Russian Chemical Bulletin, International Edition, Vol. 54, No. 1, pp. 117—123, January, 2005

2-Phosphinothioyl- and 2-phosphinoylethylcyclopentadienyl zirconium and titanium complexes. Crystal structure of $[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2P(O)Ph_2]TiCl_3$

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The intracomplex conversion of (2-diphenylphosphanoethyl)cyclopentadienyl zirconium and titanium complexes into the corresponding 2-phosphinothioyl and 2-phosphinoyl derivatives, *viz.*, $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4CH_2CH_2P(S)Ph_2]ZrCl_2$, $[\eta^5\text{-}C_5H_4CH_2CH_2P(S)Ph_2]ZrCl_3$, $[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2P(O)Ph_2]ZrCl_3 \cdot THF$, and $[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2P(O)Ph_2]TiCl_3$ (**7**), was performed. The NMR spectroscopy data revealed the following order of the coordination ability of the functional groups with respect to the Zr center: $Ph_2P{=}O > Ph_2P > Ph_2P{=}S$. An analogous order was found for the monodentate ligands ($Ph_3P{=}O > Ph_3P > Ph_3P{=}S$) with respect to $(\eta^5\text{-}C_5H_5)ZrCl_3$. The molecular structure of complex **7** was established by X-ray diffraction analysis. Coordination of the $Ph_2P{=}O$ group to the titanium atom was found retained both in the crystalline state and solution.

Key words: zirconium, titanium, 2-thiophosphanoylethylcyclopentadienes, 2-phosphanoylethylcyclopentadienes, intramolecular coordination, NMR spectroscopy, X-ray diffraction analysis.

Phosphanes are widely used as ligands in organometallic chemistry. However, the number of studies devoted to transition metal complexes with phosphane sulfide and phosphane oxide ligands is at least two orders of magnitude smaller. A few complexes of Group 4 metals with such ligands are known.[1—4] Of cyclopentadienyl complexes, only titanium derivatives, in which the $P(S)Ph_2$ or $P(O)Ph_2$ group is directly bound to the Cp ring and cannot be coordinated to the metal atom, were described.[4] At the same time, cyclopentadienyl transition metal complexes containing various functional groups (OR,[5] NRR´,[6,7] SR,[8] PRR´ [8]) in the side chain of the Cp ring are being intensively studied.

We attempted to modify the following complexes: $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)ZrCl_2$ (**1**)[9], $(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)ZrCl_3 \cdot THF$ (**2**)[9], and $(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)TiCl_3$ (**3**)[10], which have been synthesized earlier, directly in the coordination sphere of metal to prepare the corresponding $P(S)Ph_2$ and $P(O)Ph_2$ derivatives. It was also of interest to compare the coordination ability of these groups and the PPh_2 group with respect to the Zr and Ti atoms. We also studied the reaction of the $(\eta^5\text{-}C_5H_5)ZrCl_3$ complex as a model compound with Ph_3P, Ph_3PS, and Ph_3PO.

A downfield shift of the signal in the ^{31}P NMR spectrum (no less than 10 ppm) of a complex compared to that of the uncoordinated ligand can serve as a reliable criterion for the coordination of the phosphorus-containing functional group to the metal atom. Therefore, we used ^{31}P NMR spectroscopy as the main method to study the ability of phosphane sulfides and phosphane oxides to be coordinated to the metal atom.

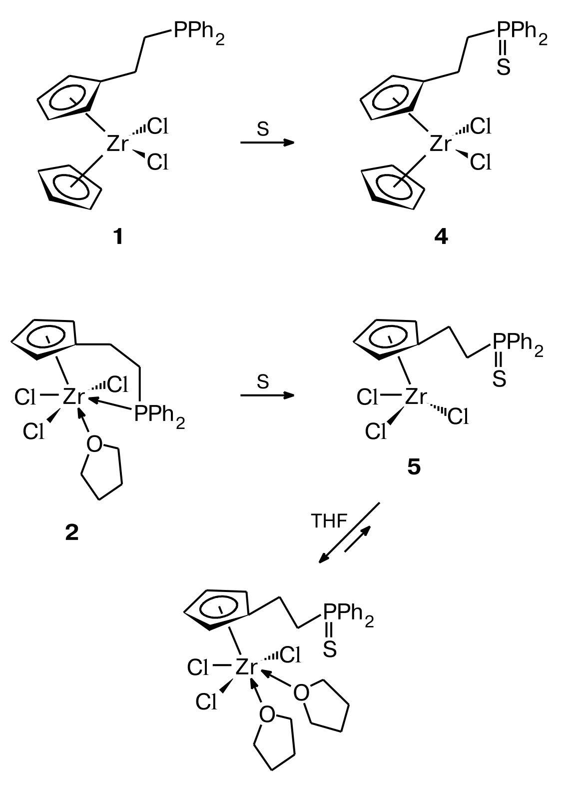
Results and Discussion

Cyclopentadienyl zirconium complexes

The reaction of bis-cyclopentadienyl complex **1** with elemental sulfur in toluene proceeds smoothly and affords the corresponding phosphane sulfide derivative **4** in nearly 100% yield (Scheme 1).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 116—122, January, 2005.

Scheme 1



Conditions and yields: toluene, ~100% yield.

As expected, coordination of the $P(S)Ph_2$ group to the Zr atom was not observed. The ^{31}P chemical shift is 43.8 ppm and appears in the region characteristic of $RCH_2CH_2P(S)Ph_2$ compounds.[11]

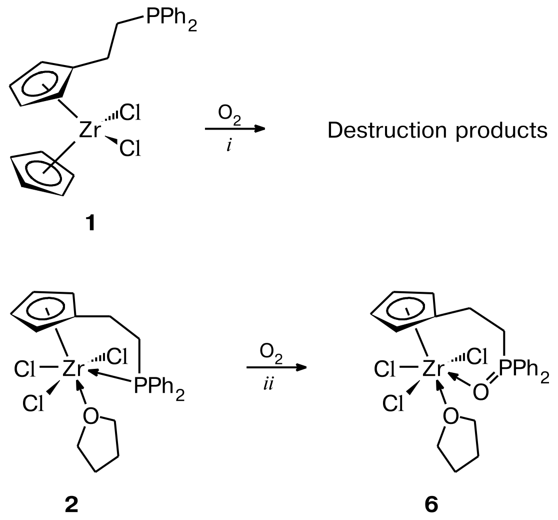
The reaction of complex **2** with one equivalent of sulfur in toluene followed by complete removal of the solvent gave half-sandwich **5** containing no THF solvate molecules in virtually quantitative yield (see Scheme 1).

The ^{31}P NMR spectra of complex **5** were recorded in two solvents, *viz.*, in THF-d_8 and CD_2Cl_2. The ^{31}P chemical shift in the spectrum of complex **5** in THF-d_8 (δ 43.5) is virtually identical to that observed for sandwich **4** and indicates that the $P(S)Ph_2$ group is not coordinated to the Zr atom. All signals in the ^1H and ^{13}C NMR spectra of complex **5**, like those for complex **4**, appear as narrow multiplets with well-resolved spin-spin coupling constants. Apparently, this is attributable to the fact that the equilibrium in a THF solution is completely shifted to **5a**, in which two coordination vacancies are occupied by THF molecules (see Scheme 1).

At room temperature, the ^{31}P NMR spectrum of complex **5** in CD_2Cl_2 shows a broadened signal at δ 43.3. In the ^1H NMR spectrum of complex **5** in CD_2Cl_2, all multiplets are strongly broadened. The broadened signal in the ^{31}P NMR spectrum splits into five narrow singlets with comparable intensities in a δ range from 42.7 to 44.5 upon a decrease in the temperature to –70 °C. An analogous splitting of the multiplets is observed in the ^1H NMR spectrum. Both at room and lower temperatures, the ^{31}P chemical shifts provide evidence that the $P(S)Ph_2$ group remains uncoordinated to the Zr atom in both cases. The observed dynamic processes are, apparently, associated with di- and oligomerization of complex **5** when solvating molecules are absent. It is known that the $(\eta^5\text{-}C_5H_5)ZrCl_3$ complex containing no coordinated solvent exists as a linear polymer with the repeating $\{Cl[(\eta^5\text{-}C_5H_5)ClZr(\mu\text{-}Cl)_2ZrCl(\eta^5\text{-}C_5H_5)]\}_n$ structural fragment.[12]

Unlike the reaction with elemental sulfur, which proceeds readily and affords diphenylphosphane sulfide derivatives **4** and **5** in approximately 100% yields, the oxidation of complexes **1** and **2** with molecular oxygen did not give satisfactory preparative results (Scheme 2). Unlike well known oxidation of phosphanes with hydrogen peroxide, which evidently cannot be used in the case under consideration, oxidation of the PPh_2 group in the complexes with molecular oxygen occurs very slowly (stirring for several days is required). In the latter case, side processes (for example, oxidation of Cp rings) prevail with the result that mixtures of unidentifiable, including insoluble, products are produced. We observed this situation in the reaction of sandwich **1** with molecular oxygen both in toluene and THF.

Scheme 2



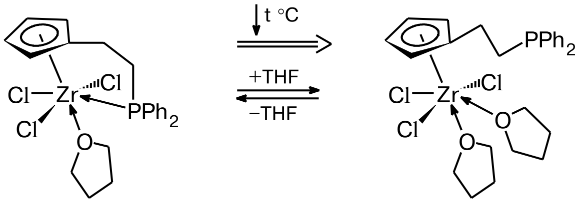
Conditions and yields: *i.* 1 atm, toluene or THF; *ii.* 1 atm, THF, ~15% yield.

Nevertheless, oxidation of half-sandwich **2** afforded (although in low yield) the corresponding phosphane oxide complex **6** (see Scheme 2), which was isolated in pure form and characterized by ^1H, ^{31}P, and ^{13}C NMR spectroscopy.

In the ^{31}P NMR spectra of complex **6** in THF-d_8 and CD_2Cl_2, $\delta(^{31}P)$ are 49.6 and 50.2, respectively, whereas the corresponding signal for phosphane oxides $RCH_2CH_2P(O)Ph_2$ is observed at δ ~30 (for three isomers of $C_5Me_4(H)CH_2CH_2P(O)Ph_2$, $\delta(^{31}P)$ = 30.0, 30.1, and 31.7[13]). The substantial (~20 ppm) shift of $\delta(^{31}P)$ for the phosphane oxide group unambiguously indicates the formation of the $Ph_2P{=}O{\rightarrow}Zr$ coordination bond in complex **6** (analogous changes in the ^{31}P chemical shifts were observed also for phosphane oxide and phosphane sulfide complexes of other transition metals[14]). The ^1H NMR spectrum in CD_2Cl_2 shows signals of THF (1 equiv. with respect to the complex based on the integral intensities of the signals) at δ 3.94 (OCH_2) and 1.76 ($OCH_2C\underline{H}_2$), which is evidence that in solution the THF molecule also remains coordinated to the Zr atom.

It was of interest to compare the dynamic behavior of half-sandwich **6** and its precursor **2** in solution. Earlier,[9] we have revealed the occurrence of equilibrium for phosphane complex **2** in a THF solution, which is associated with the replacement of the coordinated phosphane group with the second THF molecule at low temperature (Scheme 3).

Scheme 3



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Study of the dynamic behavior of complex **6** in THF-d_8 by low-temperature ^1H and ^{31}P NMR spectroscopy demonstrated that the ^{31}P NMR spectrum has two singlets at δ 50.2 and 47.1 in a ratio of 3 : 1, respectively, already at −20 °C. A further decrease in the temperature to −80 °C leads only to narrowing of these signals, whereas their relative intensities remain unchanged. Signals at δ ~30 corresponding to the uncoordinated $P(O)Ph_2$ group are absent. The ^1H NMR spectrum shows two sets of signals in the cyclopentadienyl region (signals in the region of the phenyl and bridging protons overlap with each other). These results can most likely be interpreted as a decrease in the rate of interconversion between two conformations of the pseudo-six-membered $(Zr){-}C_5H_4{-}CH_2{-}CH_2{-}P{=}O{\rightarrow}ZrCl_3$ metallacycle characterized by close but different energies. The energy barrier to their interconversion should be higher than that for the pseudo-five-membered $(Zr){-}C_5Me_4{-}CH_2{-}CH_2{-}S(Me){\rightarrow}ZrCl_3$ metallacycle, for which the corresponding energy was estimated to be 10—12 kcal mol^{-1} and the degenerate interconversion of the metallacycle became slow on the NMR time scale at temperatures lower than −70 °C.[15]

Hence, half-sandwich **6** differs from complex **5**, in which the phosphinothioyl group remains uncoordinated even in a nonsolvating solvent, and from complex **2**, in which the phosphane ligand is reversibly replaced with the THF molecule, in that its phosphinoyl group has the highest affinity for the Zr^{IV} atom compared to the PPh_2 and $P(S)Ph_2$ functional groups.

To verify this conclusion, we studied the reaction of the $(\eta^5\text{-}C_5H_5)ZrCl_3 \cdot n$THF complex ($n$ = 0.6) with Ph_3P, Ph_3PS, and Ph_3PO in CD_2Cl_2 by ^1H and ^{31}P NMR spectroscopy. Unlike the stoichiometric $(\eta^5\text{-}C_5H_5)ZrCl_3 \cdot$ DME adduct,[16] the adduct of $(\eta^5\text{-}C_5H_5)ZrCl_3$ with THF has a variable composition. This allows one to achieve the required Zr : THF ratio in the half-sandwich. In this case, it is desirable to use the starting complex with the Zr : THF ratio varying from 0 to 1 in order that both vacancies at the Zr atom be partially free, while THF be present in the system as a competitive donor. The parameters of the ^1H and ^{31}P NMR spectra of these model systems are given in Table 1.

It can be seen that phosphane sulfide is uncoordinated to the Zr atom, while THF remains completely coordinated even in the presence of a tenfold excess of Ph_3PS with respect to $(\eta^5\text{-}C_5H_5)ZrCl_3$ (see Table 1, $\delta(^1H)$ for the OCH_2 fragment in the THF molecule). The opposite situation is observed for triphenylphosphane oxide. The ^1H NMR spectrum shows signals of free THF, and the ^{31}P NMR spectrum exhibits three broadened signals in a ratio of 1 : 1 : 3. The first two signals most likely correspond to two coordinated $Ph_3P{=}O$ molecules in the apical and equatorial positions, and the third signal belongs to free phosphane oxide.

Triphenylphosphane is intermediate between phosphane sulfide and phosphane oxide. Tetrahydrofuran

Table 1. Parameters of the NMR spectra of the $(\eta^5\text{-}C_5H_5)ZrCl_3 \cdot 0.6THF + L$ system (L = Ph_3P, Ph_3PS, Ph_3PO) in CD_2Cl_2 at 25 °C

L	L : Zr	$\delta(^{31}P)^a$	$\delta(^{31}P)^b$	$\delta(^1H)^c$
$Ph_3P{=}S$	10	44.7	45.0	4.21
Ph_3P	3.5	25.2 (~0.5) −3.4 (~3)	−3.6	4.18
$Ph_3P{=}O$	5	43.1 (~1) 39.6 (~1) 29.4 (~3)	29.6	3.70

[a] Relative intensities of the signals are given in parentheses.

[b] For free L.

[c] For OCH_2 in THF.

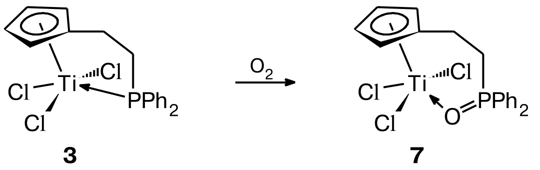
(0.6 equiv.) completely remains in the coordination sphere of the metal atom, whereas only ~0.5 equiv. of Ph_3P are coordinated. Taking into account large steric hindrance due to the presence of the triphenylphosphane molecule, Ph_3P can presumably be coordinated only at one vacancy in the complex, which is already partially occupied by THF. Therefore the total ratio of the coordinated THF and Ph_3P molecules with respect to zirconium should be 1 : 1. This ratio was actually observed within the accuracy of the integration.

Therefore, the above-considered data agree well with the results obtained for complexes **2**, **5**, and **6** with chelating phosphorus-containing cyclopentadienyl ligands. Hence, the functional groups under consideration can be arranged with a high degree of assurance in the following series of decreasing coordination ability in monocyclopentadienyl zirconium complexes: $Ph_2P{=}O > Ph_2P > Ph_2P{=}S$.

[η^5:η^1-(2-Diphenylphosphinoylethyl)cyclopentadienyl]trichlorotitanium

In addition to the above-described Zr complexes, we prepared an analogous phosphane oxide half-sandwich of titanium and studied its structure in the crystalline state and solution. The $[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2P(O)Ph_2]TiCl_3$ complex (**7**) was prepared in relatively low yield by the oxidation of half-sandwich **3** with dry oxygen in THF (Scheme 4).

Scheme 4



Conditions and yields: 1 atm, THF, 30% yield.

Crystallization from toluene afforded single crystals of complex **7** suitable for X-ray diffraction study. There are two independent geometrically similar molecules **7** per asymmetric unit. The crystal structure contains also a toluene solvate molecule disordered over two positions and located on a crystallographic inversion center. The configuration of the complex can be described as a distorted tetragonal pyramid (four-legged piano stool) containing the apical Cp ring (Fig. 1). Selected bond lengths and bond angles are given in Table 2.

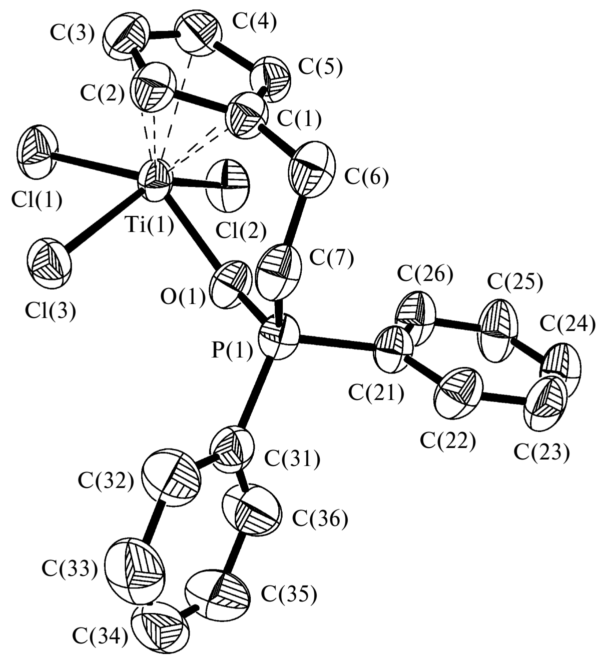


Fig. 1. Molecular structure of complex **7**. The second crystallographically independent molecule, the toluene molecule, and the hydrogen atoms are omitted.

The Ti—Cp_{cent} and Ti—Cl bond lengths averaged over two molecules (2.045 and 2.352(1) Å, respectively) are slightly larger than those in complex **3** (2.035 and 2.322(1) Å, respectively).[10] The Ti←O bond length (1.990(2) Å) correlates well with those observed in a few known phosphane oxide complexes of titanium (2.009(7) and 2.023(8) Å in $HN{\equiv}TiCl_2(OPPh_3)_2$;[1] 2.008(6) and 2.047(6) Å in $Bu^tN{\equiv}TiCl_2(OPPh_3)_2$;[2] 2.061(2) and 2.062(2) Å in $TiCl_2[\eta^2\text{-}(O)PPh_2{-}CH_2CH(Me){-}O]_2$ [3]). It should be noted that the Ti←O distance in complex **7** is substantially shorter than that in the $[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2OMe]TiCl_3$ complex (**8**) (2.214(10) Å).[17] Apparently, this fact is associated with the character of hybridization of the oxygen atom. In complex **7**, hybridization of the oxygen atom is intermediate between sp^2 and sp, whereas hybridization of the oxygen atom in **8** is intermediate between sp^2 and sp^3. This is also evidenced by the bond angles at the oxygen atom. In complex **8**, these bond angles are in a range of 112.6(11)—119.8°.[17,18] In complex **7**, the Ti—O—P angle averaged over two molecules is 140.0(1)°. This value is smaller than that in the $RN{\equiv}TiCl_2(OPPh_3)_2$ complex (R = H, Bu^t) (148.7(5)—162.5(5)°),[1,2] which is, apparently, associated with the cyclic structure of complex **7**. The phosphorus atom has a nearly tetrahedral environment. All bond angles are in a range of 107.2(2)—112.0(0)°. By contrast, the bond angles at the phosphorus atom in phosphane complex **3** vary from 100.2(2)° to 119.2(1)°,[10] which is attributable to stronger strain of the six-membered metallacycle compared to the five-membered ring.

In a solution of complex **7**, as in a solution of its zirconium analog **6**, coordination of the phosphane oxide group to the Ti atom is retained both in solvating and nonsolvating media. The signal $\delta(^{31}P)$ for complex **7** in

Table 2. Selected bond lengths (*d*) and bond angles (ω) for two independent molecules of complex **7***

Molecule **A**		Molecule **B**		Molecule **A**		Molecule **B**	
Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Ti(1)—O(1)	1.978(3)	Ti(2)—O(2)	2.001(2)	O(1)—Ti(1)—Cl(2)	81.13(8)	O(2)—Ti(2)—Cl(22)	81.28(8)
Ti(1)—C(3)	2.331(4)	Ti(2)—C(43)	2.336(4)	O(1)—Ti(1)—Cl(3)	81.94(8)	O(2)—Ti(2)—Cl(21)	139.39(8)
Ti(1)—C(2)	2.375(4)	Ti(2)—C(42)	2.370(5)	Cl(2)—Ti(1)—Cl(3)	142.96(5)	Cl(22)—Ti(2)—Cl(21)	86.19(6)
Ti(1)—C(4)	2.326(5)	Ti(2)—C(44)	2.327(4)	O(1)—Ti(1)—Cl(1)	135.60(9)	O(2)—Ti(2)—Cl(23)	81.11(8)
Ti(1)—C(5)	2.358(4)	Ti(2)—C(45)	2.359(4)	Cl(1)—Ti(1)—Cl(2)	84.54(6)	Cl(22)—Ti(2)—Cl(23)	140.05(5)
Ti(1)—C(1)	2.405(4)	Ti(2)—C(41)	2.399(4)	Cl(1)—Ti(1)—Cl(3)	84.94(5)	Cl(21)—Ti(2)—Cl(23)	84.34(6)
Ti(1)—Cl(1)	2.342(2)	Ti(2)—Cl(21)	2.340(2)	O(1)—P(1)—C(7)	110.4(2)	O(2)—P(2)—C(47)	110.0(2)
Ti(1)—Cl(3)	2.393(1)	Ti(2)—Cl(23)	2.357(1)	C(7)—P(1)—C(21)	108.3(2)	O(2)—P(2)—C(61)	108.0(2)
Ti(1)—Cl(2)	2.344(2)	Ti(2)—Cl(22)	2.338(2)	C(7)—P(1)—C(31)	110.8(2)	C(47)—P(2)—C(61)	108.7(2)
P(1)—C(31)	1.791(4)	P(2)—C(47)	1.779(5)	O(1)—P(1)—C(21)	108.2(2)	O(2)—P(2)—C(51)	112.0(2)
P(1)—C(7)	1.788(4)	P(2)—C(61)	1.787(4)	O(1)—P(1)—C(31)	111.9(2)	C(47)—P(2)—C(51)	110.6(2)
P(1)—C(21)	1.790(4)	P(2)—C(51)	1.791(4)	C(21)—P(1)—C(31)	107.2(2)	C(61)—P(2)—C(51)	107.4(2)
O(1)—P(1)	1.509(3)	O(2)—P(2)	1.510(3)	P(1)—O(1)—Ti(1)	140.1(2)	P(2)—O(2)—Ti(2)	139.8(2)

* The Ti(1)—PL(1) and Ti(2)—PL(2) distances are 2.035(2) and 2.039(2) Å, respectively; PL(1) and PL(2) are the mean planes through the C(1)—C(5) and C(41)—C(45) atoms, respectively.

CD_2Cl_2 (51.1) and THF-d_8 (49.8) is shifted downfield by ~20 ppm relative to that observed for free phosphane oxide ($\delta(^{31}P) \approx 30$). For comparison, the downfield shift of the signal in the spectrum of $HN{\equiv}TiCl_2(OPPh_3)_2$ [1] ($\delta(^{31}P) = 42.4$) is approximately 15 ppm with respect to uncoordinated Ph_3PO ($\delta(^{31}P) \approx 27$).

To summarize, we demonstrated the possibility of subjecting the phosphane ligand in cyclopentadienyl zirconium complexes to preparative inner-sphere modification with elemental sulfur giving rise to the corresponding phosphane sulfide derivatives. Analogous oxidation of phosphane complexes with molecular oxygen is accompanied by side processes and affords the target phosphane oxide complexes in low yields. Study by ^{31}P NMR spectroscopy demonstrated that the coordination ability of the functional groups in monocyclopentadienyl zirconium complexes decreases in the series $Ph_2P{=}O > Ph_2P > Ph_2P{=}S$.

Experimental

All reactions were carried out and samples for NMR spectroscopy were prepared in Schlenk-type all-sealed evacuated apparatus. The starting phosphane complexes of zirconium **1** and **2** [9] and titanium **3** [10] were prepared according to known procedures. Commercial triphenylphosphane and triphenylphosphane oxide were used. Triphenylphosphane sulfide was synthesized by the reaction of equimolar amounts of Ph_3P and sulfur in toluene. The solvents were dried according to standard procedures.

The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian VXR-400 spectrometer at 400, 100, and 162 MHz, respectively. The chemical shifts of Me_4Si or the residual protons of the corresponding deuterated solvents (δ 5.32 and 53.8 for CD_2Cl_2, δ 1.73 and 25.3 for THF-d_8) were used as the inner standard for the ^1H and ^{13}C NMR spectra, respectively. The ^{31}P NMR spectra were measured with 85% H_3PO_4 as the external standard. The temperature calibration was performed using a standard methanol sample. The mass spectra were recorded on a Kratos-MS-890 spectrometer. Elemental analysis was carried out on an automated Carlo-Erba analyzer.

(η^5-Cyclopentadienyl)trichlorozirconium; an adduct with 0.6 THF molecules was prepared starting from $CpZrCl_3 \cdot 2THF$, which was synthesized according to a known procedure[19] by the reaction of $ZrCl_4$ with $CpSiMe_3$ [20] in toluene. Then $CpZrCl_3 \cdot 2THF$ (11.9 g, 29.3 mmol) was suspended in toluene (100 mL). The suspension was heated at 100 °C for 30 min, the solvent was distilled off into a liquid nitrogen cooled trap and dried in high vacuum. The procedure was repeated. The reaction product was analyzed by ^1H NMR spectroscopy, which demonstrated that the THF : complex ratio was ~0.6. The yield was 8.9 g (virtually quantitative yield with respect to $CpZrCl_3 \cdot 2THF$).

[η^5-(2-Diphenylphosphinothioylethyl)cyclopentadienyl][η^5-cyclopentadienyl]dichlorozirconium (4). A solution of sulfur (53 mg, 1.65 mmol) in toluene (25 mL) was added to a solution of complex **1** (830 mg, 1.65 mmol) in toluene (50 mL). The reaction mixture was stirred for 4 h and then kept for 16 h. The solvent was removed, the product was twice washed on a filter with pentane, and dried in high vacuum. The product was obtained as a white powder in a yield of 840 mg (1.57 mmol, 95%). Found (%): C, 53.45; H, 4.46. $C_{24}H_{23}Cl_2PSZr$. Calculated (%): C, 53.72; H, 4.32. ^1H NMR (THF-d_8, 25 °C), δ: 2.89 (m, 2 H, CH_2P); 3.00 (m, 2 H, $C\underline{H}_2CH_2P$); 6.28 (virt. t, 2 H, H(2), H(5), $^{3+4}J_{H,H} = 5.2$ Hz); 6.36 (virt. t, 2 H, H(3), H(4), $^{3+4}J_{H,H} = 5.2$ Hz); 6.47 (s, 5 H, C_5H_5); 7.43 (m, 6 H, H_m, H_p); 7.93 (m, 4 H, H_o). ^{13}C NMR, δ: 23.71 (t, $\underline{C}H_2CH_2P$, $^1J_{C,H} = 131$ Hz); 32.61 (dt, CH_2P, $^1J_{C,H} = 131$ Hz, $^1J_{C,P} = 56.5$ Hz); 113.44 (d, C(3)H, C(4)H, $^1J_{C,H} = 174$ Hz); 116.63 (d, C_5H_5, $^1J_{C,H} = 174$ Hz); 117.77 (d, C(2)H, C(5)H, $^1J_{C,H} = 173$ Hz); 129.17 (dd, C_m, $^1J_{C,H} = 160$ Hz, $^3J_{C,P} = 11.5$ Hz); 131.87 (d, C_p, $^1J_{C,H} = 160$ Hz); 131.98 (dd, C_o, $^1J_{C,H} = 160$ Hz, $^2J_{C,P} = 9.7$ Hz); 134.27 (d, C(1), $^3J_{C,P} = 18.2$ Hz); 134.53 (d, C_{ipso}, $^1J_{C,P} = 79.0$ Hz). ^{31}P—{^1H} NMR: 43.2 (s). ^1H NMR (CD_2Cl_2, 25 °C), δ: 2.83 (m, 2 H, CH_2P); 3.01 (m, 2 H, $C\underline{H}_2CH_2P$); 6.22 (virt. t, 2 H, H(2), H(5), $^{3+4}J_{H,H}$ = 5.6 Hz); 6.29 (virt. t, 2 H, H(3), H(4), $^{3+4}J_{H,H}$ = 5.6 Hz); 6.45 (s, 5 H, C_5H_5); 7.48 (m, 6 H, H_m, H_p); 7.85 (m, 4 H, H_o). ^{13}C NMR, δ: 23.17 (t, $\underline{C}H_2CH_2P$, $^1J_{C,H}$ = 131 Hz); 32.29 (dt, CH_2P, $^1J_{C,H}$ = 131 Hz, $^1J_{C,P}$ = 56.8 Hz); 112.55 (d, C(3)H, C(4)H, $^1J_{C,H}$ = 174 Hz); 116.17 (d, C_5H_5, $^1J_{C,H}$ = 174 Hz); 117.43 (d, C(2)H, C(5)H, $^1J_{C,H}$ = 173 Hz); 128.94 (dd, C_m, $^1J_{C,H}$ = 160 Hz, $^3J_{C,P}$ = 11.8 Hz); 131.37 (dd, C_o, $^1J_{C,H}$ = 160 Hz, $^2J_{C,P}$ = 10.1 Hz); 131.80 (d, C_p, $^1J_{C,H}$ = 160 Hz); 132.98 (d, C_{ipso}, $^1J_{C,P}$ = 80.2 Hz); 133.60 (d, C(1), $^3J_{C,P}$ = 17.7 Hz). ^{31}P—{^{1}H} NMR: 43.8 (s). MS (EI, 70 eV), m/z (I_{rel} (%)): 534 $[M]^+$ (0.4), 499 $[M - Cl]^+$ (3.4), 469 $[M - C_5H_5]^+$ (24.5), 309 $[C_5H_4CH_2CH_2P(S)Ph_2]^+$ (5.8), 277 $[C_5H_4CH_2CH_2PPh_2]^+$ (23.3), 225 $[C_5H_5ZrCl_2]^+$ (41.5), 218 $[HP(S)Ph_2]^+$ (100), 185 $[PPh_2]^+$ (52.1), 183 [$C_{12}H_8P$, 9-phosphafluorene]$^+$ (64.1), 140 $[PhP(S)]^+$ (51.4), 121 $[HCPh]^+$ (32.1), 108 $[PPh]^+$ (17.6), 91 $[C_7H_7]^+$ (18.4), 77 $[Ph]^+$ (15.8), 65 $[C_5H_5]^+$ (11.3), 63 $[P=S]^+$ (14.8).

[η^5-(2-Diphenylphosphinothioylethyl)cyclopentadienyl]trichlorozirconium (5). A solution of sulfur (12.7 mg 0.40 mmol) in toluene (20 mL) was added to a solution of complex **2** (200 mg, 0.40 mmol) in toluene (30 mL). The reaction mixture was stirred for 4 h and then allowed to stand for 16 h. The solvent was distilled off at 50 °C into a liquid nitrogen cooled trap, the precipitate was washed with hexane (2×5 mL) by decantations and dried in high vacuum. The product was obtained as a white powder in a yield of 190 mg (0.37 mmol, 93%). Found (%): C, 45.31; H, 3.71. $C_{19}H_{18}Cl_3PSZr$. Calculated (%): C, 45.01; H, 3.58. ^{1}H NMR (THF-d_8, 25 °C), δ: 2.96 (m, 2 H, CH_2P); 3.15 (m, 2 H, $C\underline{H}_2CH_2P$); 6.32 (virt. t, 2 H, H(2), H(5), $^{3+4}J_{H,H}$ = 5.2 Hz); 6.40 (virt. t, 2 H, H(3), H(4), $^{3+4}J_{H,H}$ = 5.2 Hz); 7.43 (m, 6 H, H_m, H_p); 7.95 (m, 4 H, H_o). ^{13}C NMR, δ: 24.32 (t, $\underline{C}H_2CH_2P$, $^1J_{C,H}$ = 131 Hz); 32.71 (dt, CH_2P, $^1J_{C,H}$ = 130 Hz, $^1J_{C,P}$ = 58.0 Hz); 119.06 and 119.15 (both d, C(2)H, C(3)H, C(4)H, C(5)H, $^1J_{C,H}$ = 174 Hz); 129.13 (dd, C_m, $^1J_{C,H}$ = 160 Hz, $^3J_{C,P}$ = 11.6 Hz); 131.80 (dd, C_p, $^1J_{C,H}$ = 161 Hz, $^4J_{C,P}$ = 3.1 Hz); 132.04 (dd, C_o, $^1J_{C,H}$ = 161 Hz, $^2J_{C,P}$ = 9.8 Hz); 133.51 (d, C(1), $^3J_{C,P}$ = 18.2 Hz); 134.75 (d, C_{ipso}, $^1J_{C,P}$ = 78.7 Hz). ^{31}P—{^{1}H} NMR: 43.5 (s). ^{1}H NMR (CD_2Cl_2, 25 °C), δ: 3.16 (br.m, 4 H, CH_2CH_2P); 6.51 and 6.61 (both br.s, 2 H each, H(2)—H(5)); 7.52 (br.m, 6 H, H_m, H_p); 7.84 (br.m, 4 H, H_o). ^{31}P NMR, δ: 43.3 (br.s). MS (EI, 70 eV), m/z (I_{rel} (%)): 504 $[M]^+$ (0.4), 469 $[M - Cl]^+$ (2.5), 252 $[M - Cl - HP(S)Ph_2]^+$ (4.5), 218 $[HP(S)Ph_2]^+$ (100), 185 $[PPh_2]^+$ (53.3), 183 [$C_{12}H_8P$, 9-phosphafluorene]$^+$ (68.2), 140 $[PhP(S)]^+$ (61.4), 121 $[HCPh]^+$ (34.8),108 $[PPh]^+$ (36.0), 91 $[C_7H_7]^+$ (85.4), 77 $[Ph]^+$ (33.8), 63 $[P=S]^+$ (34.5), 36 $[HCl]^+$ (56.8).

Oxidation of complexes 1—3 with oxygen (general procedure). Oxidation of the complexes was carried out in an all-sealed glass apparatus equipped with two containers separated by a Teflon stopcock. In one container (~1 L), molecular oxygen was predried over P_2O_5 for 7 days. A solution of the complex (~300 mg) in THF or toluene (~5 mL) was placed in another container, which was intially separated from the first one with a breakable glass wall (better results were obtained in THF). The glass wall was broken, and the solution of the complex was stirred using a magnetic stirrer for 3 days, the apparatus being protected from daylight. Then the apparatus was evacuated, the reaction mixture was filtered off from insoluble products, and the precipitate was extracted with THF. The solvent was removed from the filtrate to a liquid nitrogen cooled trap, and the crystalline precipitate was dried in high vacuum.

[η^5:η^1-*O*-(2-Diphenylphosphinoylethyl)cyclopentadienyl]trichlorozirconium (6). The reaction with the use of complex **2** (280 mg, 0.51 mmol) in THF afforded the target complex in a yield of 40 mg (0.08 mmol, 15%) as a powdered white compound (>95% purity based on the NMR spectroscopic data). ^{1}H NMR (THF-d_8, 25 °C), δ: 2.89—3.05 (m, 4 H, CH_2CH_2P); 6.40 (virt. t, 2 H, H(2), H(5), $^{3+4}J_{H,H}$ = 5.2 Hz); 6.46 (virt. t, 2 H, H(3), H(4), $^{3+4}J_{H,H}$ = 5.2 Hz); 7.60 (m, 4 H, H_m); 7.69 (m, 2 H, H_p); 8.00 (m, 4 H, H_o). ^{13}C NMR, δ: 21.39 (dt, $\underline{C}H_2CH_2P$, $^1J_{C,H}$ = 133 Hz, $^2J_{C,P}$ = 5.2 Hz); 25.04 (dt, CH_2P, $^1J_{C,H}$ = 134 Hz, $^1J_{C,P}$ = 70 Hz); 118.19 (d, C(3)H, C(4)H, $^1J_{C,H}$ = 176 Hz); 120.23 (d, C(2)H, C(5)H, $^1J_{C,H}$ = 174 Hz); 126.39 (s, C(1)); 128.18 (d, C_{ipso}, $^1J_{C,P}$ = 106 Hz); 129.90 (dd, C_m, $^1J_{C,H}$ = 164 Hz, $^3J_{C,P}$ = 12.5 Hz); 132.93 (dd, C_o, $^1J_{C,H}$ = 164 Hz, $^2J_{C,P}$ = 11.3 Hz); 134.27 (dd, C_p, $^1J_{C,H}$ = 163 Hz, $^4J_{C,P}$ = 3.1 Hz). ^{31}P—{^{1}H} NMR: 49.6 (s). ^{1}H NMR (CD_2Cl_2, 25 °C), δ: 1.76 (m, 4 H, THF); 2.87—3.03 (m, 4 H, CH_2CH_2P); 3.94 (m, 4 H, THF); 6.51 (virt. t, 2 H, H(2), H(5), $^{3+4}J_{H,H}$ = 5.6 Hz); 6.58 (virt. t, 2 H, H(3), H(4), $^{3+4}J_{H,H}$ = 5.6 Hz); 7.60 (m, 4 H, H_m); 7.71 (m, 2 H, H_p); 7.84 (m, 4 H, H_o). ^{31}P—{^{1}H} NMR: 50.2 (s).

[η^5:η^1-*O*-(2-Diphenylphosphinoylethyl)cyclopentadienyl]trichlorotitanium (7). The reaction with the use of complex **3** (300 mg, 0.65 mmol) in THF afforded phosphane oxide complex **7** in a yield of 94 mg (0.20 mmol, 30%) as an orange powdered compound. Found (%): C, 50.87; H, 4.10. $C_{19}H_{18}Cl_3OPTi$. Calculated (%): C, 50.99; H, 4.05. ^{1}H NMR (CD_2Cl_2, 25 °C), δ: 2.95—3.05 (m, 4 H, CH_2CH_2P); 6.87 and 7.03 (both virt. t, 2 H each, H(2)—H(5), $^{3+4}J_{H,H}$ = 5.4 Hz); 7.61 (m, 4 H, H_m); 7.70 (m, 2 H, H_p); 7.86 (m, 4 H, H_o). ^{13}C—{^{1}H} NMR: 21.52 (br.s, $\underline{C}H_2CH_2P$); 25.11 (d, CH_2P, $^1J_{C,P}$ = 69 Hz); 124.99, 125.36 (C(2)H, C(3)H, C(4)H, C(5)H); 125.60 (C(1)); 128.93 (d, C_{ipso}, $^1J_{C,P}$ = 81 Hz); 129.78 (d, C_m, $^3J_{C,P}$ = 13.5 Hz); 132.09 (d, C_o, $^2J_{C,P}$ = 10.8 Hz); 134.24 (C_p). ^{31}P—{^{1}H} NMR: 51.1 (s). ^{1}H NMR (THF-d_8, 25 °C), δ: 2.99 (m, 2 H, $C\underline{H}_2CH_2P$); 3.17 (m, 2 H, CH_2P); 6.82 and 6.93 (both virt. t, 2 H each, H(2)—H(5), $^{3+4}J_{H,H}$ = 5.3 Hz); 7.57 (m, 4 H, H_m); 7.65 (m, 2 H, H_p); 7.99 (m, 4 H, H_o). ^{31}P—{^{1}H} NMR: 49.8 (s). MS (EI, 70 eV), m/z (I_{rel} (%)): 411 $[M - Cl]^+$ (0.2), 368 $[M - C_5H_4{=}CH_2]^+$ (0.3), 367 $[M - C_5H_4Me]^+$ (0.3), 294 $[C_5H_5CH_2CH_2P(O)Ph_2]^+$ (21.4), 216 $[C_5H_4CH_2CH_2P(O)Ph]^+$ (7.1), 215 $[CH_2P(O)Ph_2]^+$ (38.9), 202 $[HP(O)Ph_2]^+$ (100), 201 $[P(O)Ph_2]^+$ (45.9), 183 [$C_{12}H_8P$, 9-phosphafluorene]$^+$ (11.4), 125 $[HP(O)Ph]^+$ (18.9), 121 $[CH=PPh]^+$ (2.9), 108 $[PPh]^+$ (5.0), 91 $[C_7H_7]^+$ (22.6), 77 $[C_6H_5]^+$ (33.7).

Single crystals of complex **7** suitable for X-ray diffraction analysis were prepared by slow crystallization from toluene.

X-ray diffraction study of compound 7 was carried out on an automated Enraf-Nonius CAD4 diffractometer at room temperature using Mo-Kα radiation (λ = 0.71073 Å, graphite monochromator). Crystals of **7** ($C_{19}H_{18}Cl_3OPTi \cdot 0.25C_7H_8$, M = 470.59) are triclinic, space group $P\bar{1}$, a = 11.455(3), b = 13.663(8), c = 14.050(6) Å, α = 78.82(4), β = 83.09(4), γ = 89.44(4)°, V = 2141(2) Å^3, Z = 4, d_{calc} = 1.460 g cm^{-3}, μ(Mo-Kα) = 0.857 mm^{-1}, F(000) = 962. Intensities of 7306 reflections (5913 independent reflections, R_{int} = 0.0294) were measured using the ω-scanning mode in the angle range 2.19 < θ < 24.97° ($-13 \le h \le 8$, $-16 \le k \le 16$, $-3 \le l \le 16$). The intensities of reflections were corrected for the Lorentz and polarization factors.[21] Absorption was ignored. The structure was solved by direct methods (SHELXS-86).[22] All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method against F^2 (SHELXL-97).[23] All hydrogen atoms (except for the H atoms in the toluene solvate molecule) were revealed from difference electron density maps and refined isotropically. The hydrogen atoms of the C_7H_8 molecule were placed in calculated positions and refined using a riding model. The final reliability factors were $R_1 = 0.0425$, $wR_2 = 0.1108$ for 4795 reflections with $I > 2\sigma(I)$; 658 parameters were refined; GOOF = 0.997, min/max $\Delta\rho = -0.497/0.479$ e Å^{-3}.

This study was financially supported by the Foundation of the President of the Russian Federation (Program for Support of Young Scientists, Grant MK-3697.2004.3).

References

1. P. J. McKarns, G. P. A. Yap, A. L. Rheingold, and C. H. Winter, *Inorg. Chem.*, 1996, **35**, 5968.
2. C. H. Winter, P. H. Sheridan, T. S. Lewkebandara, M. J. Heeg, and J. W. Proscia, *J. Am. Chem. Soc.*, 1992, **114**, 1095.
3. R. J. Cross, L. J. Farrugia, P. D. Newman, R. D. Peacock, and D. Stirling, *J. Chem. Soc., Dalton Trans.*, 1996, 1637.
4. E. Delgado, M. A. Garsia, E. Hernandes, N. Mansilla, L. A. Martinez-Cruz, J. Tornero, and R. Torres, *J. Organomet. Chem.*, 1998, **560**, 27.
5. U. Siemeling, *Chem. Rev.*, 2000, **100**, 1495.
6. P. Jutzi and T. Redeker, *Eur. J. Inorg. Chem.*, 1998, 663.
7. P. Jutzi and U. Siemeling, *J. Organomet. Chem.*, 1995, **500**, 175.
8. H. Butenschön, *Chem. Rev.*, 2000, **100**, 1527.
9. D. P. Krut´ko, M. V. Borzov, E. N. Veksler, A. V. Churakov, and J. A. K. Howard, *Polyhedron*, 1998, **17**, 3889.
10. D. P. Krut´ko, M. V. Borzov, E. N. Veksler, A. V. Churakov, and K. Mach, *Polyhedron*, 2003, **22**, 2885.
11. I. M. Aladzheva, O. V. Bykhovskaya, D. I. Lobanov, P. V. Petrovskii, T. A. Mastryukova, and M. I. Kabachnik, *Zh. Obshch. Khim.*, 1995, **65**, 1586 [*Russ. J. Gen. Chem.*, 1995, **65** (Engl. Transl.)].
12. L. M. Engelhardt, R. I. Papasergio, C. L. Raston, and A. H. White, *Organometallics*, 1984, **3**, 18.
13. D. P. Krut´ko, M. V. Borzov, E. N. Veksler, R. S. Kirsanov, and A. V. Churakov, *Eur. J. Inorg. Chem.*, 1999, 1973.
14. T. C. Blagborough, R. Davis, and P. Ivison, *J. Organomet. Chem.*, 1994, **467**, 85.
15. D. P. Krut´ko, M. V. Borzov, V. S. Petrosyan, L. G. Kuz´mina, and A. V. Churakov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 984 [*Russ. Chem. Bull.*, 1996, **45**, 940 (Engl. Transl.)].
16. N. J. Wells, J. C. Huffman, and K. G. Caulton, *J. Organomet. Chem.*, 1981, **213**, C17.
17. Q. Huang, Y. Qian, G. Li, and Y. Tang, *Transition Met. Chem.*, 1990, **15**, 483.
18. F. H. Allen, *Acta Crystallogr., Sect. B*, 2002, **58**, 380.
19. K. W. Krebs, H. Engelhard, and G. E. Nischk, *Ger. Offen.*, 1959322; *Chem. Abstr.*, 1971, **75**, P88763.
20. K. C. Frish, *J. Am. Chem. Soc.*, 1971, **75**, 6050.
21. K. Harms, *XCAD4, Program for the Lp-Correction of Nonius CAD4 Data*, Marburg (Germany), 1997.
22. G. M. Sheldrick, *Acta. Crystallogr., Sect. A*, 1990, **46**, 467.
23. G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen (Germany), 1997.

Received February 24, 2004;
in revised form June 10, 2004