Formation of Novel P-Functionalized Ligands by Insertion Reactions of RNCX (R = Ph, X = O, S; $R = Pr^{i}$, X = O into the Zr-P Bond of $[Cp_2^2ZrCl(PHCy)]$ (Cp^o = η^{5} -C₅EtMe₄, Cy = Cyclohexyl) and [Cp'₂ZrCl{PH(TRIP)}] $(Cp' = \eta^{5} - C_{5}MeH_{4}, TRIP = 2, 4, 6 - Pr^{i}_{3}C_{6}H_{2})$

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Received February 23, 2000

 $[Cp^{\circ}_{2}ZrCl(PHCy)]$ (1; $Cp^{\circ} = \eta^{5}-C_{5}EtMe_{4}$, Cy = cyclohexyl) and $[Cp'_{2}ZrCl\{PH(TRIP)\}]$ (2; $Cp' = \eta^5 - C_5 MeH_4$, TRIP = 2,4,6-Prⁱ₃C₆H₂) readily insert RNCX (R = Ph, X = S, O; R = Prⁱ, X = O to give $[Cp_{2}^{\circ}ZrCl{\eta^{2}-XC(PHCy)NR}]$ (X = S, R = Ph (3); X = O, R = Ph (4); X = O, $R = Pr^{i}$ (5)) and $[Cp'_{2}ZrCl{\eta^{2}-XC{PH(TRIP)}NR}]$ (X = S, R = Ph (6); X = O, R = Ph (7); $X = O, R = Pr^{i}$ (8)). 3–8 were characterized spectroscopically (IR, NMR, MS), and crystal structure determinations on 4-6 showed an η^2 bonding mode (X,N) of the XC(PHR')NR (R' = Cy, TRIP) ligands. Of the two possible coordination modes of the ligand, 4 and 5 are obtained exclusively as the endo isomer, in which the NR group is adjacent to the Zr-Cl bond, while for **6**–**8**, both isomers (*endo* and *exo*) are formed (1:8 (**6**), 1:30 (**7**) and 1:5 (**8**)), whereby the *exo* isomer is favored. The *exo* isomer of **6** was structurally characterized.

Introduction

Since the first report on zirconocene(IV) complexes with terminal dialkyl- or diarylphosphanido ligands in 1983 by Baker et al.,¹ several other group 4 complexes with such ligands have been described; however, complexes of this type with P-functionalized phosphanido ligands are still rare.^{2–8}

While zirconocene complexes with terminal P(SiMe₃)₂ groups are easily accessible,^{4,5} complexes containing terminal primary phosphanido ligands of general formula [Cp^Z₂ZrCl(PHR)] are only obtained with certain combinations of substituted cyclopentadienyl ligand and P-R substituent. Thus, PH-functionalized zirconocene complexes were only obtained from reactions of [Cp₂- $ZrCl_2$ with LiPH(2,4,6-R'_3C_6H_2) (R' = Me, {}^6Pr^{i}, {}^7Bu^{t}{}^8), i.e., a sterically less demanding ligand at Zr and a bulky substituent at phosphorus ("small/large"), or from [Cp*2-MX₂] and LiPHR (Cp^{*} = η^{5} -C₅Me₅; M = Zr, X = Cl, R = Cy (cyclohexyl); M = Hf, X = I, Cl, R = Cy, X = I, R = Ph),⁹ i.e., a bulky substituent at Zr or Hf and a

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sterically less demanding substituent at phosphorus ("large/small").

The insertion of polar, multiply bonded systems into the Zr-P bond of the P-functionalized zirconocene monophosphanido complexes allows the synthesis within the coordination sphere of zirconium of novel P-functionalized phosphino ligands which are either difficult to synthesize or are inaccessible by other routes.^{2,10,11} Thus, CS_2 ,¹² diazoalkanes,¹³ phenylacetylene,¹⁰ carbo-diimides,^{14,15} and isonitriles¹⁵ are readily inserted into the Zr-P bond of the P-functionalized zirconocene monophosphanido complexes $[Cp_2ZrCl{P(SiMe_3)_2}]$ $(Cp^{Z} = Cp, Cp' (Cp' = \eta^{5} \cdot C_{5}MeH_{4}))$. Only a few insertion reactions of the dialkyl- or diarylphosphanido complexes $[Cp*HfCl_2(PBu^t_2)]$ (with CO¹⁶) and $[Cp*_2HfH(PPh_2)]$ (with CO_2^9) have been reported. Up to now, insertion reactions of CS₂, PhNCS,³ and MeCN¹⁷ with [Cp°₂ZrCl-(PHCy)] (**1**; Cp° = η^5 -C₅EtMe₄), of ketones, aldehydes, and nitriles with $[Cp_2ZrMe(PHMes^*)]$ (Mes^{*} = 2,4,6-But₃C₆H₂),^{6b} and of acetonitrile and benzaldehyde with the chelate complex [Cp*2Zr(1-PH-2-CH2-4,6-Me2C6H2)]18

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10.1021/om000170k CCC: \$19.00 © 2000 American Chemical Society Publication on Web 05/23/2000

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have been reported. A systematic study of the influence of the steric and electronic factors of Cp^Z and R on the course of the insertion reaction has not yet been undertaken.

We now report the insertion reactions of RNCX (R =Ph, X = O, S; $R = Pr^{i}$, X = O) into the Zr-P bond of [Cp[°]₂ZrCl(PHCy)]³ (1) (large/small) and [Cp[′]₂ZrCl{PH-(TRIP)}]⁷ (**2**; TRIP = 2,4,6-Prⁱ₃C₆H₂) (small/large). Preliminary results of the insertion reaction of 1 with PhNCS have been reported elsewhere.³

Results and Discussion

Synthesis and Characterization. Recently, we observed that [Cp°2ZrCl(PHCy)] (1) undergoes insertion of PhNCS into the Zr–P bond, yielding $[Cp^{\circ}_{2}ZrCl\{\eta^{2}-$ SC(PHCy)NPh}] (3). We have now extended these investigations to the complex $[Cp'_2ZrCl{PH(TRIP)}]$ (2) and the isocyanates RNCO ($R = Ph, Pr^{i}$).

Compound 1 was previously obtained in low yield (24-38%) by reaction of [Cp°₂ZrCl₂]¹⁹ and LiPHCy²⁰ at -70 °C in THF.³ We have optimized the preparation by carrying out the reaction at -40 °C in 1,2-dimethoxyethane (DME), which gave 1 in 77% yield.

RNCX (R = Ph, X = S, O; R = Pr^{i} , X = O) readily inserts into the Zr-P bond of 1 and 2 to give [Cp°2ZrCl- $\{\eta^2 - XC(PHCy)NR\}\}$ (X = S, R = Ph (3);³ X = O, R = Ph (4); X = O, $R = Pr^{i}$ (5)) and $[Cp'_{2}ZrCl\{\eta^{2}-XC\{PH(TRIP)\}\}$ -NR}] (X = S, R = Ph (6); X = O, R = Ph (7); X = O, $R = Pr^{i}$ (8)) (Scheme 1). The insertion products are colorless or yellow solids (3-6) or oils (7, 8), which are stable to air for a short period of time. Complexes 4-8 were characterized spectroscopically (IR, NMR, MS). Crystal structure determinations carried out on 4-6 showed an η^2 bonding mode (X,N) of the XC(PHR')NR $(\mathbf{R}' = \mathbf{C}\mathbf{y}, \mathbf{T}\mathbf{R}\mathbf{I}\mathbf{P})$ ligands (vide infra). Because of the chelating action of the N-phenylthiophosphinoamidato and *N*-phenyl- or *N*-isopropylphosphinoamidato ligand, two isomers could, in principle, be formed in each case

Table 1. Comparison of ³¹P NMR and Selected ¹H NMR Data of 1-8

compd	$\delta(^{31}\text{P})$ (ppm)	$^{1}J_{\mathrm{PH}}$ (Hz)	ratio	$\delta(^{1}\mathrm{H})_{\mathrm{P}-H}$ (ppm)
1 ³	71.7	209.0		3.49
2 ⁷	-4.6	230.0		4.86
3 (endo) ³	-16.1	226.9		3.86
4 (endo)	-50.8	224.8		3.79
5 (endo)	-52.2	215.4		3.95
6a (<i>endo</i>)	-48.8	246.2	1:8	
6b (<i>exo</i>)	-69.6	241.3		5.00
7a (endo)	-75.5	244.6	1:30	
7b (<i>exo</i>)	-99.9	241.3		5.03
8a (<i>endo</i>)	-86.9	233.2	1:5	
8b (<i>exo</i>)	-100.2	234.9		5.29

(Scheme 1), one with the NR group adjacent to the chloro ligand (endo isomer) and the other with the X group adjacent to the chloro ligand (exo isomer). Complexes 3,³ 4, and 5 were obtained exclusively as the *endo* isomer with the NPh group adjacent to the Zr-Cl bond. For **6**–**8**, both isomers were formed, with the *exo* isomer being favored, as shown by ³¹P NMR studies (Table 1) and crystal structure determination. Apparently, the bulky cyclopentadienyl ligand Cp° favors the formation of the endo isomer, in which the steric interaction between the Cp° ligands and the NR group is weakest, while the less bulky Cp' (or Cp)²¹ ligands favor the *exo* isomer, in which the Cl-NR interaction is minimized.

The N-phenylthiophosphinoamidato and N-phenyl- or *N*-isopropylphosphinoamidato ligands in 4-8 are expected to show a bidentate (O,N or S,N) coordination mode, as was observed previously for **3** (ν (CN) 1488 and ν (CS) 1022 cm⁻¹),³ [Cp₂Zr(Cl){ η^2 -SC(H)NPh}] (ν (CN) 1562 cm⁻¹),²¹ [Cp'₂ZrCl{ η^2 -NPhC{P(SiMe_3)₂}NPh}]¹⁴ (N,N' coordination; ν (CN) 1485 and 1431 cm⁻¹) and [Cp₂- $ZrCl{\eta^2-S_2CP(SiMe_3)_2}^{12}$ (S,S' coordination; ν (CS) 978 and 923 cm^{-1}). For **6**, the two strong absorptions at 1490 cm⁻¹ (ν (CN)) and at 1013 cm⁻¹ (ν (CS)) were assigned by comparison with the products of carbodiimide, CS_2 , and PhNCS insertion.^{3,12,14,21,22}

The complexes $[Cp_2Zr(Me)\{\eta^2-OC(Me)NR\}]$ (R = Ph, 1-naphthyl)²³ and $[Cp_2Zr(Cl){\eta^2-OC(H)NR}]$ (R = Ph, Cy)²⁴ show strong absorptions at 1600 (R = Ph), 1655 (R = 1-naphthyl),²³ and 1675 cm⁻¹ (R = Ph, Cy),²⁴ which were assigned to the $\nu(CN)$ vibrations. The RNCO insertion products 4 and 5 exhibit strong absorptions at 1597 and 1502 cm⁻¹ (4) and 1600 and 1506 cm⁻¹ (5), which can be assigned to ν (CN) and ν (CO) vibrations.

Molecular Structures of 4-6. In 4 and 5, the zirconium atom is coordinated by two Cp° rings, one chloro ligand, and the O and N atoms of the *N*-phenyl-(4) or N-isopropylphosphinoamidato ligand (5), thus achieving a coordination number of 5 (Figures 1 and 2, Table 2). In **6**, the zirconium atom is coordinated by two Cp' rings, one chloro ligand, and the S and N atoms of the *N*-phenylthiophosphinoamidato ligand, thus also achieving a coordination number of 5 (Figure 3, Table 2). The overall structures are comparable to those of the previously reported complex 3,3 the thioformamido

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Figure 1. Molecular structure of $[Cp^{\circ}_2ZrCl\{\eta^2-OC(PHCy)-NPh\}]$ (4) showing the atom-numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP).²⁶ Hydrogen atoms (other than P–H) are omitted for clarity.



Figure 2. Molecular structure of $[Cp^{\circ}_2ZrCl\{\eta^2-OC(PHCy)-NPr^i\}]$ (5) showing the atom numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP).²⁶ Hydrogen atoms (other than P–H) are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and BondAngles (deg) of 3,3 4, 5, and 6

	- 0			
	3 ³	4	5	6
Zr-Cl	2.523(1)	2.5035(9), 2.5028(9)	2.5217(7)	2.5176(9)
Zr-S	2.769(1)			2.658(1)
Zr-O		2.268(2), 2.262(2)	2.273(2)	
Zr-N	2.361(4)	2.309(3), 2.327(3)	2.349(2)	2.418(2)
S-C*a	1.718(5)			1.723(3)
0-C*		1.290(4), 1.289(4)	1.299(3)	
N-C*	1.296(6)	1.309(4), 1.311(4)	1.299(4)	1.311(4)
P-C*	1.842(4)	1.855(4), 1.857(3)	1.882(3)	1.847(3)
P-H	1.258(2)	1.30(4), 1.26(4)	0.960	1.33(3)
C*-N-Zr	106.5(3)	93.2(2), 92.5(2)	92.0(2)	102.5(2)
S-C*-N	114.4(3)			113.9(2)
O-C*-N		114.2(3), 114.5(3)	115.7(2)	
S-Zr-N	58.8(1)			60.2(1)
O-Zr-N		56.95(9), 56.90(9)	56.83(7)	

^a C*: **3**, C(23); **4/1**, C(35); **4/2**, C(70); **5**, C(23); **6**, C(13).

complex [Cp₂Zr(Cl){ η^2 -SC(H)NPh}],²¹ the phosphaguanidino complex [Cp'_2ZrCl{ η^2 -NPhC{P(SiMe_3)_2}NPh}]¹⁴ (N,N' coordination), and the CS₂ insertion product [Cp₂-ZrCl{ η^2 -S₂CP(SiMe₃)₂}]¹² (S,S' coordination), as well as



Figure 3. Molecular structure of $[Cp'_2ZrCl{\eta^2-SC{PH-(TRIP)}NPh}]$ (6) showing the atom-numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP).²⁶ Hydrogen atoms (other than P–H) are omitted for clarity.

the related complex $[Cp_2Zr(Me)\{\eta^2-OC(Me)NPh\}]^{23}$ (O,N coordination). The guanidino ligand, the phosphinodithioformato ligand, and the formamido ligand are bonded to the zirconium atom almost symmetrically in a bidentate fashion (phosphaguanidino ligand, Zr-N =2.309(5), 2.348(5) Å;¹⁴ phosphinodithioformato ligand, Zr-S = 2.733(7), 2.640(8) Å;¹² formamido ligand, Zr-O = 2.298(4), Zr-N = 2.297(4) Å²³), as are the *N*-phenyl- (4: Zr-N = 2.309(3) and 2.327(3) Å, Zr-O = 2.268(2) and 2.262(2) Å) and *N*-isopropylphosphinoamidato ligands (5: Zr-N = 2.349(2) Å, Zr-O = $\hat{2}.273(2)$ Å). In $\hat{6}$ (Zr-N = 2.418(2) Å, Zr-S = 2.658(1) Å) and the related complex $[Cp_2Zr(Cl){\eta^2-SC(H)NPh}]^{21}$ (Zr-N = 2.408(9) Å, Zr-S = 2.659(4) Å), the N,S coordination is unsymmetrical. The Zr-N bond lengths of 4-6 are comparable to those of the N,N'-bonded ligand, and the Zr–S bond length of **6** is comparable to those of the S,S'-bonded ligand. However, in all these complexes, delocalization of the π electrons of the N₂C, NCS, and NCO fragments can be assumed, as the C-N, C-S, and C-O bonds are shorter than expected for single bonds, and the N and C atoms of the N_2C (C-N = 1.331(7), 1.323(7) Å),¹⁴ NCO (4, N-C(35) = 1.309(4) Å, O-C(35) = 1.209(4) Å; **5**, N-C(23) = 1.299-(4) Å, O-C(23) = 1.299(3) Å) and NCS fragments (3, N-C(23) = 1.296(6) Å, S-C(23) = 1.718(5) Å; 6, N-C(13) = 1.311(4) Å, S-C(13) = 1.723(3) Å) are coordinated in a trigonal-planar fashion. As in 3^3 , the chlorine atom and the ZrXCN fragments (X = O, S) in **4–6** are coplanar. The P atom of the pyramidal PHR group deviates from this plane by 0.070 (P1) and 0.001 Å (P2) (4), 0.149 Å (5) and 0.393 Å (6). The mean P-C bond length of 1.86 Å is indicative of single bonds (Table 2).

Of the two possible coordination modes of the ligand, for **4** and **5** the only one observed is that in which the NR group is adjacent to the Zr-Cl bond (*endo* isomer), while the *exo* isomer is observed for **6**.

Experimental Section

All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. NMR spectra were recorded on an Avance DRX 400 spectrometer (Bruker). NMR standards: ¹H NMR (400 MHz), trace amounts of protonated solvent, C_6D_6 ; ¹³C NMR (100.6 MHz), internal solvent; ³¹P NMR (162 MHz), external 85% H₃PO₄. The IR spectra were recorded as KBr mulls on a Perkin-Elmer FT-IR spectrometer System 2000 in the range 350–4000 cm⁻¹. The mass spectra were recorded with a Sektorfeldgerät AMD 402 (AMD Intectra GmbH; EI, 70 eV). The melting points were determined in sealed capillaries under argon and are uncorrected. $\mathbf{2}^7$ and $\mathbf{3}^3$ were prepared by literature procedures. PhNCS, PhNCO, and PrⁱNCO are commercially available and were kept over molecular sieves prior to use.

Improved Synthesis of $[Cp_2ZrCl(PHCy)]$ (1). At -40 °C 1.2 g (9.8 mmol) of LiPHCy in 15 mL of DME was added to a solution of 4.5 g (9.7 mmol) of $[Cp_2ZrCl_2]$ in 30 mL of DME. The solution was kept at this temperature for 3 h, during which time the color changed to dark red. After the mixture was stirred at room temperature for 12 h, LiCl was filtered off, and the mother liquor was kept at room temperature. Pure 1 crystallized in 77% yield. The spectroscopic data are in agreement with those reported in the literature.³

 $[Cp^{\circ}_{2}ZrCl{\eta^{2}-OC(PHCy)NPh}]$ (4). At room temperature 0.51 mL (4.66 mmol) of PhNCO was added to a solution of 2.48 g (4.59 mmol) of 1 in 50 mL of pentane. Immediately, the color of the solution changed from dark red to yellow. A ³¹P NMR spectrum of the reaction mixture (C₆D₆) showed only one signal at -50.8 ppm (d, ${}^{1}J_{PH} = 224.8$ Hz). Colorless crystals were obtained on concentrating the solution (at room temperature). Yield: 81%. Mp: 142 °C. ¹H NMR (C₆D₆): δ 0.95 (t, 6H, CH_2CH_3 , ${}^3J_{HH} = 7.4$ Hz), 0.98–1.80 (m, br, 11H, Cy), 1.89, 1.90, 1.93, and 1.96 (s, each 3H, C₅Me₄Et), 1.97 (s, 6H, C₅Me₄-Et), 2.00 (s, 2H, C₅Me₄Et), 2.01 (s, 4H, C₅Me₄Et), 2.48 (q, br, 4H, CH_2CH_3), 3.79 (d, 1H, P-H, ${}^1J_{PH} = 227$ Hz), 6.96-6.98 (m, 1H, Ph), 7.19–7.25 (m, 4H, Ph). ¹³C NMR (C₆D₆): δ 12.55– 12.90 (s, C₅Me₄Et), 15.28 and 15.38 (s, C₅Me₄CH₂CH₃), 21.00 and 21.04 (s, C₅Me₄CH₂CH₃), 26.94 (s, C4 of Cy), 27.59 (d, C3 or C5 of Cy, ${}^{3}J_{PC} = 14.5$ Hz), 27.95 (d, C3 or C5 of Cy, ${}^{3}J_{PC} =$ 7.4 Hz), 31.54 (d, C2 or C6 of Cy, ${}^{2}J_{PC} = 5.9$ Hz), 33.20 (d, C2 or C6 of Cy, ${}^{2}J_{PC} = 5.8$ Hz), 33.69 (d, C1 of Cy, ${}^{1}J_{PC} = 23.0$ Hz), 120.25, 120.41, 120.90, 121.04, 121.74, 122.04, 122.13, and 122.70 (each s, C₄Me₄CEt), 125.59 (s, C₄Me₄CEt), 126.45, 126.70, 126.83, and 126.85 (each s, C2-C6 of Ph), 146.13 (s, C1 of Ph), 184.48 (d, NCP, ${}^{1}J_{PC} = 34.4$ Hz). EI MS: m/z 657 (4%, M⁺), 545 (0.5%, M⁺ – Ph – Cl), 508 (100%, M⁺ – Cp°), 423 (11%, Cp°₂ZrCl⁺), 387 (9%, Cp°₂Zr⁺), 359 (2%, M⁺ – 2 Cp°), 307 (5%, ZrNPhCPCy⁺), 291 (13%, Cp°ZrClO⁺), 269 (14%, (C₅-Et)₂Zr⁺), 218 (4%, PhNCPHCy⁺), 149 (20%, Cp°⁺), 135 (21%, C₅EtMe₃⁺), 119 (21%, PhNCO⁺), 103 (5%, PhNC⁺), and fragmentation thereof. Anal. Calcd for C₃₅H₅₁ClNOPZr (659.41): C, 63.7; H, 7.8; N, 2.1. Found: C, 62.9; H, 8.4; N, 2.0.

 $[Cp^{\circ}_{2}ZrCl\{\eta^{2}-OC(PHCy)NPr^{i}\}]$ (5). At room temperature 0.36 mL (3.69 mmol) of PriNCO was added to a solution of 1.99 g (3.69 mmol) of 1 in 50 mL of pentane. Immediately, the color of the solution changed from dark red to yellow. The solution was stirred for 24 h. A ³¹P NMR spectrum of the reaction mixture (C_6D_6) showed only one signal at -52.2 ppm (d, ${}^{1}J_{\rm PH} = 215.4$ Hz). Colorless crystals were obtained on concentrating the solution. Yield: 85%. Mp: 133 °C. ¹H NMR (C₆D₆): δ 0.94 (t, 6H, CH₂CH₃, ³J_{HH} = 8.1 Hz), 1.20-2.75 (m, br, 11H, Cy), 1.34 (d, 6H, Me₂CH, ³J_{HH} = 6.4 Hz), 1.90 (s, 6H, C₅Me₄Et), 1.93 (s, 6H, C₅Me₄Et), 1.95 (s, 12H, C₅Me₄Et), 2.44 (q, br, 4H, CH_2CH_3 , ${}^3J_{HH} = 7.2$ Hz), 3.81 (sept, br, 1H, Me_2CH), 3.95 (d, 1H, P–H, ${}^{1}J_{PH} = 215.5$ Hz). ${}^{13}C$ NMR (C₆D₆): δ 12.53, 12.70, 12.72, 12.90, 12.97, and 13.03 (each s, C₅Me₄Et), 15.31 and 15.40 (each s, C₅Me₄CH₂CH₃), 21.04 and 21.08 (each s, C₅Me₄*C*H₂CH₃), 25.00 (s, *Me*₂CH), 26.98 (s, C4 of Cy), 27.71 (d, C3 or C5 of Cy, ${}^{3}J_{PC} = 14.9$ Hz), 28.20 (d, C3 or C5 of Cy, ${}^{3}J_{PC} = 7.1$ Hz), 30.88 (d, C2 or C6 of Cy, ${}^{2}J_{PC} = 5.5$ Hz), 33.45 (d, C2 or C6 of Cy, ${}^{2}J_{PC} = 5.1$ Hz), 34.01 (d, C1 of Cy, ${}^{1}J_{PC} =$ 24.3 Hz), 51.39 (d, Me₂*C*H, ${}^{3}J_{PC} = 10.0$ Hz), 120.03, 120.34, 120.56, 120.60, 121.90, 121.97, 122.28, and 122.70 (each s, C₄-Me₄CEt), 126.14 and 126.44 (each s, C₄Me₄CEt), 180.72 (d, NCP, ${}^{1}J_{PC} = 33.7$ Hz). EI MS: m/z 625 (4%, M⁺), 590 (2%, M^+ – Cl), 476 (97%, M^+ – Cp°), 423 (23%, Cp°₂ZrCl⁺), 290 (28%, C₅Me₃ZrCl⁺ or ZrOC(PCy)NPrⁱ⁺), 268 (21%, (C₅-Et)₂ZrNC⁺), 200 (7%, OC(PHCy)NPrⁱ⁺), 149 (29%, Cp°⁺), 141 (17%, NCPHCy⁺), 134 (15%, C₅EtMe₃⁺), 116 (53%, PHCy⁺), 91 (7%, Zr⁺), 83 (100%, Cy⁺), 43 (97%, Prⁱ⁺), and fragmentation thereof. Anal. Calcd for C₃₂H₅₃ClNOPZr (625.39): C, 63.7; H, 7.8; N, 2.1. Found: C, 62.9; H, 8.4; N, 2.0.

 $[Cp'_2ZrCl{\eta^2-SC{PH(TRIP)}NPh}]$ (6). At room temperature 0.45 mL (3.77 mmol) of PhNCS was added to a suspension of 1.78 g (3.42 mmol) of 2 in 50 mL of pentane. The color of the reaction mixture became lighter, and after 30 min a colorless solid had formed. The mixture was stirred for 2 h, during which time the solution turned yellow. The solid was isolated by filtration, washed with pentane, and dried in vacuo. A ³¹P NMR spectrum of the solid (C₆D₆) showed two signals at -48.8 ppm (d, ${}^{1}J_{PH} = 246.2$ Hz, endo isomer, **6a**) and -69.6ppm (d, ${}^{1}J_{PH} = 241.3$ Hz, *exo* isomer, **6b**) in the ratio 1:8. The mother liquor was further concentrated, and a colorless solid was obtained. Recrystallization from toluene yielded colorless crystals of 6b (yield 70%). Mp: 110 °C (melts and turns yellow). The assignment of the signals in the ¹³C NMR spectrum of **6b** was made on the basis of a 2D NMR spectrum (1H/13C). 6a was not obtained in pure form.

6b. ¹H NMR (C₆D₆): δ 1.18 (d, 6H, *Me*₂CH, ³*J*_{HH} = 6.2 Hz), 1.28 (d, 6H, Me_2 CH, ${}^{3}J_{HH} = 6.2$ Hz), 1.39 (d, 6H, Me_2 CH, ${}^{3}J_{\rm HH} = 6.7$ Hz), 2.20 (s, 3H, C₅H₄Me), 2.23 (s, 3H, C₅H₄Me), 2.76 (sept, 1H, Me_2CH, $^3J_{\rm HH}$ = 6.9 Hz), 3.76 (sept, br, 2H, Me₂C*H*), 5.00 (d, 1H, P–H, ${}^{1}J_{PH} = 238.9$ Hz), 5.48 (m, 1H, C₅H₄Me), 5.56 (m, 1H, C₅H₄Me), 5.61 (m, 1H, C₅H₄Me), 5.68 (m, 3H, C₅H₄Me), 6.07 (m, 2H, C₅H₄Me), 7.02 (m, 1H, Ph), 7.18–7.09 (m, Ph and 2,4,6-Pri₃C₆H₂). ¹³C NMR (C₆D₆): δ 16.26 (s, C₅H₄Me), 24.67 (s, Me₂CH of p-Prⁱ), 25.19 (s, Me₂CH of o-Prⁱ), 25.39 (s, Me₂CH of o-Prⁱ), 34.32 (s, Me₂CH of o-Prⁱ), 34.46 (s, Me₂*C*H of *p*-Prⁱ), 108.72, 110.14, 113.53, 114.22, 115.89, 116.10, 118.00, 118.64, and 119.63 (each s, C₅H₄Me), 122.53 (d, C3/ C5 of 2,4,6- $Pr_{3}^{i}C_{6}H_{2}$, ${}^{3}J_{PC} = 4.7$ Hz), 124.69, 126.20, 129.72, and 130.16 (each s, C2-C6 of Ph), 140.0 (s, C1 of Ph), 151.44 (d, C2/C6 of 2,4,6-Pr $_{3}^{i}C_{6}H_{2}$, $^{2}J_{PC} = 3.9$ Hz), 152.58 (s, C4 of 2,4,6-Prⁱ₃ C_6 H₂), 155.65 (d, br, C1 of 2,4,6-Prⁱ₃ C_6 H₂, ¹ $J_{PC} = 14.2$ Hz), 206.4 (d, N*C*P, ${}^{1}J_{PC} = 54.6$ Hz). EI MS: m/z 538 (1%, Cp'₂-Zr(Cl)NPhC(S)PHC₆CH₃⁺), 506 (3%, Cp'₂Zr(Cl)NPhCPHC₆- CH_{3}^{+}), 496 (0.5%, $Zr(Cl){SC{PH(TRIP)}}NPh}^{+}$), 370 (20%, $SC\{PH(TRIP)\}NPh^+ \ or \ Cp'Zr(Cl)SC(P)NPh^+), \ 338 \ (64\%,$ $PhNCPH(TRIP)^{+}),\;317\;(5\%,\;Cp'_{2}ZrClS^{+}),\;282\;(9\%,\;Cp'_{2}ZrS^{+}),$ 246 (25%, CP(TRIP)+), 235 (21%, PH(TRIP)+), 219 (4%, PC₆H₂-Pri₂CH₃CH⁺), 203 (72%, TRIP⁺), 191 (11%, PC₆H₂Pri₂⁺), 166 (100%, SCPNPh⁺), 160 (14%, PC₆H₂PrⁱC⁺ or C₆H₂Prⁱ₂⁺), 149 (16%, $PHC_{6}H_{2}Pr^{i\,+}),$ 135 (50%, $PHC_{6}H_{2}CHCH_{3}^{+}$ or $PhNCS^{+}),$ 118 (11%, PC₆CH₃⁺ or C₆H₂Prⁱ₂⁺), 91 (30%, Zr⁺), 77 (62%, Ph⁺), 64 (8%, $C_5H_4^+$), 43 (66%, Pr^{i+}) and fragmentation thereof (molecular ion peak is not observed). Anal. Calcd for C₃₄H₄₃-ClNSPZr (655.39): C, 62.3; H, 6.6; N, 2.1; S, 4.9. Found: C, 62.3; H, 5.9; N, 2.1; S, 4.3.

[Cp'_2ZrCl{ η^2 -**OC**{**PH(TRIP)**}**NPh**}**]** (7). At room temperature 0.4 mL (3.66 mmol) of PhNCO was added to a suspension of 1.56 g (3.00 mmol) of **2** in 50 mL of pentane. The solid dissolved at once, and a clear yellow-orange solution was obtained. The mixture was stirred for 12 h, during which time the solution turned pale yellow. A ³¹P NMR spectrum of the solution (C₆D₆) showed two signals at -75.5 ppm (d, ¹J_{PH} = 244.6 Hz, 7a) and -99.9 ppm (d, ¹J_{PH} = 241.3 Hz, 7b) in the ratio 1:30. The solvent was evaporated, and an oily yellow residue was obtained which did not solidify. Further purification of the major isomer was not achieved.

7b. ¹H NMR (C₆D₆): δ 1.14 (d, 6H, *Me*₂CH, ³*J*_{HH} = 6.9 Hz), 1.21 (d, 6H, *Me*₂CH, ³*J*_{HH} = 6.5 Hz), 1.33 (d, 6H, *Me*₂CH, ³*J*_{HH} = 6.7 Hz), 1.85 (s, 3H, C₅H₄*Me*), 2.12 (s, 3H, C₅H₄*Me*), 2.71 (sept, 1H, Me₂C*H*, ³*J*_{HH} = 6.8 Hz), 3.69 (sept, br, 2H, Me₂C*H*), 5.03 (d, 1 H, P-H, ¹*J*_{PH} = 242.7 Hz), 5.61, 5.68, 5.73, 5.74, 5.83, 5.86 (each m, each 1H, C₅*H*₄Me), 5.96 (m, 2H, C₅*H*₄-Me), 6.96-7.07, 7.11, 7.18-7.23 (each m, 7H, Ph and 2,4,6Prⁱ₃C₆H₂). ¹³C NMR (C₆D₆): δ 15.64 and 16.02 (each s, C₅H₄*Me*), 24.67, 24.70, 25.57 (each s, *Me*₂CH), 34.16, 34.29, and 35.41 (each s, Me₂CH), 110.45, 110.61, 113.54, 114.24, 115.05, 115.29, 115.69, 115.89, 118.02, and 119.70 (each s, C₅H₄Me), 122.27 (d, C3/C5 of 2,4,6-Prⁱ₃C₆H₂, ³J_{PC} = 3.8 Hz), 126.15, 126.48, 126.95, and 127.56 (each s, C2–C6 of Ph), 139.81 (s, C1 of Ph), 146.77 (s, br, C2/C6 of 2,4,6-Prⁱ₃C₆H₂), 151.89 (s, C4 of 2,4,6-Prⁱ₃C₆H₂), 154.77 (d, br, C1 of 2,4,6-Prⁱ₃C₆H₂), 185.88 (d, br, N*C*P, ¹J_{PC} ≈ 35 Hz).

[Cp'₂ZrCl{ η^2 -OC{PH(TRIP)}NPrⁱ]] (8). At room temperature 0.26 mL (2.65 mmol) of PrⁱNCO was added to a suspension of 1.32 g (2.54 mmol) of 2 in 50 mL of pentane. The mixture was stirred for 10 h, during which time the solution turned orange. The ³¹P NMR spectrum of the solution (C₆D₆) showed two signals at -86.9 ppm (d, ¹J_{PH} = 233.2 Hz, 8a) and -100.2 ppm (d, ¹J_{PH} = 234.9 Hz, 8b) in the ratio 1:5. The solvent was evaporated, and an oily residue was obtained. By washing with hexane, the isomer 8b was enriched (ratio 1:12) but did not solidify.

8b. ¹H NMR (C₆D₆): δ 1.17 (d, 6H, *Me*₂CH of TRIP, ³*J*_{HH} = 6.9 Hz), 1.30 (d, 6H, Me_2 CH of TRIP, ${}^{3}J_{HH} = 6.7$ Hz), 1.36 (d, 6H, Me_2 CH of TRIP, ${}^{3}J_{HH} = 6.6$ Hz), 1.44 (d, 3H, Me_2 CH of $Pr^{i}N$, ${}^{3}J_{HH} = 6.3$ Hz), 1.47 (d, 3H, $Me_{2}CH$ of $Pr^{i}N$, ${}^{3}J_{HH} = 6.4$ Hz), 1.84 (s, 3H, C₅H₄Me), 2.07 (s, 3H, C₅H₄Me), 2.75 (sept, 1H, Me₂CH), 3.75 (sept, br, 3H, Me₂CH, ${}^{3}J_{HH} = 6.3$ Hz), 5.29 (d, 1H, P–H, ${}^{1}J_{PH} = 235.2$ Hz), 5.55 and 5.63 (each m, each 1H, C₅H₄Me), 5.65 (m, 2H, C₅H₄Me), 5.77, 5.80, 5.88, and 5.93 (each m, each 1H, C₅H₄Me), 7.14 (s, 2H, 2,4,6-Prⁱ₃C₆H₂). ¹³C NMR (C₆D₆): δ 15.67 and 16.03 (each s, C₅H₄*Me*), 24.36, 24.48, 24.70, 24.73, 24.80, and 25.59 (each s, Me₂CH of TRIP and Prⁱ-NCP), 34.21 (s, Me₂CH of o-Prⁱ), 35.43 (s, Me₂CH of p-Prⁱ), 53.00 (d, Me₂*C*H of Prⁱ-NCP, ${}^{3}J_{PC} = 8.7$ Hz), 110.72, 112.07, 112.91, 115.03, 115.52, 115.58, and 116.08 (each s, C₅H₄Me), 122.33 (d, C3 or C5 of 2,4,6- $Pr_{3}^{i}C_{6}H_{2}$, ${}^{3}J_{PC} = 4.1$ Hz), 123.60 (d, C3 or C5 of 2,4,6- $Pr_{3}^{i}C_{6}H_{2}$, ${}^{3}J_{PC} = 6.4$ Hz), 126.41 (s, C2 or C6 of 2,4,6- $Pr^{i}_{3}C_{6}H_{2}$), 127.33 (s, C2 or C6 of 2,4,6- $Pr^{i}_{3}C_{6}H_{2}$), 151.92 (s, C4 of 2,4,6-Prⁱ₃C₆H₂), 154.88 (d, C1 of 2,4,6-Prⁱ₃C₆H₂, ${}^{1}J_{PC} = 12.3$ Hz), 182.31 (d, N*C*P, ${}^{1}J_{PC} = 34.5$ Hz).

Data Collection and Structural Refinement of 4–6. Crystallographic data are given in Table 3. Data (λ (Mo K α) = 0.710 73 Å) were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for determination of the unit cell parameters. Empirical absorption correction was carried out with SADABS.²⁵ The structures were solved by direct methods (SHELXTL PLUS²⁶). Restrictions for **4** and **5**: Zr, Cl, P, N, O, and C atoms anisotropic.

(25) Sheldrick, G. M. SADABS-a Program for Empirical Absorption Correction; University of Göttingen, Göttingen, Germany, 1998.

Table 3. Crystal Data and Structure RefinementDetails for 4–6

	4	5	6
formula	C ₃₅ H ₅₁ Cl-	C ₃₂ H ₅₃ Cl-	C ₃₄ H ₄₃ Cl-
	NOPZr	NOPZr	NPSZr
$M_{ m r}$	659.41	625.39	655.39
temp (K)	213(2)	223(2)	223(2)
cryst syst	triclinic	monoclinic	triclinic
space group	P1 (No. 2)	$P2_1/n$ (No. 14)	P1 (No. 2)
a (Å)	10.097(1)	16.366(1)	9.689(1)
b (Å)	17.825(1)	11.037(1)	13.260(1)
c (Å)	19.553(1)	18.673(1)	14.087(1)
α (deg)	104.96(1)	90	70.75(1)
β (deg)	91.95(1)	106.37(1)	76.65(1)
γ (deg)	91.37(1)	90	76.74(1)
$V(Å^3)$	3395.8(3)	3236.3(1)	1639.1(1)
Ζ	4	4	2
ρ_{calcd} (Mg m ⁻³)	1.290	1.284	1.328
F(000)	1392	1328	684
cryst size (mm)	$0.25 \times 0.25 \times$	$0.25 \times 0.20 \times$	$0.25 \times 0.25 \times$
	0.20	0.20	0.20
abs coeff (mm ⁻¹)	0.476	0.496	0.552
$2\theta_{\rm max}$ (deg)	2.2 - 56.2	3.0 - 54.4	3.1 - 55.8
no. of rflns collected	18 695	24 776	10 837
no. of indep rflns	13 495	6547	6771
R _{int}	0.0330	0.0459	0.0288
no. of params	1135	334	525
R1 $(I \geq 2\sigma(I))$	0.0534	0.0405	0.0402
wR2 (all data)	0.1125	0.1353	0.1101
$(\Delta/\rho)_{\rm min}$ (e Å ⁻³)	0.444	0.963	0.495
$(\Delta/ ho)_{ m max}$ (e Å ⁻³)	-0.826	-0.828	-0.534

Restrictions for **6**: Zr, Cl, P, N, S, and C atoms anisotropic. H atoms were located by difference maps and refined isotropically (for **4** and **6**). For **5**, H atoms were refined (fixed U_{eq}) in calculated positions.

Acknowledgment. We gratefully acknowledge support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of crystal data, atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **4–6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000170K

⁽²⁶⁾ SHELXTL PLUS; Siemens Analytical X-ray Instruments, Madison, WI, 1990: XS, Program for Crystal Structure Solution; XL, Program for Crystal Structure Determination; XP, Interactive Molecular Graphics.