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Insertion of Acetonitrile into the Zr−P Bond of $[Cp^{\circ}_2ZrCl(PHCy)]$ (Cy = Cyclohexyl, $Cp^{\circ} = \eta^5\text{-}C_5EtMe_4$) Followed by PHCy Elimination To Give $[Cp^{\circ}_2(Cl)Zr(\mu\text{-}N{=}CMe{-}CMe{=}N)Zr(Cl)Cp^{\circ}_2]$[†]

Ulrike Segerer, Steffen Blaurock, Joachim Sieler, and Evamarie Hey-Hawkins*

Institut für Anorganische Chemie der Universität, Talstrasse 35, D-04103 Leipzig, Germany

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$[Cp^{\circ}_2ZrCl(PHCy)]$ (Cy = cyclohexyl, $Cp^{\circ} = \eta^5\text{-}C_5EtMe_4$) undergoes insertion of MeCN into the Zr−P bond, yielding $[Cp^{\circ}_2ZrCl\{N{=}C(Me)(PHCy)\}]$ (**1**). Isomers with a *Z* (**1a**) or *E* (**1b**) configuration at the C−N double bond are obtained in a ratio of 13:1. At room temperature, **1** slowly decomposes in solution with elimination of a PHCy fragment and formation of $[Cp^{\circ}_2(Cl)Zr(\mu\text{-}N{=}CMe{-}CMe{=}N)Zr(Cl)Cp^{\circ}_2]$ (**2**). Two isomers are obtained with a trans (**2a**) or cis (**2b**) arrangement around the C−N double bonds of the bridging butane-2,3-diimino(2-)-*N*,*N′* ligand. **1a**, **2a**, and **2b** were isolated and characterized by IR, MS, and NMR spectroscopy (^1H, ^{31}P, ^{13}C), and crystal structure determinations were carried out on **1a** and **2a**. In the solid state, the short Zr−N bonds and the almost linear Zr−N−C angles of **1a** and **2a** indicate the presence of Zr−N double bonds.

Although the first dinuclear zirconocene phosphanido complexes were prepared as early as 1966,[1] these complexes remained largely unexplored until 1983, when Baker et al.[2] prepared the first zirconocene(IV) complexes with terminal dialkyl- or diarylphosphanido ligands. To date, several group 4 complexes with dialkyl- or diarylphosphanido ligands are known; however, complexes of this type with P-functionalized phosphanido ligands are still rare.[3]

For some time we have been interested in the preparation of zirconocene phosphanido complexes with P−H-functionalized ligands and their synthetic potential. Thus, the insertion of polar multiple-bond systems such as CS_2,[4,5] diazoalkanes,[6] phenylacetylene,[7] carbodiimides,[5,8,9] phenylisothiocyanate,[5] or isonitriles[9] into the Zr−P bond of P-functionalized zirconocene monophosphanido complexes $[Cp^R_2ZrCl\{P(SiMe_3)_2\}]$ [$Cp^R = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_4Me$ (Cp′)] or $[Cp^{\circ}_2ZrCl(PHCy)]$ ($Cp^{\circ} = \eta^5\text{-}C_5EtMe_4$) allows the synthesis within the coordination sphere of zirconium of novel P-functionalized phosphino ligands which are either difficult to synthesize or inaccessible by other routes.[7,10] Similarly, insertion of ketones[11] and benzonitrile[11] was observed. We now report the insertion of acetonitrile into the Zr−P bond of the P−H-functionalized zirconocene monophosphanido complex $[Cp^{\circ}_2ZrCl(PHCy)]$ to give $[Cp^{\circ}_2ZrCl\{N{=}C(Me)(PHCy)\}]$ (**1**). At room temperature, **1** slowly decomposes in solution with elimination of a PHCy fragment to give $[Cp^{\circ}_2(Cl)Zr(\mu\text{-}N{=}CMe{-}CMe{=}N)Zr(Cl)Cp^{\circ}_2]$ (**2**).

Results and Discussion

Synthesis and Properties of 1 and 2. Whereas insertion of acetonitrile into the Zr−P bond of $[Cp'_2ZrCl\{P(SiMe_3)_2\}]$ is not observed,[12] $[Cp^{\circ}_2ZrCl(PHCy)]$ undergoes insertion of MeCN into the Zr−P bond, yielding $[Cp^{\circ}_2ZrCl\{N{=}C(Me)(PHCy)\}]$ (**1**). In the ^{31}P NMR spectrum of the reaction mixture signals are observed for isomers of **1** with a *Z* (**1a**: −17.3 ppm, d, $^1J_{P-H}$ 208.9 Hz) or *E* (**1b**: −11.3 ppm, d, $^1J_{P-H}$ 217.0 Hz) configuration at the C−N double bond in a ratio of 13:1 (Scheme 1).

The related alkylideneamido complexes with an $M{-}N{=}CR^1R^2$ fragment are readily accessible by hydrozirconation of nitriles,[3,13] and *E* and *Z* isomers are observed for $R^1 \neq R^2$.[3,13] The phosphinoarylideneamido complex $[Cp_2Zr(Me)\{N{=}C(Ph)PHMes^*\}]$ was obtained from methyl zirconocene chloride, benzonitrile, and $LiPHMes^*$.[11] Hydrozirconation of $(N^iPr_2)_2PCN$ gives $[Cp_2ZrCl\{N{=}CHP(N^iPr_2)_2\}]$, the only other zirconocene compound in which a phosphinoalkylideneamido ligand is present.[14] However, when diphenylcyanophosphine

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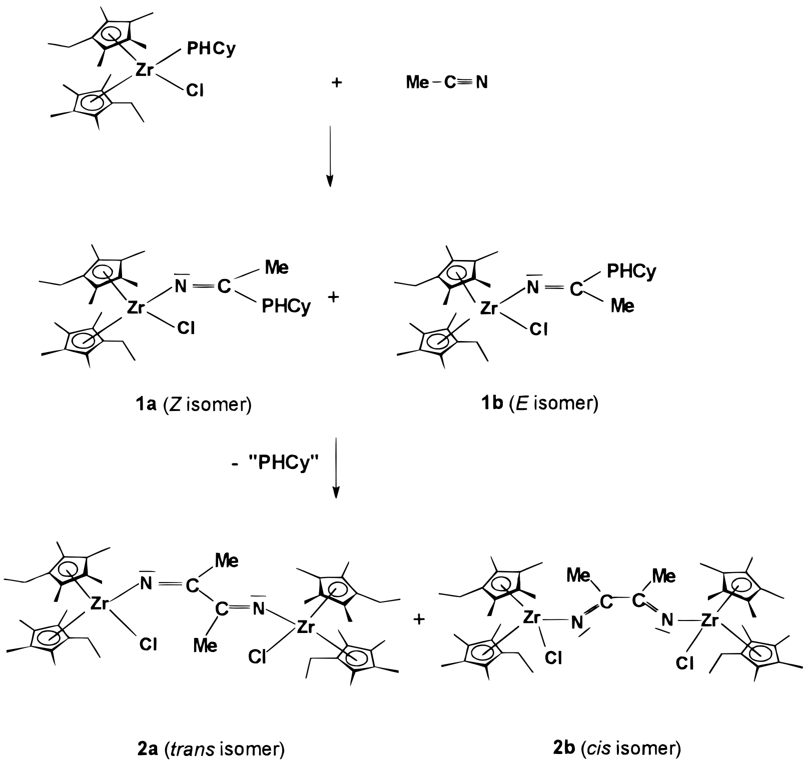
Scheme 1



is employed in this reaction, the resulting hydrozirconation product is unstable.[14] The possible existence of two isomers for $[Cp_2Zr(Me)\{N{=}C(Ph)PHMes^*\}]$[11] and $[Cp_2ZrCl\{N{=}CHP(N^iPr_2)_2\}]$[14] was not discussed. Nitriles also insert into the Zr−P bond of the thermally unstable iminozirconiophosphorane $[Cp_2ZrCl(PMe_2{=}NMes^*)]$ at −40 °C to give the cyclic compound $[Cp_2ZrCl(N{=}CR{-}PMe_2{=}NMes^*)]$ ($Mes^* = 2,4,6\text{-}{}^tBu_3C_6H_2$, R = Me, ^{i}Pr, Ph).[15]

Insertion reactions of nitriles into metal−nitrogen (amide) bonds are also known.[16] Thus, benzonitrile reacts with $[\{Ti(NMe_2)_3\}_2]$ to give $[Ti\{N{=}C(Ph)NMe_2\}_3]$ as a red oil.[17] The other group 4 metal amides $[M(NMe_2)_4]$ (M = Zr, Hf) react exothermically with benzo- or *p*-toluonitrile to give $[M\{N{=}C(R)NMe_2\}_4]$.[18]

The signals of the insertion products **1a** and **1b** are shifted to high field relative to $[Cp°_2ZrCl(PHCy)]$ (71.7 ppm, d, $^1J_{P-H}$ 209 Hz).[5] Only **1a** can be obtained in pure form from the reaction mixture. In **1a**, eight singlets are observed for the Me groups of the inequivalent Cp° ligands in the ^{1}H NMR spectrum. The P−H group gives rise to a doublet of doublets at 4.00 ppm ($^1J_{P-H}$ 208.9 Hz, $^2J_{P-H}$ 5.1 Hz). In the comparable complex $[Cp_2Zr(Me)\{N{=}C(Ph)PHMes^*\}]$, the P−H signal is at 6.17 ppm (d, $^1J_{P-H}$ 234.3 Hz).[11] In the ^{1}H NMR spectrum of **1a**, the methyl group of the inserted acetonitrile molecule is observed as a doublet at 1.96 ppm ($^3J_{P-H}$ 6.0 Hz) (pure acetonitrile: 1.727 ppm, s). In the ^{13}C NMR spectrum of **1a**, the C=N moiety gives rise to a doublet at 177.10 ppm ($^1J_{P-C}$ 26.6 Hz), which is comparable to $[Cp_2Zr(Me)\{N{=}C(Ph)PHMes^*\}]$ (177.9 ppm, $^1J_{P-C}$ 30.5 Hz)[11] and $[Cp_2ZrCl\{N{=}CHP(N^iPr_2)_2\}]$ (184.56 ppm, $^1J_{P-C}$ 13.7 Hz).[14] A doublet ($^2J_{P-C}$ 9.3 Hz) is observed for the methyl group (*Me*−C−P) of **1a** at 34.09 ppm. The ^{13}C chemical shifts and P−C coupling constants of the cyclohexyl ring of **1a** are comparable to those of the starting material and other insertion products thereof.[5]

The C=N stretching vibration in **1a** gives rise to a strong band at 1651 cm^{-1}, which is comparable to that of the related complex $[Cp_2ZrCl\{N{=}CHP(N^iPr_2)_2\}]$ (1654 cm^{-1}).[14] The aminoalkylideneamido complexes $[Ti\{N{=}C(Ph)NMe_2\}_3]$[17] and $[M\{N{=}C(R)NMe_2\}_4]$ (M = Zr, Hf; R = Bz, *p*-toluene)[18] show a strong C=N stretching vibration between 1571 and 1595 cm^{-1}, but no absorption between 2000 and 2500 cm^{-1} for a nitrile adduct. The P−H stretching band of **1a** is shifted to lower wavenumbers (2270 cm^{-1}) relative to the starting material $[Cp°_2ZrCl(PHCy)]$ (2311 cm^{-1}).[5]

At room temperature, **1** slowly decomposes in solution with elimination of a PHCy fragment, which dimerizes to $P_2H_2Cy_2$ (^{31}P: −84.6 ppm, m, −87.8 ppm, m, two diastereomers), which is also unstable and slowly decomposes to $(PCy)_4$ (^{31}P: −68.0 ppm, s) and PH_2Cy (−111.0 ppm, t). The resulting zirconocene product, $[Cp°_2(Cl)Zr(\mu\text{-}N{=}CMe{-}CMe{=}N)Zr(Cl)Cp°_2]$ (**2**), has a bridging butane-2,3-diimino(2-)-*N*,*N′* ligand with a trans (**2a**) or cis (**2b**) arrangement around the C−N double bonds (Scheme 1). In contrast, benzonitrile inserts into the Zr−P bond of $[Cp_2Zr(Me)(PHMes^*)]$ to give $[Cp_2Zr(Me)\{N{=}C(Ph)PHMes^*\}]$,[11] which has only one ^{31}P NMR signal at −44.8 ppm (d, $^1J_{P-H}$ 233.9 Hz).[11] However, no structural data are available, and decomposition in solution is not mentioned in the paper.

There are only four other reports of reductive coupling of alkyl- or arylnitriles. The two-electron reductive

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Table 1. Summary of Crystal Data for 1a and 2a

	1a	2a
formula	$C_{30}H_{49}ClNPZr$	$C_{48}H_{74}Cl_2N_2Zr_2$
fw	581.34	932.44
cryst size, mm	0.5 × 0.3 × 0.2	0.25 × 0.25 × 0.2
cryst. syst.	monoclinic	triclinic
space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a, Å	10.596(1)	8.750(1)
b, Å	18.588(1)	10.623(1)
c, Å	15.553(1)	13.635(1)
α, deg	90	73.608(1)
β, deg	98.46(1)	77.941(1)
γ, deg	90	72.720(1)
V, Å^3	3029.94(4)	1150.0(2)
Z	4	1
temp, K	220(2)	213(2)
$F(000)$	1232	490
D_{calcd}, mg m^{-3}	1.274	1.346
μ, mm^{-1}	0.522	0.603
2θ range, deg	3.4−55.8	3.1−52.2
no. of data collected	27729	5174
no. of unique data	6780	3793
R_{int}	0.0374	0.0238
no. of params	491	325
R [$I > 2\sigma(I)$]	0.0352	0.0474
wR2 (all data)	0.0861	0.1114
GooF	1.076	1.093

coupling of acetonitrile to form a (μ-butane-2,3-diimino-(2-)-*N*,*N'*)ditungsten complex, [{LW(CO)$_2$}$_2${μ-N=CMe−CMe=N}], was observed in the reaction of [LW(CO)$_3$Br] [L = HB(Me$_2$pz)$_3$] with NaS^{i}Pr in acetonitrile. Here, the oxidation product is ^{i}PrSS^{i}Pr.[19] Reduction of titanocene dichloride with Zn in the presence of benzyl cyanide gave the (μ-alkylideneamido)titanocene complex [(Cp$_2$-TiCl)$_2${μ-N=C(Bz)−C(Bz)=N}] with C−C bond formation between the two benzyl cyanide molecules.[20] Similarly, [Cp$_2$TiR] reacts with R′CN to give [(Cp$_2$TiR)$_2$(μ-N=CR′−CR′=N)] (R = Ph, *o*-, *m*-, *p*-MeC$_6$H$_4$, Bz, C$_6$F$_5$, Cl; R′ = Ph, *o*-MeC$_6$H$_4$, Me).[21] The related binuclear complex [{WCl$_3$[1-NH-2-(H$_2$N)C$_6$H$_4$]}$_2$(μ-1,2-N$_2$C$_6$H$_4$)] was obtained from the reaction of WCl$_6$ with *o*-phenylenediamine in 2-propanol.[22] The complexes [{MCl$_4$(CH$_3$-CN)}$_2${μ-N=CMe−CMe=N}]$^{2-}$ and [(MCl$_5$)$_2${μ-N=CMe−CMe=N}]$^{4-}$ (M = Nb, Ta) were obtained from the reaction of MCl$_4$ with acetonitrile in the presence of zinc followed by addition of (Ph$_3$P)$_2$NCl, LiCl, or CsCl.[23]

The strong C=N stretching band of **2b** at 1667 cm^{-1} lies in the range observed for [(Cp$_2$TiR)$_2$(μ-N=CR′−CR′=N)] (R = Ph, *o*-, *m*-, *p*-MeC$_6$H$_4$, Bz, C$_6$F$_5$, Cl; R′ = Ph, *o*-MeC$_6$H$_4$, Me) (1638−1705 cm^{-1}).[21]

Molecular Structure of 1a and 2a. 1a crystallizes in the monoclinic space group $P2_1/n$ (no. 14), and **2a** in the triclinic space group $P\bar{1}$ (no. 2) (Table 1). In **1a** and **2a**, the zirconium atom is coordinated in a distorted tetrahedral fashion by two Cp° rings, one chloro ligand, and the N atom.

We carried out a structure determination on the *Z* isomer of **1** (**1a**, Figure 1, Table 2). The short Zr−N distance [Zr(1)−N(1) 2.029(2) Å] indicates the presence of a Zr−N double bond. This is also supported by the near linearity of the Zr−N−C bond [174.2(2)°]. The C=N bond length [N(1)−C(23) 1.260(3) Å] is also in the range expected for a double bond. The atoms Cl(1), Zr(1), N(1), and C(23) are coplanar with a *Z* orientation of the Zr−N=C moiety (Cl and PHCy group are cis).

Table 2. Selected Bond Lengths [Å] and Bond Angles [deg] for 1a

Zr(1)−N(1)	2.029(2)	Zr(1)−Cl(1)	2.5107(6)
P(1)−C(25)	1.846(3)	P(1)−C(23)	1.866(3)
P(1)−H(1P)	1.359(1)	N(1)−C(23)	1.260(3)
C(6)−C(7)	1.534(5)	C(17)−C(18)	1.532(4)
C(23)−C(24)	1.508(4)		
C(Cy)-C(Cy)	1.498(5)−1.549(6)		
Zr(1)−C(Cp°)	2.549(2)−2.586(2)		

N(1)−Zr(1)−Cl(1)	100.07(6)	C(25)−P(1)−C(23)	103.2(1)
C(25)−P(1)−H(1P)	105.5(1)	C(23)−P(1)−H(1P)	100.06(9)
C(23)−N(1)−Zr(1)	174.2(2)	N(1)−C(23)−C(24)	124.4(3)
N(1)−C(23)−P(1)	123.1(2)	C(24)−C(23)−P(1)	112.1(2)
C(30)−C(25)−P(1)	110.0(2)	C(26)−C(25)−P(1)	113.9(2)

Table 3. Selected Bond Lengths [Å] and Bond Angles [deg] for 2a

Zr(1)−N	2.018(3)	Zr(1)−Cl	2.497(1)
N−C(23)	1.266(5)	C(23)−C(23a)	1.524(8)
C(23)−C(24)	1.510(7)		
Zr(1)−C(Cp°)	2.531(5)−2.585(4)		

N−Zr(1)−Cl	99.5(1)	C(23)−N−Zr(1)	177.9(3)
N−C(23)−C(24)	123.7(4)	N−C(23)−C(23a)	120.8(5)
C(24)−C(23)−C(23a)	115.5(5)		

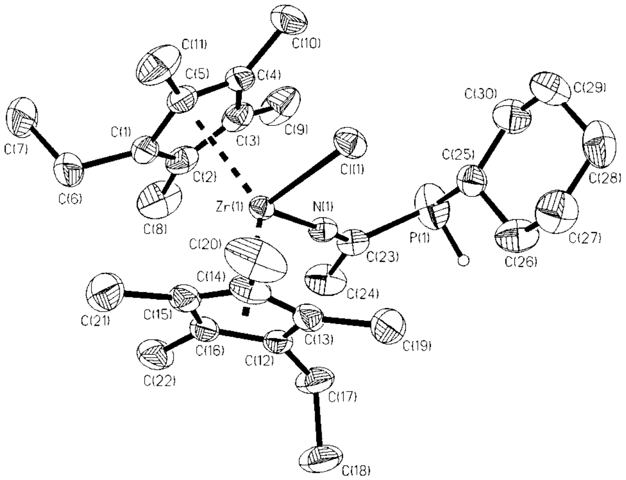

Figure 1. Molecular structure of [Cp°$_2$ZrCl{N=C(Me)-(PHCy)}] (**1a**) showing the atom-numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP).[24] Hydrogen atoms (other than P−H) are omitted for clarity.

The zirconocene products obtained by decomposition of **1** have a bridging butane-2,3-diimino(2-)-*N*,*N′* ligand with a trans or cis arrangement of the C−N double bonds. We carried out a crystal stucture determination on the trans isomer (**2a**, Figure 2, Table 3). The molecule is located on an inversion center which bisects the C−C bond of the butane-2,3-diimino(2-)-*N*,*N′* ligand. As in **1a**, the short Zr−N bond of 2.018(3) Å and the almost linear Zr−N−C arrangement [177.9(3)°] in **2a** indicate the presence of a Zr−N multiple bond. The related complex [(Cp$_2$TiCl)$_2${μ-N=C(Bz)−C(Bz)=N}] [Ti−N−C 168.3(4)°, C−N 1.260(5) Å, C−C 1.519(6) Å][20] exhibits bond lengths and angles for the M−N=C−C=N−M fragment similar to those of **2a**. In [{LW(CO)$_2$}$_2${μ-N=CMe−CMe=N}] [L = HB(Me$_2$pz)$_3$], a bridging butane-2,3-

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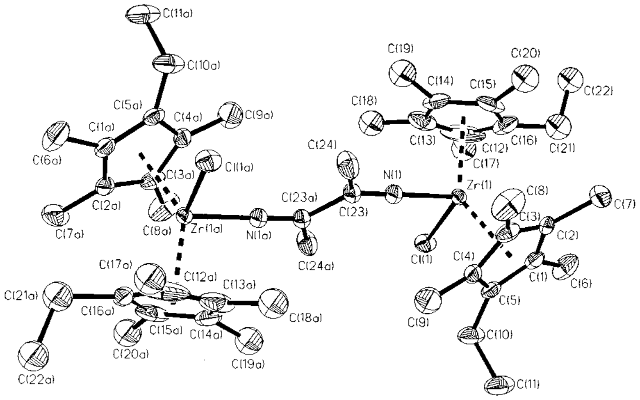

Figure 2. Molecular structure of [Cp°$_2$(Cl)Zr(μ-N=CMe−CMe=N)Zr(Cl)Cp°$_2$] (**2a**) showing the atom-numbering scheme employed (SHELXTL PLUS; XP).[24] Hydrogen atoms are omitted for clarity.

diimino(2-)-*N*,*N*′ ligand with a trans arrangement comparable to that in **2a** is present.[19] Here the C−C distance [1.40(4) Å][19] is shorter than expected for a single bond, while in **2a**, the C(23)−C(23a) bond length of 1.524(8) Å and the C=N distance [N−C(23) 1.266(5) Å] are as expected for a N=C−C=N fragment. The binuclear complex [{WCl$_3$[1-NH-2-(H$_2$N)C$_6$H$_4$]}$_2$(μ-1,2-N$_2$C$_6$H$_4$)] has a cis configuration of the C=N double bonds due to geometric requirements.[22] Here, the C=N bond length [1.316(20) Å] is larger, and the C−C distance [1.415(33) Å] smaller than in **2a**.[22] Comparable bond lengths and angles were observed for the Zr−N−C fragment in zirconocene alkylideneamido complexes, in which the Zr−N bond lengths range from 2.013 to 2.063 Å, C=N ranges from 1.259(1) to 1.266(4) Å, and the Zr−N−C linkages are almost linear (164−174°).[13] For the structurally characterized complex [{NbCl$_4$(CH$_3$CN)}$_2$-{μ-N=CMe−CMe=N}]$^{2-}$, the data suggest that the π bonding is delocalized over the Nb(NCMeCMeN)Nb fragment.[23]

Experimental Section

General Remarks. All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. The NMR spectra were recorded with an AVANCE DRX 400 spectrometer (Bruker). ^{1}H NMR: internal standard solvent (benzene), external standard TMS. ^{13}C NMR: external standard TMS, internal standard solvent. ^{31}P NMR: external standard 85% H$_3$PO$_4$. The IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer in the range 350−4000 cm^{-1}. X-ray structural analyses: Siemens SMART CCD diffractometer. The melting points were determined in sealed capillaries under argon and are uncorrected. [Cp°$_2$ZrCl(PHCy)][5] was prepared by literature procedures.

Preparation of [Cp°$_2$ZrCl{N=C(Me)(PHCy)}] (1). Acetonitrile (0.2 mL, 0.16 g, 3.80 mmol) was added to a solution of [Cp°$_2$ZrCl(PHCy)] (1.53 g, 2.84 mmol) in toluene (20 mL). After 20 min the color of the solution changed from red to orange. A ^{31}P NMR spectrum showed two products [**1a** (*Z* isomer, −17.3 ppm, 208.9 Hz) and **1b** (*E* isomer, −11.3 ppm, 217.0 Hz), ratio 13:1]. The solution was concentrated and cooled to −28 °C. After several days, pale yellow-green crystals of **1a** had formed. Yield: ca. 1.2 g (ca. 73%). Mp: 89 °C. C$_{30}$H$_{49}$ClNPZr (581.34): calcd C 62.09, H 8.51, N 2.41, Cl 6.11; found C 61.81, H 8.63, N 2.50, Cl 6.19.

1a decomposes in solution at room temperature.

^{1}H NMR (400 MHz, C$_6$D$_6$): δ 0.92 (t, $^3J_{\mathrm{H-H}}$ = 7.6 Hz, 3H, C$_5$Me$_4$CH$_2$C*H*$_3$), 0.95 (t, $^3J_{\mathrm{H-H}}$ = 7.6 Hz, 3H, C$_5$Me$_4$CH$_2$C*H*$_3$), 1.0−1.8 (br, 11H, Cy), 1.837 (s, 3H, C$_4$C*H*$_3$CEt), 1.845 (s, 3H, C$_4$C*H*$_3$CEt), 1.85 (s, 3H, C$_4$C*H*$_3$CEt), 1.86 (s, 3H, C$_4$C*H*$_3$CEt), 1.89 (s, 3H, C$_4$C*H*$_3$CEt), 1.90 (s, 3H, C$_4$C*H*$_3$CEt), 1.905 (s, 3H, C$_4$C*H*$_3$CEt), 1.91 (s, 3H, C$_4$C*H*$_3$CEt), 1.96 (d, $^3J_{\mathrm{P-H}}$ = 6.0 Hz, 3H, C*H*$_3$CP), 2.380 (q, $^3J_{\mathrm{H-H}}$ = 7.6 Hz, 2H, C*H*$_2$CH$_3$), 2.384 (q, $^3J_{\mathrm{H-H}}$ = 7.6 Hz, 2H, C*H*$_2$CH$_3$), 4.00 (d/d, $^1J_{\mathrm{P-H}}$ = 208.9 Hz, $^2J_{\mathrm{P-H}}$ = 5.1 Hz, 1H, P-*H*). ^{31}P NMR (162 MHz, C$_6$D$_6$): δ −17.3 ppm (d, $^1J_{\mathrm{P-H}}$ = 208.9 Hz, P-*H*). ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ 177.10 (d, $^1J_{\mathrm{P-C}}$ = 26.6 Hz, CH$_3$*C*N), 124.86 (s, C$_4$Me$_4$*C*Et), 124.63 (s, C$_4$Me$_4$*C*Et), 119.86 (s, *C*$_4$Me$_4$CEt), 119.74 (s, *C*$_4$Me$_4$CEt), 119.68 (s, *C*$_4$Me$_4$CEt), 119.05 (s, *C*$_4$Me$_4$CEt), 118.91 (s, *C*$_4$Me$_4$CEt), 118.20 (s, *C*$_4$CH$_3$CEt), 36.18 (d, $^1J_{\mathrm{P-C}}$ = 4.5 Hz, C1), 34.09 (d, $^2J_{\mathrm{P-C}}$ = 9.3 Hz, *C*H$_3$CN), 30.74 (d, $^3J_{\mathrm{P-C}}$ = 7.8 Hz, C3/C5), 28.39 (d, $^2J_{\mathrm{P-C}}$ = 20 Hz, C2/C6), 27.04 (s, C4), 20.91 (s, *C*H$_2$CH$_3$), 20.79 (s, *C*H$_2$CH$_3$), 15.60 (s, CH$_2$*C*H$_3$), 15.50 (s, CH$_2$*C*H$_3$), 12.56 (s, C$_4$*C*H$_3$CEt), 12.50 (s, C$_4$*C*H$_3$CEt), 12.45 (s, C$_4$*C*H$_3$CEt), 12.32 (s, C$_4$*C*H$_3$CEt), 12.30 (s, C$_4$*C*H$_3$CEt), 12.26 (s, C$_4$*C*H$_3$CEt). Mass (EI, 70 eV): *m*/*z* 459 (M$^+$ − Cl − 2C$_2$H$_5$ − 2CH$_3$, 10), 439 [M$^+$ − C(CH$_3$)PHCy, 16], 290 [Cp°Zr(Cl)N$^+$, 100], 254 (Cp°ZrN$^+$, 16), 149 (Cp°$^+$, 35), 134 [(Cp° − CH$_3$)$^+$, 36], 119 (C$_5$Me$_4^+$, 41), 105 (C$_5$Me$_3^+$, 15), 91 (Zr$^+$, 22), 83 (Cy$^+$, 35), 70 [NC(CH$_3$)P$^+$, 24], 41 (NCCH$_3^+$, 44), and fragmentation products thereof. IR: ν(P−H) 2270 (m), ν(C=N) 1651 (st) cm^{-1}.

Preparation of [Cp°$_2$(Cl)Zr(μ-N=CMe−CMe=N)Zr(Cl)-Cp°$_2$] (2). Acetonitrile (0.2 mL, 0.16 g, 3.80 mmol) was added to a solution of [Cp°$_2$ZrCl(PHCy)] (1.53 g, 2.84 mmol) in toluene (20 mL). After 20 min the color of the solution changed from red to orange. A ^{31}P NMR spectrum showed two products [**1a** (*Z* isomer) and **1b** (*E* isomer), vide supra]. The solution was concentrated and kept at room temperature for 1 month, after which a small amount of yellow crystals of **2a** (*trans*-**2**) had formed and were isolated. The solution was concentrated until a yellow solid precipitated. This was shown to consist of a mixture of **2a** and **2b** (ca. 0.85 g, ca. 64%) by ^{1}H NMR spectroscopy. Repeated recrystallization from pentane/toluene gave pure **2b** (*cis*-**2**) as orange microcrystals.

2a: Mp: 179 °C. C$_{48}$H$_{74}$Cl$_2$N$_2$Zr$_2$ (932.44): calcd. C 61.83, H 8.00, N 3.00, Cl 7.60; found C 61.93, H 8.65, N 3.21, Cl 7.59.

2b: Mp: >300 °C, >55 °C dec. C$_{48}$H$_{74}$Cl$_2$N$_2$Zr$_2$ (932.44): calcd. C 61.83, H 8.00, N 3.00, Cl 7.60; found C 62.03, H 8.99, N 3.33, Cl 7.66.

2a: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 0.84 (t, $^3J_{\mathrm{H-H}}$ = 7.5 Hz, 6H, C$_5$Me$_4$CH$_2$C*H*$_3$), 1.87 (s, 12H, C$_4$C*H*$_3$CEt), 1.92 (s, 12H, C$_4$C*H*$_3$CEt), 2.11 (s, 3H, C*H*$_3$CN), 2.44 (q, $^3J_{\mathrm{H-H}}$ = 7.5 Hz, 4H, C*H*$_2$CH$_3$). Additionally, a singlet at 0.59 ppm is observed, which could not be asigned. ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ ca. 129.9, s, signal is obscured by signals of solvent (N=*C*Me*C*Me=N ?), 126.3 (s, C$_4$Me$_4$*C*Et), 124.6 (s, *C*$_4$Me$_4$Et), 123.2 (s, *C*$_4$Me$_4$Et), 22.1 (s, *C*H$_3$CN), 21.1 (s, *C*H$_2$CH$_3$), 15.0 (s, CH$_2$*C*H$_3$), 12.8 [s, C$_4$(*C*H$_3$)$_4$CEt], 12.6 [s, C$_4$(*C*H$_3$)$_4$CEt]. Mass (EI, 70 eV): *m*/*z* 465.5 (M$^+$/2, 23.7), 421 (M$^+$/2 − C$_2$H$_5$ − CH$_3$, 100), 316 (M$^+$/2 − Cp°, 13.6), 275 (Cp°ZrCl$^+$, 8.5), 149 (Cp°$^+$, 10.2), 134 [(Cp° − CH$_3$)$^+$, 10.3], 120 (C$_5$Me$_4^+$, 7.6), 105 (C$_5$Me$_3^+$, 3.4), 91 (Zr$^+$, 3.7), 41 (NCCH$_3^+$, 5.1), and fragmentation products thereof.

2b: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 0.96 (t, $^3J_{\mathrm{H-H}}$ = 7.5 Hz, 6H, C$_5$Me$_4$CH$_2$C*H*$_3$), 1.89 (s, 12H, C$_4$C*H*$_3$CEt), 1.93 (s, 6H, C$_4$C*H*$_3$CEt), 1.96 (s, 6H, C$_4$C*H*$_3$CEt), 2.14 (s, 3H, C*H*$_3$CN), 2.40 (q, $^3J_{\mathrm{H-H}}$ = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 2.41 (q, $^3J_{\mathrm{H-H}}$ = 7.5 Hz, 2H, C*H*$_2$CH$_3$). ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ 173.0 (s, ?), 124.0 (s, C$_4$Me$_4$*C*Et), 119.3 (s, *C*$_4$Me$_4$Et), 119.2 (s, *C*$_4$Me$_4$Et), 118.7 (s, *C*$_4$Me$_4$Et), 118.0 (s, *C*$_4$Me$_4$Et), 29.7 (s, *C*H$_3$CN), 20.9 (s, *C*H$_2$-CH$_3$), 15.5 (s, CH$_2$*C*H$_3$), 12.5 [s, C$_4$(*C*H$_3$)$_4$CEt], 12.4 [s, C$_4$(*C*H$_3$)$_4$-CEt], 12.2 [s, C$_4$(*C*H$_3$)$_4$CEt]; apparently, the *C*N signal is obscured by signals of solvent. Mass (EI, 70 eV): *m*/*z* 466 (M$^+$/2, 20.7), 423 (M$^+$/2 − C$_2$H$_5$ − CH$_3$, 100), 387 (M$^+$/2 − C$_2$H$_5$ − CH$_3$ − Cl, 17.5), 275 (Cp°ZrCl$^+$, 35.7), 258 (Cp°ZrCl$^+$ − CH$_3$, 22.1), 149 (Cp°$^+$, 16.4), 134 [(Cp° − CH$_3$)$^+$, 22.1], 119 (C$_5$Me$_4^+$, 17.1), 105 (C$_5$Me$_3^+$ and ZrN$^+$, 15.7), 91 (Zr$^+$, 16.1), and fragmentation products thereof. IR: ν(C=N) 1667 (st) cm^{-1}.

X-ray Structure Determinations. Data of **1a** and **2a** (Mo Kα, $\lambda = 0.71073$ Å) were collected with a Siemens CCD (SMART). All observed reflections were used for determination of the unit cell parameters. The structures were solved by direct methods (SHELXTL PLUS[24]) and subsequent difference Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL PLUS[24]). Restrictions for **1a**: C, Cl, N, P, and Zr atoms anisotropic, H atoms located and refined isotropically. Absorption correction with SADABS. Restrictions for **2a**: C, Cl, N, and Zr atoms anisotropic, H atoms of Cp° ring C(17) − C(22) refined in fixed positions, other H atoms located and refined isotropically. Absorption correction with SADABS.

The methyl and ethyl groups of one of the Cp° rings (atoms C(12)−C(22)) in **2a** have large thermal parameters. While the program SHELX97 gives splitting positions for the methyl and ethyl groups (C(17)−C(21)), no splitting positions were given for the cyclopentadienyl ring C atoms C(12)−C(16), as the anisotropic displacement parameters were not large enough. Although refinement of the atoms C(17)−C(21) in splitting positions results in a lower *R* value (wR2 decreases from 0.11 to 0.08), this approach results in meaningless bond angles.

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Supporting Information Available: Tables of crystal data, atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **1a** and **2a.** This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] *SHELXTL PLUS*; Siemens Analyt. X-ray Inst. Inc., 1990. XS: Program for Crystal Structure Solution, XL: Program for Crystal Structure Determination, XP: Interactiv Molecular Graphics.