade, G.H. Wallbridge, G.R. Willey, J. Chem. Soc., Dalton Trans. (1983) 2555.
[3] R.T. Baker, J.F. Whitney, S.S. Wreford, Organometallics 2 (1983) 1049.
[4] L. Weber, G. Meine, R. Boese, N. Augart, Organometallics 6 (1987) 2484.
[5] F. Lindenberg, E. Hey-Hawkins, J. Organomet. Chem. 435 (1992) 291.
[6] Z. Hou, T.L. Breen, D.W. Stephan, Organometallics 12 (1993) 3158.
[7] E. Hey-Hawkins, S. Kurz, J. Organomet. Chem. 479 (1994) 125.
[8] R. Bohra, P.B. Hitchcock, M.F. Lappert, W.-P. Leung, J. Chem. Soc., Chem. Commun. (1989) 728.
[9] Z. Hou, D.W. Stephan, J. Am. Chem. Soc. 114 (1992) 10088.
[10] E. Urnėžius, S.J. Klippenstein, J.D. Protasiewicz, Inorg. Chim. Acta 297 (2000) 181.
[11] D.M. Roddick, B.D. Santarsiero, J.E. Bercaw, J. Am. Chem. Soc. 107 (1985) 4670.
[12] A.M. Arif, A.H. Cowley, C.M. Nunn, M. Pakulski, J. Chem. Soc., Chem. Commun. (1987) 994.
[13] E. Hey, M.F. Lappert, J.L. Atwood, S.G. Bott, Polyhedron 7 (1988) 2083.
[14] J. Ho, Z. Hou, R. Rosseau, D.W. Stephan, Organometallics 13 (1994) 1918.
[15] E. Hey-Hawkins, S. Kurz, G. Baum, Z. Naturforsch. 50b (1995) 239.
[16] U. Segerer, E. Hey-Hawkins, Polyhedron 16 (1997) 2537.
[17] R.T. Baker, P.J. Krusic, T.H. Tulip, J.C. Calabrese, S.S. Wreford, J. Am. Chem. Soc. 107 (1985) 4670.
[18] J. Pikies, E. Baum, E. Matern, J. Chojnacki, R. Grubba, A. Robaszkiewicz, J. Chem. Soc., Chem. Commun. (2004) 2478.
[19] R. Grubba, A. Wiśniewska, K. Baranowska, E. Matern, J. Pikies, Dalton Trans. 40 (2011) 2017.
[20] 18th International Conference on Phosphorus Chemistry, July 11–15. 2010, Wroclaw, Poland, Book of Abstracts, p. 69.
[21] (a) G. Hägele, M. Engelhardt, W. Boenigk, Simulation und automatisierte Analyse von NMR-Spektren, VCH, Weinheim, 1987.;
(b) Program Daisy, part of Bruker Topspin 2.1 pl 6.
[22] P.M. Druce, B.M. Kingstone, M.F. Lappert, T.R. Spalding, R.C. Srivastava, J. Chem. Soc. (A) (1969) 2106.
[23] I. Kovacs, E. Matern, G. Fritz, Z. Anorg. Allg. Chem. 622 (1996) 935.
[24] W. Domańska-Babul, K. Baranowska, R. Grubba, E. Matern, J. Pikies, Polyhedron 26 (2007) 2491.
[25] E.C. Lund, T. Livinghouse, Organometallics 9 (1990) 2426.
[26] E. Matern, G. Fritz, J. Pikies, Z. Anorg. Allg. Chem. 623 (1997) 1769.
[27] H. Schumann, H.J. Kroth, Z. Naturforsch. 32B (1977) 513.
[28] E. Fluck, K. Issleib, Chem. Ber. 98 (1965) 2674.
[29] J. Tong, S. Liu, S. Zhang, S.Z. Li, Spectrochim. Acta 67A (2007) 837.
[30] Oxford Diffraction: CRYSALIS CCD and CRYSALIS RED, Version 1.171. Oxford Diffraction Ltd., Abingdon, England, 2008.
[31] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.