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°$_2$ZrCl(PHCy)] (Cp° = η^5-C_5EtMe_4, Cy = Cyclohexyl) and [Cp′$_2$ZrCl{PH(TRIP)}] (Cp′ = η^5-C_5MeH_4, TRIP = 2,4,6-Pr$^i_3C_6H_2$)

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[Cp°$_2$ZrCl(PHCy)] (**1**; Cp° = η^5-C_5EtMe_4, Cy = cyclohexyl) and [Cp′$_2$ZrCl{PH(TRIP)}] (**2**; Cp′ = η^5-C_5MeH_4,TRIP = 2,4,6-Pr$^i_3C_6H_2$) readily insert RNCX (R = Ph, X = S, O; R = Pr^i, X = O) to give [Cp°$_2$ZrCl{η^2-XC(PHCy)NR}] (X = S, R = Ph (**3**); X = O, R = Ph (**4**); X = O, R = Pr^i (**5**)) and [Cp′$_2$ZrCl{η^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(SiMe$_3$)$_2$ groups are easily accessible,[4,5] complexes containing terminal primary phosphanido ligands of general formula [Cp$^Z_2$ZrCl(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 [Cp$_2$ZrCl$_2$] with LiPH(2,4,6-R′$_3C_6H_2$) (R′ = Me,[6] Pr^i,[7] Bu^t [8]), i.e., a sterically less demanding ligand at Zr and a bulky substituent at phosphorus ("small/large"), or from [Cp*$_2$MX$_2$] and LiPHR (Cp* = η^5-C_5Me_5; 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 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] carbodiimides,[14,15] and isonitriles[15] are readily inserted into the Zr−P bond of the P-functionalized zirconocene monophosphanido complexes [Cp$^Z_2$ZrCl{P(SiMe$_3$)$_2$}] (Cp^Z = Cp, Cp′ (Cp′ = η^5-C_5MeH_4)). Only a few insertion reactions of the dialkyl- or diarylphosphanido complexes [Cp*HfCl$_2$(PBu$^t_2$)] (with CO[16]) and [Cp*$_2$HfH(PPh$_2$)] (with CO_2[9]) have been reported. Up to now, insertion reactions of CS_2, PhNCS,[3] and MeCN[17] with [Cp°$_2$ZrCl(PHCy)] (**1**; Cp° = η^5-C_5EtMe_4), of ketones, aldehydes, and nitriles with [Cp$_2$ZrMe(PHMes*)] (Mes* = 2,4,6-Bu$^t_3C_6H_2$),[6b] and of acetonitrile and benzaldehyde with the chelate complex [Cp*$_2$Zr(1-PH-2-CH$_2$-4,6-Me$_2C_6H_2$)][18]

(1) (a) Baker, R. T.; Krusic, P. J.; Tulip, T. H.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 6763. (b) Baker, R. T.; Whitney, J. F.; Wreford, S. S. *Organometallics* **1983**, *2*, 1049.
(2) (a) Stephan, D. W. *Angew. Chem.* **2000**, *112*, 322. (b) Segerer, U.; Felsberg, R.; Blaurock, S.; Hadi, G. A.; Hey-Hawkins, E. *Phosphorus, Sulfur Silicon Relat. Elem.* **1999**, *144−146*, 477. (c) Hey-Hawkins, E. *Chem. Rev.* **1994**, *94*, 1661.
(3) Segerer, U.; Hey-Hawkins, E. *Polyhedron* **1997**, *16*, 2537.
(4) Hey-Hawkins, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc., Dalton Trans.* **1991**, 939.
(5) Lindenberg, F.; Hey-Hawkins, E. *J. Organomet. Chem.* **1992**, *435*, 291.
(6) (a) Hey, E.; Müller, U. *Z. Naturforsch.* **1989**, *44B*, 1538. (b) Breen, T. L.; Stephan, D. W. *Organometallics* **1996**, *15*, 4509.
(7) Hey-Hawkins, E.; Kurz, S.; Baum, G. *Z. Naturforsch.* **1995**, *50B*, 239.
(8) Kurz, S.; Hey-Hawkins, E. *J. Organomet. Chem.* **1994**, *479*, 125.
(9) Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 1760.
(10) Hey-Hawkins, E.; Lindenberg, F. *Chem. Ber.* **1992**, *125*, 1815.
(11) (a) Appel, R.; Moors, R. *Angew. Chem.* **1986**, *98*, 570. (b) Fritz, G.; Härer, J.; Stoll, K.; Vaahs, T. *Phosphorus Sulfur Relat. Elem.* **1983**, *18*, 65. (c) Lindenberg, F.; Sieler, J.; Hey-Hawkins, E. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *108*, 279.
(12) Hey, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc., Chem. Commun.* **1987**, 421.
(13) Hey, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *Polyhedron* **1988**, *7*, 2083.
(14) Hey-Hawkins, E.; Lindenberg, F. *Z. Naturforsch.* **1993**, *48B*, 951.
(15) Lindenberg, F.; Sieler, J.; Hey-Hawkins, E. *Polyhedron* **1996**, *15*, 1459.
(16) Roddick, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4670.
(17) Segerer, U.; Hey-Hawkins, E. *Organometallics* **1999**, *18*, 2838.

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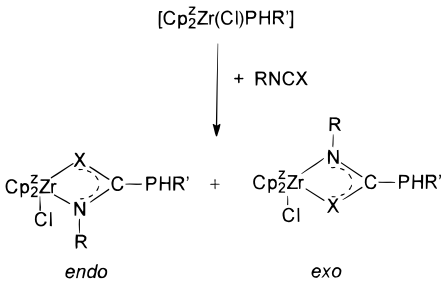
Scheme 1



Cp^z = Cp° (η^5-C_5EtMe_4), R' = Cy: X = S, R = Ph (**3**); X = O, R = Ph (**4**); X = O, R = Pr^i (**5**)

Cp^z = Cp' (η^5-C_5MeH_4), R' = TRIP (2,4,6-Pr$^i_3C_6H_2$): X = S, R = Ph (**6**); X = O, R = Ph (**7**); X = O, R = Pr^i (**8**)

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°$_2$ZrCl(PHCy)][3] (**1**) (large/small) and [Cp′$_2$ZrCl{PH(TRIP)}][7] (**2**; TRIP = 2,4,6-Pr$^i_3C_6H_2$) (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°$_2$ZrCl(PHCy)] (**1**) undergoes insertion of PhNCS into the Zr−P bond, yielding [Cp°$_2$ZrCl{η^2-SC(PHCy)NPh}] (**3**). We have now extended these investigations to the complex [Cp′$_2$ZrCl{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°$_2$ZrCl$_2$][19] and LiPHCy[20] 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°$_2$ZrCl{η^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{η^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 (R′ = Cy, TRIP) 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 (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 ^{31}P 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.

Table 1. Comparison of ^{31}P NMR and Selected ^{1}H NMR Data of 1−8

compd	$\delta(^{31}P)$ (ppm)	$^1J_{PH}$ (Hz)	ratio	$\delta(^1H)_{P-H}$ (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 (*endo*)	−48.8	246.2	1:8	
6b (*exo*)	−69.6	241.3		5.00
7a (*endo*)	−75.5	244.6	1:30	
7b (*exo*)	−99.9	241.3		5.03
8a (*endo*)	−86.9	233.2	1:5	
8b (*exo*)	−100.2	234.9		5.29

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] [Cp$_2$Zr(Cl){η^2-SC(H)NPh}] (ν(CN) 1562 cm^{-1}),[21] [Cp′$_2$ZrCl{η^2-NPhC{P(SiMe$_3$)$_2$}NPh}][14] (N,N′ coordination; ν(CN) 1485 and 1431 cm^{-1}) and [Cp$_2$ZrCl{η^2-S$_2$CP(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$_2$Zr(Me){η^2-OC(Me)NR}] (R = Ph, 1-naphthyl)[23] and [Cp$_2$Zr(Cl){η^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 ν(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

(18) (a) Hou, Z.; Stephan, D. W. *J. Am. Chem. Soc.* **1992**, *114*, 10088. (b) Hou, Z.; Breen, T. L.; Stephan, D. W. *Organometallics* **1993**, *12*, 3158.
(19) Kurz, S.; Hey-Hawkins, E. *Z. Kristallogr.* **1993**, *205*, 61.
(20) (a) Hey-Hawkins, E.; Kurz, S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *90*, 281. (b) Frenzel, C.; Lönnecke, P.; Hey-Hawkins, E. *Z. Anorg. Allg. Chem.*, manuscript in preparation.
(21) Mei, W.; Shiwei, L.; Meizhi, B.; Hefu, G. *J. Organomet. Chem.* **1993**, *447*, 227.
(22) Weidlein, J.; Müller, U.; Dehnicke, K. *Schwingungsfrequenzen I, Hauptgruppenelemente*; G. Thieme Verlag: Stuttgart, Germany, 1981.
(23) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1985**, *24*, 655.
(24) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278.

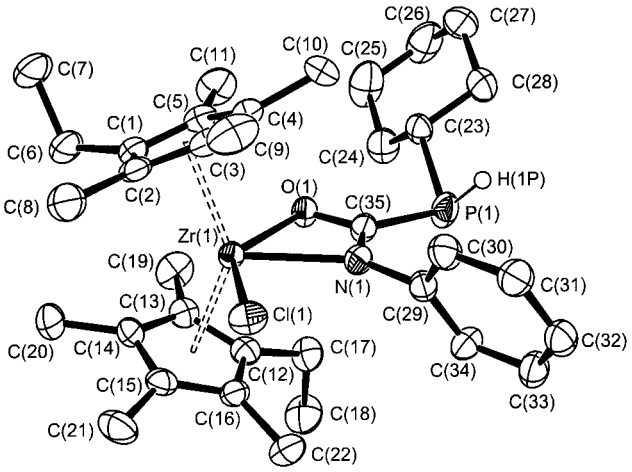


Figure 1. Molecular structure of [Cp°$_2$ZrCl{η^2-OC(PHCy)-NPh}] (**4**) showing the atom-numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP).[26] Hydrogen atoms (other than P−H) are omitted for clarity.

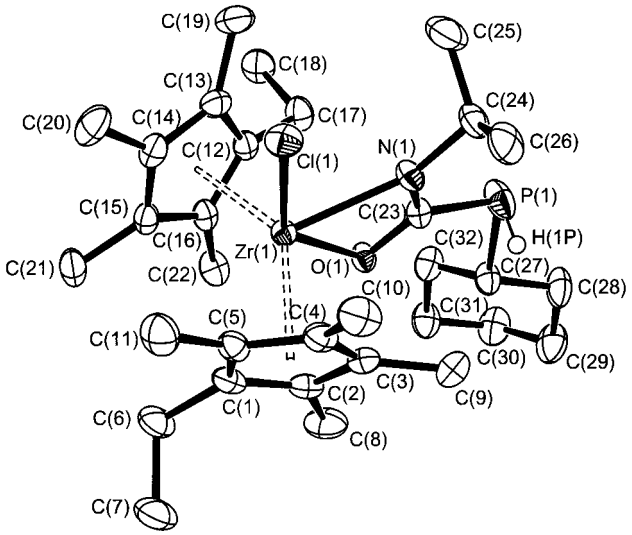


Figure 2. Molecular structure of [Cp°$_2$ZrCl{η^2-OC(PHCy)-NPr^i}] (**5**) showing the atom numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP).[26] Hydrogen atoms (other than P−H) are omitted for clarity.

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

	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)
O−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 [Cp$_2$Zr(Cl){η^2-SC(H)NPh}],[21] the phosphaguanidino complex [Cp′$_2$ZrCl{η^2-NPhC{P(SiMe$_3$)$_2$}NPh}][14] (N,N′ coordination), and the CS_2 insertion product [Cp$_2$-ZrCl{η^2-S$_2$CP(SiMe$_3$)$_2$}][12] (S,S′ coordination), as well as

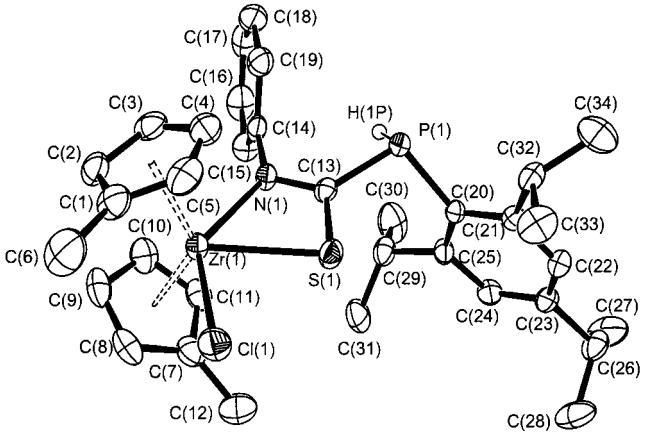


Figure 3. Molecular structure of [Cp′$_2$ZrCl{η^2-SC{PH-(TRIP)}NPh}] (**6**) showing the atom-numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP).[26] Hydrogen atoms (other than P−H) are omitted for clarity.

the related complex [Cp$_2$Zr(Me){η^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) Å[23]), 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 = 2.273(2) Å). In **6** (Zr−N = 2.418(2) Å, Zr−S = 2.658(1) Å) and the related complex [Cp$_2$Zr(Cl){η^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 N_2C, 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: ^{1}H NMR (400 MHz), trace amounts

of protonated solvent, C_6D_6; ^{13}C NMR (100.6 MHz), internal solvent; ^{31}P NMR (162 MHz), external 85% H_3PO_4. 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. **2**[7] and **3**[3] were prepared by literature procedures. PhNCS, PhNCO, and Pr^iNCO are commercially available and were kept over molecular sieves prior to use.

Improved Synthesis of [Cp°$_2$ZrCl(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°$_2$ZrCl$_2$] 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°$_2$ZrCl{η^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 ^{31}P NMR spectrum of the reaction mixture (C_6D_6) showed only one signal at −50.8 ppm (d, $^1J_{PH}$ = 224.8 Hz). Colorless crystals were obtained on concentrating the solution (at room temperature). Yield: 81%. Mp: 142 °C. ^1H NMR (C_6D_6): 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, C_5Me_4Et), 1.97 (s, 6H, C_5Me_4-Et), 2.00 (s, 2H, C_5Me_4Et), 2.01 (s, 4H, C_5Me_4Et), 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). ^{13}C NMR (C_6D_6): δ 12.55−12.90 (s, C_5Me_4Et), 15.28 and 15.38 (s, $C_5Me_4CH_2CH_3$), 21.00 and 21.04 (s, $C_5Me_4CH_2CH_3$), 26.94 (s, C4 of Cy), 27.59 (d, C3 or C5 of Cy, $^3J_{PC}$ = 14.5 Hz), 27.95 (d, C3 or C5 of Cy, $^3J_{PC}$ = 7.4 Hz), 31.54 (d, C2 or C6 of Cy, $^2J_{PC}$ = 5.9 Hz), 33.20 (d, C2 or C6 of Cy, $^2J_{PC}$ = 5.8 Hz), 33.69 (d, C1 of Cy, $^1J_{PC}$ = 23.0 Hz), 120.25, 120.41, 120.90, 121.04, 121.74, 122.04, 122.13, and 122.70 (each s, C_4Me_4CEt), 125.59 (s, C_4Me_4CEt), 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, $^1J_{PC}$ = 34.4 Hz). EI MS: *m*/*z* 657 (4%, M^+), 545 (0.5%, M^+ − Ph − Cl), 508 (100%, M^+ − Cp°), 423 (11%, Cp°$_2$ZrCl$^+$), 387 (9%, Cp°$_2$Zr$^+$), 359 (2%, M^+ − 2 Cp°), 307 (5%, ZrNPhCPCy$^+$), 291 (13%, Cp°ZrClO$^+$), 269 (14%, (C_5-Et)$_2$Zr$^+$), 218 (4%, PhNCPHCy$^+$), 149 (20%, Cp°$^+$), 135 (21%, $C_5EtMe_3^+$), 119 (21%, PhNCO$^+$), 103 (5%, PhNC$^+$), and fragmentation thereof. Anal. Calcd for $C_{35}H_{51}ClNOPZr$ (659.41): C, 63.7; H, 7.8; N, 2.1. Found: C, 62.9; H, 8.4; N, 2.0.

[Cp°$_2$ZrCl{η^2-OC(PHCy)NPr^i}] (5). At room temperature 0.36 mL (3.69 mmol) of Pr^iNCO 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 ^{31}P NMR spectrum of the reaction mixture (C_6D_6) showed only one signal at −52.2 ppm (d, $^1J_{PH}$ = 215.4 Hz). Colorless crystals were obtained on concentrating the solution. Yield: 85%. Mp: 133 °C. ^1H NMR (C_6D_6): δ 0.94 (t, 6H, CH_2CH_3, $^3J_{HH}$ = 8.1 Hz), 1.20−2.75 (m, br, 11H, Cy), 1.34 (d, 6H, Me_2CH, $^3J_{HH}$ = 6.4 Hz), 1.90 (s, 6H, C_5Me_4Et), 1.93 (s, 6H, C_5Me_4Et), 1.95 (s, 12H, C_5Me_4Et), 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, $^1J_{PH}$ = 215.5 Hz). ^{13}C NMR (C_6D_6): δ 12.53, 12.70, 12.72, 12.90, 12.97, and 13.03 (each s, C_5Me_4Et), 15.31 and 15.40 (each s, $C_5Me_4CH_2CH_3$), 21.04 and 21.08 (each s, $C_5Me_4CH_2CH_3$), 25.00 (s, Me_2CH), 26.98 (s, C4 of Cy), 27.71 (d, C3 or C5 of Cy, $^3J_{PC}$ = 14.9 Hz), 28.20 (d, C3 or C5 of Cy, $^3J_{PC}$ = 7.1 Hz), 30.88 (d, C2 or C6 of Cy, $^2J_{PC}$ = 5.5 Hz), 33.45 (d, C2 or C6 of Cy, $^2J_{PC}$ = 5.1 Hz), 34.01 (d, C1 of Cy, $^1J_{PC}$ = 24.3 Hz), 51.39 (d, Me_2CH, $^3J_{PC}$ = 10.0 Hz), 120.03, 120.34, 120.56, 120.60, 121.90, 121.97, 122.28, and 122.70 (each s, C_4-Me_4CEt), 126.14 and 126.44 (each s, C_4Me_4CEt), 180.72 (d, NCP, $^1J_{PC}$ = 33.7 Hz). EI MS: *m*/*z* 625 (4%, M^+), 590 (2%, M^+ − Cl), 476 (97%, M^+ − Cp°), 423 (23%, Cp°$_2$ZrCl$^+$), 290 (28%, $C_5Me_3ZrCl^+$ or ZrOC(PCy)NPr^{i+}), 268 (21%, (C_5-Et)$_2$ZrNC$^+$), 200 (7%, OC(PHCy)NPr^{i+}), 149 (29%, Cp°$^+$), 141 (17%, NCPHCy$^+$), 134 (15%, $C_5EtMe_3^+$), 116 (53%, PHCy$^+$), 91 (7%, Zr$^+$), 83 (100%, Cy$^+$), 43 (97%, Pr^{i+}), and fragmentation thereof. Anal. Calcd for $C_{32}H_{53}ClNOPZr$ (625.39): C, 63.7; H, 7.8; N, 2.1. Found: C, 62.9; H, 8.4; N, 2.0.

[Cp′$_2$ZrCl{η^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 ^{31}P NMR spectrum of the solid (C_6D_6) showed two signals at −48.8 ppm (d, $^1J_{PH}$ = 246.2 Hz, *endo* isomer, **6a**) and −69.6 ppm (d, $^1J_{PH}$ = 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 ^{13}C NMR spectrum of **6b** was made on the basis of a 2D NMR spectrum ($^1H/^{13}C$). **6a** was not obtained in pure form.

6b. ^1H NMR (C_6D_6): δ 1.18 (d, 6H, Me_2CH, $^3J_{HH}$ = 6.2 Hz), 1.28 (d, 6H, Me_2CH, $^3J_{HH}$ = 6.2 Hz), 1.39 (d, 6H, Me_2CH, $^3J_{HH}$ = 6.7 Hz), 2.20 (s, 3H, C_5H_4Me), 2.23 (s, 3H, C_5H_4Me), 2.76 (sept, 1H, Me_2CH, $^3J_{HH}$ = 6.9 Hz), 3.76 (sept, br, 2H, Me_2CH), 5.00 (d, 1H, P−H, $^1J_{PH}$ = 238.9 Hz), 5.48 (m, 1H, C_5H_4Me), 5.56 (m, 1H, C_5H_4Me), 5.61 (m, 1H, C_5H_4Me), 5.68 (m, 3H, C_5H_4Me), 6.07 (m, 2H, C_5H_4Me), 7.02 (m, 1H, Ph), 7.18−7.09 (m, Ph and 2,4,6-$Pr^i_3C_6H_2$). ^{13}C NMR (C_6D_6): δ 16.26 (s, C_5H_4Me), 24.67 (s, Me_2CH of *p*-Pr^i), 25.19 (s, Me_2CH of *o*-Pr^i), 25.39 (s, Me_2CH of *o*-Pr^i), 34.32 (s, Me_2CH of *o*-Pr^i), 34.46 (s, Me_2CH of *p*-Pr^i), 108.72, 110.14, 113.53, 114.22, 115.89, 116.10, 118.00, 118.64, and 119.63 (each s, C_5H_4Me), 122.53 (d, C3/C5 of 2,4,6-$Pr^i_3C_6H_2$, $^3J_{PC}$ = 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-$Pr^i_3C_6H_2$, $^2J_{PC}$ = 3.9 Hz), 152.58 (s, C4 of 2,4,6-$Pr^i_3C_6H_2$), 155.65 (d, br, C1 of 2,4,6-$Pr^i_3C_6H_2$, $^1J_{PC}$ = 14.2 Hz), 206.4 (d, NCP, $^1J_{PC}$ = 54.6 Hz). EI MS: *m*/*z* 538 (1%, Cp′$_2$-Zr(Cl)NPhC(S)PHC$_6$CH$_3^+$), 506 (3%, Cp′$_2$Zr(Cl)NPhCPHC$_6$-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%, PC_6H_2-$Pr^i_2CH_3CH^+$), 203 (72%, TRIP$^+$), 191 (11%, $PC_6H_2Pr^i_2^+$), 166 (100%, SCPNPh$^+$), 160 (14%, $PC_6H_2Pr^iC^+$ or $C_6H_2Pr^i_2^+$), 149 (16%, $PHC_6H_2Pr^{i+}$), 135 (50%, $PHC_6H_2CHCH_3^+$ or PhNCS$^+$), 118 (11%, $PC_6CH_3^+$ or $C_6H_2Pr^i_2^+$), 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 $C_{34}H_{43}$-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′$_2$ZrCl{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 ^{31}P NMR spectrum of the solution (C_6D_6) 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 (C_6D_6): δ 1.14 (d, 6H, Me_2CH, $^3J_{HH}$ = 6.9 Hz), 1.21 (d, 6H, Me_2CH, $^3J_{HH}$ = 6.5 Hz), 1.33 (d, 6H, Me_2CH, $^3J_{HH}$ = 6.7 Hz), 1.85 (s, 3H, C_5H_4Me), 2.12 (s, 3H, C_5H_4Me), 2.71 (sept, 1H, Me_2CH, $^3J_{HH}$ = 6.8 Hz), 3.69 (sept, br, 2H, Me_2CH), 5.03 (d, 1 H, P−H, $^1J_{PH}$ = 242.7 Hz), 5.61, 5.68, 5.73, 5.74, 5.83, 5.86 (each m, each 1H, C_5H_4Me), 5.96 (m, 2H, C_5H_4-Me), 6.96−7.07, 7.11, 7.18−7.23 (each m, 7H, Ph and 2,4,6-

$Pr^i_3C_6H_2$). ^{13}C NMR (C_6D_6): δ 15.64 and 16.02 (each s, C_5H_4Me), 24.67, 24.70, 25.57 (each s, Me_2CH), 34.16, 34.29, and 35.41 (each s, Me_2CH), 110.45, 110.61, 113.54, 114.24, 115.05, 115.29, 115.69, 115.89, 118.02, and 119.70 (each s, C_5H_4Me), 122.27 (d, C3/C5 of 2,4,6-$Pr^i_3C_6H_2$, $^3J_{PC}$ = 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-$Pr^i_3C_6H_2$), 151.89 (s, C4 of 2,4,6-$Pr^i_3C_6H_2$), 154.77 (d, br, C1 of 2,4,6-$Pr^i_3C_6H_2$), 185.88 (d, br, NCP, $^1J_{PC} \approx$ 35 Hz).

[Cp′$_2$ZrCl{η^2-OC{PH(TRIP)}NPr^i}] (8). At room temperature 0.26 mL (2.65 mmol) of Pr^iNCO 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 ^{31}P NMR spectrum of the solution (C_6D_6) 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 (C_6D_6): δ 1.17 (d, 6H, Me_2CH of TRIP, $^3J_{HH}$ = 6.9 Hz), 1.30 (d, 6H, Me_2CH of TRIP, $^3J_{HH}$ = 6.7 Hz), 1.36 (d, 6H, Me_2CH of TRIP, $^3J_{HH}$ = 6.6 Hz), 1.44 (d, 3H, Me_2CH of Pr^iN, $^3J_{HH}$ = 6.3 Hz), 1.47 (d, 3H, Me_2CH of Pr^iN, $^3J_{HH}$ = 6.4 Hz), 1.84 (s, 3H, C_5H_4Me), 2.07 (s, 3H, C_5H_4Me), 2.75 (sept, 1H, Me_2CH), 3.75 (sept, br, 3H, Me_2CH, $^3J_{HH}$ = 6.3 Hz), 5.29 (d, 1H, P−H, $^1J_{PH}$ = 235.2 Hz), 5.55 and 5.63 (each m, each 1H, C_5H_4Me), 5.65 (m, 2H, C_5H_4Me), 5.77, 5.80, 5.88, and 5.93 (each m, each 1H, C_5H_4Me), 7.14 (s, 2H, 2,4,6-$Pr^i_3C_6H_2$). ^{13}C NMR (C_6D_6): δ 15.67 and 16.03 (each s, C_5H_4Me), 24.36, 24.48, 24.70, 24.73, 24.80, and 25.59 (each s, Me_2CH of TRIP and Pr^i-NCP), 34.21 (s, Me_2CH of *o*-Pr^i), 35.43 (s, Me_2CH of *p*-Pr^i), 53.00 (d, Me_2CH of Pr^i-NCP, $^3J_{PC}$ = 8.7 Hz), 110.72, 112.07, 112.91, 115.03, 115.52, 115.58, and 116.08 (each s, C_5H_4Me), 122.33 (d, C3 or C5 of 2,4,6-$Pr^i_3C_6H_2$, $^3J_{PC}$ = 4.1 Hz), 123.60 (d, C3 or C5 of 2,4,6-$Pr^i_3C_6H_2$, $^3J_{PC}$ = 6.4 Hz), 126.41 (s, C2 or C6 of 2,4,6-$Pr^i_3C_6H_2$), 127.33 (s, C2 or C6 of 2,4,6-$Pr^i_3C_6H_2$), 151.92 (s, C4 of 2,4,6-$Pr^i_3C_6H_2$), 154.88 (d, C1 of 2,4,6-$Pr^i_3C_6H_2$, $^1J_{PC}$ = 12.3 Hz), 182.31 (d, NCP, $^1J_{PC}$ = 34.5 Hz).

Data Collection and Structural Refinement of 4−6. Crystallographic data are given in Table 3. Data (λ(Mo Kα) = 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 PLUS[26]). 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 Refinement Details for 4−6

	4	**5**	**6**
formula	$C_{35}H_{51}ClNOPZr$	$C_{32}H_{53}ClNOPZr$	$C_{34}H_{43}ClNPSZr$
M_r	659.41	625.39	655.39
temp (K)	213(2)	223(2)	223(2)
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (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)
Z	4	4	2
ρ_{calcd} (Mg m^{-3})	1.290	1.284	1.328
F(000)	1392	1328	684
cryst size (mm)	0.25 × 0.25 × 0.20	0.25 × 0.20 × 0.20	0.25 × 0.25 × 0.20
abs coeff (mm^{-1})	0.476	0.496	0.552
$2\theta_{max}$ (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 ($I > 2\sigma(I)$)	0.0534	0.0405	0.0402
wR2 (all data)	0.1125	0.1353	0.1101
$(\Delta/\rho)_{min}$ (e Å^{-3})	0.444	0.963	0.495
$(\Delta/\rho)_{max}$ (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.

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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.