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Preparation of Zwitterionic 18-Electron d^0-Anionic-Metallocene Complexes Induced by *β*-Heterosubstituted Azazirconaindenes

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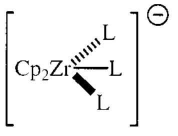
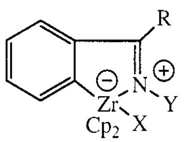
Formal [2+2] and [2+1] cycloaddition reactions between the azazirconaindenes **1a**,**b** and aldehydes RCHO (R = Ph, −CH=CHMe-(*E*), Fc), heterocumulenes [R−N=C=O (R = Ph, 1-naphthyl), Me−N=C=S, Cy−N=C=N−Cy], and the azide $(PhO)_2P(O)N_3$ afford stable pentavalent zirconocene compounds **2**−**8**, respectively. The single-crystal X-ray structure of **4** is reported. Zr−X (X = C, O, N) distances in **4** are in the range of Cp_2Zr-X σ-bonds in pentavalent zirconium complexes and not in that of π-X-coordination. This is in accord with a formal description for these compounds as iminium zirconate complexes.

Introduction

Bis(cyclopentadienyl) complexes Cp_2M (M = Ti, Zr, Hf) can exhibit metal centers with 14 to 18 electrons and valence coordination number from 3 to 5.[1] Pentacoordinate complexes play a pivotal role in group 4 stoichiometric and catalytic reactions.[2] As an example, an α-agostic interaction involving a five-coordinate geometry in chain propagation mechanism studies has been proposed to rationalize the stereospecific polymerization of α-olefins using metallocene group 4 d^0 complexes.[3] Although anionic transition metal complexes are important organometallic reagents in organic synthesis,[4] pentacoordinate anionic group 4 metallocene $[Cp_2ML_3]^-$ complexes are rare. They have been postulated as intermediates in a number of stoichiometric and catalytic reactions.[5] Only very few of these metal **A** species have been spectroscopically[6] and structurally characterized.[7] No general route to prepare these anionic five-coordinated compounds have been described; therefore their chemistry remain largely unexplored. Most of the reported **A** compounds exhibit electrostatic anion−cation pairing resulting in dimer, trimer, oligomer, or polymeric structures.[7,8]



A



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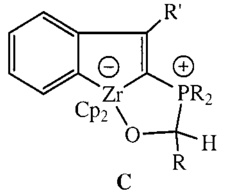
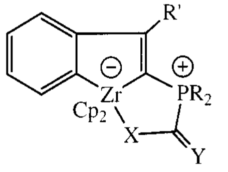


C



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For the past three years, we have been interested in the study of 18-electron five-valent anionic zirconocene complexes.[9,10] Herein we report the synthesis and structural characterization of a variety of stable mono-

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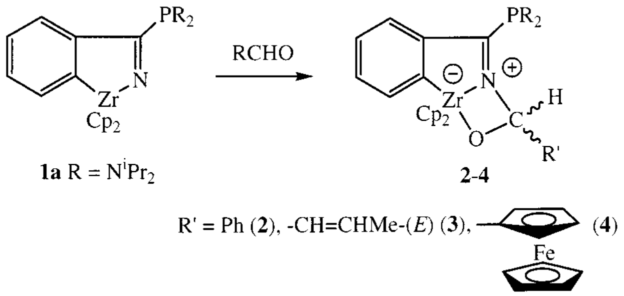
Scheme 1. Addition of Aldehydes on Azazirconaindene 1



meric five-coordinated anionic bis(cyclopentadienyl) azazirconaindene complexes.

Results and Discussion

We recently reported the preparation of stable iminium 18-electron zirconate species **B**.[10] The reaction can formally be described as a formal 1,2-addition of an activated C−H or M−Cl bond onto the Zr−N moiety of the corresponding azazirconaindene complexes **1a**,**b**. Addition at room temperature of aldehydes RCHO (R = Ph, −CH=CHMe-(*E*), [Fc]) to a solution of azazirconaindene **1a** in toluene gave in good yield the stable complex products **2**−**4** (Scheme 1). From their elemental analyses and mass spectra, compounds **2**−**4** appear to have a correct composition for a formally 1/1 adduct of the starting reagents [**1a**·RCHO]. Complexes **2**−**4** exhibit the characteristic spectroscopic features of five-coordinated zirconate species. ^{31}P NMR spectra showed the clean formation of a unique phosphorus product in the region expected for pentavalent azazirconaindene complexes. As already observed for the phosphonium zirconates **C**,[9] in the ^{13}C and ^{1}H NMR the signals of the OCH fragment are significantly shifted to high field at 94−98 and 6.6−7.2 ppm, respectively. Moreover the signal in ^{13}C NMR appeared as a doublet with a $^{3}J_{CP}$ coupling constant in the range of 20 Hz. The NMR data are consistent with the carbonyl function of the aldehyde moiety bridged to the zirconium and nitrogen atoms.

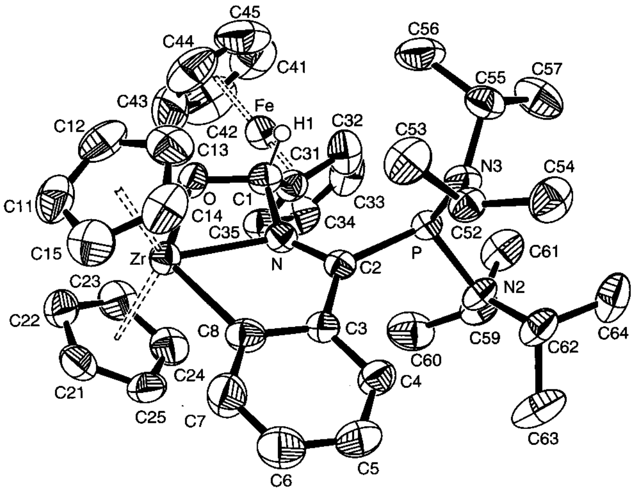


Figure 1. X-ray crystal structure of **4** (CAMERON drawing with thermal ellipsoids at 50% probability).

Table 1. Crystal Data, Data Collection, and Structure Refinement of 4

empirical formula	$C_{40}H_{52}N_3OPFeZr$
fw	768.89
temperature	160(2) K
wavelength	0.71073 Å
cryst syst, space group	monoclinic, $P2_1/c$
unit cell dimensions	$a = 9.865(2)$ Å
	$b = 19.463(4)$ Å
	$\beta = 99.42(3)°$
	$c = 19.495(4)$ Å
volume	3692.6(13) Å^3
Z, calcd density	4, 1.383 mg/m^3
abs coeff	0.753 mm^{-1}
F(000)	1608
cryst size	0.17 × 0.15 × 0.10 mm
cryst form	parallelepiped
cryst color	orange-yellow
tube power	1.80 kW
tube voltage	50 kV
tube current	36 mA
collimator size	0.5 mm
detector distance	80.0 mm
2θ range	2.9−48.4 deg
d(*hkl*) range	14.228−0.867 Å
ϕ movement mode	rotation
ϕ start	0.0°
ϕ end	200.2°
ϕ incr.	1.3°
no. of exposures	154
irradiation/exposure	6.00 min
measurement duration	26 h
index ranges	$-10 \le h \le 10$, $-20 \le k \le 20$, $-21 \le l \le 21$
no. of reflns collected/unique	19 108/5158 [*R*(int) = 0.0876]
completeness to $2\theta = 23.26$	97.4%
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	5158/0/436
abs corr	none
goodness-of-fit on F^2	0.878
weighting scheme where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2]$
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0394, wR2 = 0.0769
R indices (all data)	R1 = 0.0851, wR2 = 0.0899
largest diff peak and hole	0.379 and −0.486 e Å^{-3}

To confirm the spectroscopic assignments of the azazirconocene complexes **2**−**4** obtained from **1a** and the corresponding aldehyde derivatives RCHO, the structure of **4** was solved by X-ray crystallography studies and corroborates the formation of the suggested cycloadduct (Figure 1, Table 1). The zirconium atom is coordinated to two η^5-cyclopentadienyl ligands with three different Zr−X (X = C, N, O) atoms arranged around the central metal in a pseudo-tetrahedral geometry.[11] Features at the Cp$_2$Zr unit are typical for bent metallocene complexes.[12] The Zr−C(Cp) distances are in a narrow range between 2.499(3) and 2.561(3) Å, and the bond angle between the centroids of the Cp rings

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(12) There is no sign of slippage to give (η^3-Cp)-coordination of the cyclopentadienyl rings. For a comparison with typical examples of other d^0-configurated early transition metal bent metallocene complexes see ref 1 and: Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium and Hafnium*; Academic Press: New York, 1974; and references therein.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4

Distances			
Zr–C(8)	2.338(5)	Zr–N	2.242(4)
Zr–O	2.106(3)	C(1)–O	1.389(6)
N(1)–C(1)	1.492(6)	N–C(2)	1.294(6)
C(2)–C(3)	1.492(6)	C(3)–C(8)	1.416(7)
Angles			
O–Zr–N	60.32(13)	O–Zr–C(8)	128.28(16)
C(1)–O-Zr	105.1(2)	O–C(1)–N	98.8(4)
Zr–C(8)–C(3)	116.8(3)	Zr–C(8)–C(7)	127.3(4)
Zr–N–C(2)	128.6(3)	Zr–N–C(1)	95.5(3)

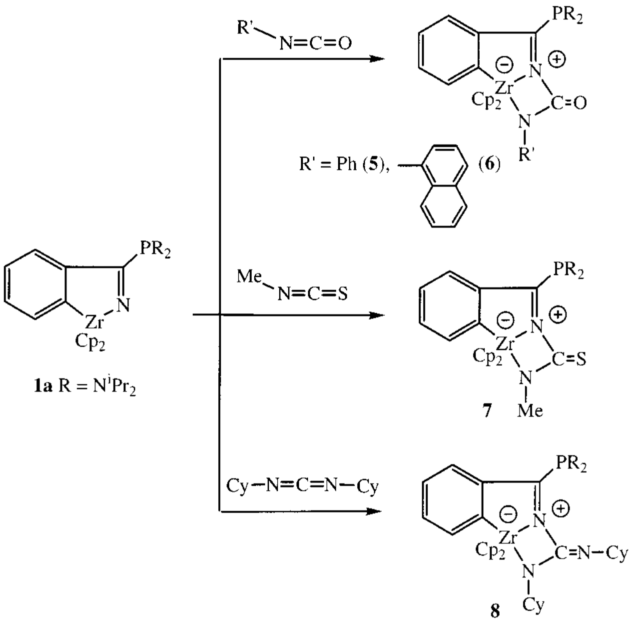
D(1)–Zr–D(2) is 131.1°. The remaining bonding sites around the zirconium atom are used to coordinate three Zr–X atoms. The atoms of the metallapolycycle skeleton lie in the equatorial plane that bisects the Cp$_2$Zr fragment with a maximum deviation from the ideal plane for the carbon atom C(2) of 0.11 Å. The geometry around the C- and N-sp^2 atoms linked to zirconium is not distorted to any great extent. C(1) is tetrahedrally coordinated with angles near the ideal tetrahedral angle. The ferrocene fragment is turned away from the zirconium center with a Zr–O–C1–C31 torsion angle of 128.8°. The large C(8)–Zr–O angle of 128.28(15)° in **4** (Table 2) is typical for five-coordinated Cp$_2$Zr(IV) complexes[9,10,13] and is due to the necessity of achieving good orbital overlap with the single acceptor $1a_1$ orbital available in **1a** for bonding of a fifth ligand, as well as the resolving of the steric requirements of the ligands.

The Zr–X (X = C, N, O) bond lengths in the equatorial plane that bisects the Cp groups represent the truly outstanding structural features in **4** (Table 2).

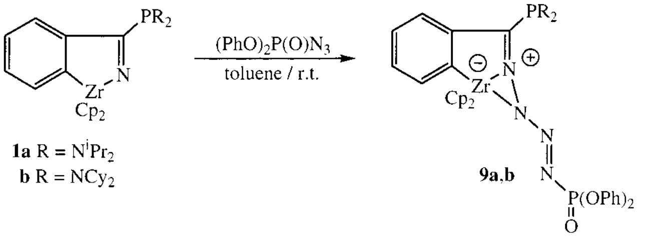
The Zr–C(8)-sp^2 external bond length is halfway from typical neutral four-coordinated Cp$_2$Zr(IV)–C σ-bonds and Cp$_2$Zr(IV)–olefin π-type interaction.[14] This elongation for the Zr–C-sp^2 bond in **4** is consistent with the results from Lauher and Hoffmann's work,[15] which predicts that the effect of the zirconium atom achieving an 18-electron configuration will result in lengthening of the metal–ligand bonds compared to those in 16-electron [Cp$_2$MX$_2$] complexes. Moreover the elongation of the Zr–C-sp^2 bonds is also possibly the result of the lower Lewis acidity of the five-coordinate metallocenes.

The Zr–N distance of 2.242(4) Å in **4** is in the range of Cp$_2$Zr–N σ-bonds in pentavalent zirconium cyclic or linear amides[16] and not of π-N-coordination.[17,18] The Zr–O bond length of 2.106(3) Å is close to those observed in alkoxy/aryloxy zirconium(IV) complexes.[18,19] Interestingly the Zr–X (X = N, O) bond distances are shorter than those previously observed in our group for the iminium zirconate complexes.[10] It is very likely due to the strain of the four-membered heterocycle.

Scheme 2. Addition of Heterocumulenes on Azazirconaindene 1



Scheme 3. Addition of Azides on Azazirconaindenes 1a,b



The final result is an 18-electron complex since all three Zr–X atoms linked to zirconium are two-electron donors and the two η^5-C$_5$H$_5$ rings each provides six electrons to the d^0 Zr(IV) center. The metal–ligand bonding situation in **4** is best described as consisting of three different σ-bonds. Therefore this product could be formally represented as an iminium zirconate complex.

The iminium azazirconate species **5**–**8** were obtained in toluene at room temperature in good isolated yield (64–77%) by treatment of **1a** with an equimolar amount of the corresponding heterocumulenes (R–N=C=O, Me–N=C=S, Cy–N=C=N–Cy) (Scheme 2). Complexes **5**–**8** were characterized by NMR spectroscopy (^{31}P, ^{1}H, ^{13}C). In ^{31}P NMR, the chemical shift at 70–80 ppm for **5**–**8** (to be compared with $\delta = 45.5$ ppm for **1a**) is typical for azazirconate complexes. ^{1}H NMR signals revealed the presence in the final product of the two η^5-cyclo-

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(17) Zr–N distances of 2.45–2.50 Å suggest dative interactions in zirconocene(IV) complexes.

(18) The Cambridge Structural Database was used to determine the mean Zr–X (X = O, N) bond distances in complexes of the type Cp$_2$-Zr–X: Allen, F. H.; Kennard, O. *Chem. Autom. News* **1993**, *8*, 31.

(19) For Zr-O σ/π-bonding situation see: Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. In *Structure Correlation*; Bürgi, H.-B., Dunitz, J. D., Eds., VCH: Weinheim, 1994; Vol. 2, pp 816–824. For Zr–O σ/π-distances in five-valent neutral and anionic complexes see for example: Ho, S. C. H.; Straus, D. A.; Armantrout, J.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2210. Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068. Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946.

pentadienyl ligands of the initial zirconium fragment and the presence of the aromatic protons of the azaindene skeleton. The deshielded chemical shift at 193−196 ppm observed in ^{13}C NMR is indicative of the lateral Zr−C bond. One of the most characteristic NMR data is obtained for the signal of the central carbon atom of the starting heterocumulene reagent R−N═*C*═X (X = O, S, NCy) which is significantly shifted to low field in the final product (δ = 150.9 (**5**), 151.0 (**6**), 186.5 (**7**), 153.5 (**8**) to be compared with δ = 133.4 (PhNCO), 136.2 (1-naphthyl-NCO), 129.0 (MeNCS), 139.7 (CyNCNCy)). The same trend was observed for the phosphonium zirconate complexes **D**. Moreover the signals appear in each case as a doublet ($6 < {}^3J_{\mathrm{CP}} < 33$ Hz), which confirms the linkage of the heterocumulenes on the Zr−N of the starting zirconaazaindene skeleton. IR spectra clearly showed the presence of the C = X (X = O, S, NCy) function in **5**−**8**. Finally correct elemental analyses were obtained for all the complexes. We already demonstrated in the formation of the phosphonium zirconate complexes that with isocyanates and isothiocyanates the preferred coordination site in these systems is the nitrogen atom. The η^1-bonding mode of the carbamoyl group is very strong since only one regioisomer was observed.

When a toluene solution of **1a**,**b** and $N_3P(O)(OPh)_2$ was stirred at room temperature for 15 min, the formation of a unique complex **9a**,**b** was detected by ^{31}P NMR. Two broad singlets appeared: the first one in the region observed for pentavalent azazirconaindene complexes at 54.1 (**9a**) and 58.3 (**9b**) ppm for the PNR_2 fragment and the second one at 1.3 (**9a**) and 2.0 (**9b**) ppm for $P(OPh)_2$ corresponding to the −N−N═N−P(O)-(OPh)$_2$ linkage. IR spectroscopy showed the presence of a nitrogen−nitrogen double bond (ν(N═N) = 2000 (**9a**) and 2070 (**9b**) cm^{-1}) in the azido ligand as well as that of the imino group (ν(C═N) = 1606 (**9a**) and 1596 (**9b**) cm^{-1}). Finally mass spectrometry (FAB/MNBA) (*m/z* 829 [M$^{\bullet+}$]) corroborates the structure assigned to **9a**. In marked contrast to the phosphonium zirconate complexes **D**, when **9a**,**b** were heated under reflux in toluene, a multitude of phosphorus products was observed by ^{31}P NMR.

The scope and limitations of this methodology for the synthesis of anionic zirconocene species as well as studies of the chemical properties and reactivity of these iminium azazirconaindene complexes are currently under active investigations.

Experimental Section

General Procedures. All manipulations were conducted under an argon atmosphere with standard Schlenk techniques. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker MSL 400, AM-250, AC-200, and AC-80 Fourier transform spectrometers. Positive chemical schifts are given downfield relative to Me_4Si (^{1}H, ^{13}C, ^{29}Si) or H_3PO_4 (^{31}P), respectively. Mass spectrum analyses and elemental analyses were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS. Solvents were freshly distilled from sodium/benzophenone ketyl (THF) or lithium aluminum hydride (pentane). C_6D_6, CD_2Cl_2, and $CDCl_3$ were treated with CaH_2, distilled, and stored under argon. Aldehydes RCHO (R = Ph, −CH═CHMe-(*E*), $FeCp_2$), MeNCS, RNCO (R = Ph, naphthyl), and CyN═C═NCy were purchased from Aldrich and used without further purification.

Preparation of Complex 2. To a solution of **1** (0.126 g, 0.228 mmol) in toluene (4 mL) was added benzaldehyde (0.023 mL, 0.228 mmol) at room temperature. The mixture was stirred at room temperature for 30 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (15 mL) and filtered. The volatiles were removed from the solution to give **2** as a yellow solid in 72% yield (0.108 g). IR (KBr): 1566 cm^{-1} ν(C═N). ^{31}P{^{1}H} NMR (C_6D_6): δ 66.3 (s) ppm. ^{1}H NMR (C_6D_6): δ 0.96 (d, 6H, J_{HH} = 6.7 Hz, CH_3), 1.01 (d, 6H, J_{HH} = 6.5 Hz, CH_3), 1.03 (d, 6H, J_{HH} = 5.4 Hz, CH_3), 1.05 (d, 6H, J_{HH} = 5.8 Hz, CH_3), 3.45 (m, 4H, NCH), 5.92 (s, 5H, CH_{Cp}), 6.06 (s, 5H, CH_{Cp}), 7.16−7.25 (m, 5H, CH_{arom} and CHO), 7.39 (m, 2H, CH_{arom}), 7.65 (d, 2H, J_{HH} = 7.1 Hz, CH_{arom}), 8.41 (d, 1H, J_{HH} = 7.3 Hz, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 24.2 (d, J_{CP} = 7.7 Hz, CH_3), 24.4 (d, J_{CP} = 5.7 Hz, CH_3), 25.5 (d, J_{CP} = 7.1 Hz, CH_3), 49.9 (d, J_{CP} = 2.9 Hz, NCH), 50.2 (br, NCH), 97.9 (d, J_{CP} = 22.5 Hz, CHO), 110.8 (s, CH_{Cp}), 111.0 (s, CH_{Cp}), 123.1, 127.8, 128.2, 128.6, and 141.2 (s, CH_{arom}), 130.0 (d, J_{CP} = 5.2 Hz, CH_{arom}), 146.0 (s, C_{arom}), 150.4 (d, J_{CP} = 5.6 Hz, ZrC*C*), 190.4 (d, J_{CP} = 69.2 Hz, PC═N), 195.7 (s, ZrC) ppm. Anal. Calcd for $C_{36}H_{48}N_3POZr$ (660.98): C, 65.41; H, 7.32; N, 6.35. Found: C, 65.50; H, 7.40; N, 6.37.

Preparation of Complex 3. To a solution of **1** (0.438 g, 0.790 mmol) in toluene (8 mL) was added crotonaldehyde (0.065 mL, 0.790 mmol) at room temperature. The mixture was stirred at room temperature for 30 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatiles were removed from the solution to give **3** as a yellow solid in 80% yield (0.394 g). IR (KBr): 1571 cm^{-1} ν(C═N). ^{31}P{^{1}H} NMR (C_6D_6): δ 62.9 (s) ppm. ^{1}H NMR (C_6D_6): δ 0.96 (d, 6H, J_{HH} = 5.1 Hz, CH_3), 1.06 (d, 6H, J_{HH} = 6.7 Hz, CH_3), 1.10 (d, 6H, J_{HH} = 6.7 Hz, CH_3), 1.20 (d, 6H, J_{HH} = 6.4 Hz, CH_3), 1.73 (d, 3H, J_{HH} = 6.4 Hz, ═CH*CH*$_3$), 3.54 (m, 4H, NCH), 5.98 (s, 5H, CH_{Cp}), 6.00 (s, 5H, CH_{Cp}), 6.10 (dq, 1H, J_{HH} = 15.4 Hz, J_{HH} = 6.4 Hz, ═*C*HCH$_3$), 6.30 (dd, J_{HH} = 15.4 Hz, J_{HH} = 4.5 Hz, C*H*═CHCH$_3$), 6.80 (d, 1H, J_{HH} = 4.5 Hz, CHO), 6.98−7.34 (m, 3H, CH_{arom}), 8.15 (d, 1H, J_{HH} = 7.3 Hz, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 18.5 (s, ═CH*CH*$_3$), 24.1 (d, J_{CP} = 7.4 Hz, CH_3), 24.4 (d, J_{CP} = 6.9 Hz, CH_3), 25.4 (d, J_{CP} = 7.2 Hz, CH_3), 49.2 (d, J_{CP} = 13.3 Hz, NCH), 50.0 (d, J_{CP} = 13.3 Hz, NCH), 96.2 (d, J_{CP} = 21.9 Hz, CHO), 110.5 (s, CH_{Cp}), 110.8 (s, CH_{Cp}), 122.8, 129.8, and 140.8 (s, CH_{arom}), 126.4 and 127.9 (s, ═CH), 134.8 (d, J_{CP} = 5.1 Hz, CH_{arom}), 149.5 (s, ZrC*C*), 189.5 (d, J_{CP} = 69.0 Hz, PC═N), 196.5 (s, ZrC) ppm. Anal. Calcd for $C_{33}H_{48}N_3POZr$ (624.95): C, 63.42; H, 7.74; N, 6.72. Found: C, 63.31; H, 7.80; N, 6.78.

Preparation of Complex 4. To a solution of **1** (0.297 g, 0.537 mmol) in toluene (7 mL) was added ferrocenecarboxaldehyde (0.115 g, 0.537 mmol) at room temperature. The mixture was stirred at room temperature for 10 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (30 mL) and filtered. The volatiles were removed from the solution to give **4** as a yellow solid in 79% yield (0.326 g). IR (KBr): 1541 cm^{-1} ν(C═N). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 68.5 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 0.70 (d, 6H, J_{HH} = 6.7 Hz, CH_3), 0.86 (d, 6H, J_{HH} = 6.5 Hz, CH_3), 0.90 (d, 6H, J_{HH} = 6.6 Hz, CH_3), 0.98 (d, 6H, J_{HH} = 6.6 Hz, CH_3), 3.20 (m, 2H, NCH), 3.50 (m, 2H, NCH), 3.82, 3.86, 4.23, and 4.43 (br, CH of FeC_5H_4), 3.99 (s, 5H, CH_{FeCp}), 5.72 (s, 5H, CH_{Cp}), 5.83 (s, 5H, CH_{Cp}), 6.56 (s, 1H, CHO), 6.71−7.11 (m, 3H, CH_{arom}), 7.94 (d, 1H, J_{HH} = 7.7 Hz, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 23.1 (d, J_{CP} = 7.4 Hz, CH_3), 23.7 (d, J_{CP} = 6.2 Hz, CH_3), 23.9 (d, J_{CP} = 4.9 Hz, CH_3), 25.7 (d, J_{CP} = 6.0 Hz, CH_3), 47.5 (d, J_{CP} = 14.0 Hz, NCH), 48.8 (d, J_{CP} = 14.0 Hz, NCH), 66.5, 67.5, 71.6, and 72.0 (s, CH of FeC_5H_4), 68.9 (s, CH_{FeCp}), 93.8 (s, C of FeC_5H_4), 93.9 (d, J_{CP} = 20.3 Hz, CHO), 109.8 (s, CH_{Cp}), 110.1 (s, CH_{Cp}), 122.1, 127.0, 129.3 and 140.0 (s, CH_{arom}), 149.5 (d, J_{CP} = 2.9 Hz, ZrC*C*), 189.8 (d, J_{CP} = 75.2 Hz, PC═N), 194.3 (d, J_{CP} = 3.3 Hz, ZrC) ppm. Anal. Calcd for $C_{40}H_{52}N_3POZrFe$ (768.91): C, 62.48; H, 6.81; N, 5.46. Found: C, 62.39; H, 6.89; N, 5.51.

Preparation of Complex 5. To a solution of **1** (0.169 g, 0.306 mmol) in toluene (5 mL) was added phenyl isocyanate (0.033 mL, 0.306 mmol) at room temperature. The mixture was stirred at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatiles were removed from the solution to give **5** as a red solid in 75% yield (0.154 g). IR (KBr): 1588 cm^{-1} ν(C=N), 1681 cm^{-1} ν(C=O). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 69.6 (s) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.14 (br, 12H, CH$_3$), 1.29 (br, 12H, CH$_3$), 4.01 (m, 4H, NCH), 5.87 (s, 10H, CH$_{\mathrm{Cp}}$), 6.96−7.76 (m, 8H, CH$_{\mathrm{arom}}$), 8.69 (m, 1H, CH$_{\mathrm{arom}}$) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 23.7 (br, CH$_3$), 25.3 (br, CH$_3$), 49.3 (d, J_{CP} = 14.4 Hz, NCH), 109.3 (s, CH$_{\mathrm{Cp}}$), 121.9, 122.6, 122.9, 128.2, 128.4, and 141.5 (s, CH$_{\mathrm{arom}}$), 131.6 (d, J_{CP} = 3.7 Hz, CH$_{\mathrm{arom}}$), 148.4 (s, C$_{\mathrm{arom}}$), 150.9 (d, J_{CP} = 33.0 Hz, C=O), 156.6 (s, ZrC*C*), 196.1 (d, J_{CP} = 6.7 Hz, ZrC), 198.3 (d, J_{CP} = 82.1 Hz, PC=N) ppm. Anal. Calcd for $C_{36}H_{47}N_4POZr$ (673.98): C, 64.15; H, 7.03; N, 8.31. Found: C, 64.08; H, 7.12; N, 8.27.

Preparation of Complex 6. To a solution of **1** (0.513 g, 0.926 mmol) in toluene (10 mL) was added 1-naphthyl isocyanate (0.133 mL, 0.926 mmol) at room temperature. The mixture was stirred at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (30 mL) and filtered. The volatiles were removed from the solution to give **6** as a red solid in 77% yield (0.516 g). IR (KBr): 1531 cm^{-1} ν(C=N), 1691 cm^{-1} ν(C=O). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 67.3 (s) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.22 (d, 12H, J_{HH} = 6.2 Hz, CH$_3$), 1.40 (d, 12H, J_{HH} = 6.3 Hz, CH$_3$), 4.05 (m, 4H, NCH), 5.96 (s, 10H, CH$_{\mathrm{Cp}}$), 7.18−8.02 (m, 10H, CH$_{\mathrm{arom}}$), 8.91 (m, 1H, CH$_{\mathrm{arom}}$) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 23.7 (d, J_{CP} = 8.0 Hz, CH$_3$), 25.1 (d, J_{CP} = 6.1 Hz, CH$_3$), 49.4 (d, J_{CP} = 15.0 Hz, NCH), 109.4 (s, CH$_{\mathrm{Cp}}$), 121.5, 123.1, 124.6, 124.9, 125.3, 125.7, 126.0, 128.5, and 141.3 (s, CH$_{\mathrm{arom}}$), 129.9 and 134.9 (s, C$_{\mathrm{arom}}$), 132.2 (d, J_{CP} = 2.9 Hz, CH$_{\mathrm{arom}}$), 145.3 (s, C$_{\mathrm{arom}}$), 151.0 (d, J_{CP} = 28.5 Hz, C=O), 157.5 (s, ZrC*C*), 196.5 (d, J_{CP} = 4.6 Hz, ZrC), 199.3 (d, J_{CP} = 87.7 Hz, PC=N) ppm. Anal. Calcd for $C_{40}H_{49}N_4POZr$ (724.05): C, 66.35; H, 6.82; N, 7.73. Found: C, 66.30; H, 6.91; N, 7.83.

Preparation of Complex 7. To a solution of **1** (0.317 g, 0.572 mmol) in toluene (7 mL) was added methyl isothiocyanate (0.039 mL, 0.572 mmol) at room temperature. The mixture was stirred at room temperature for 20 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatiles were removed from the solution to give **7** as a red solid in 68% yield (0.244 g). IR (KBr): 1526 cm^{-1} ν(C=N). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 80.2 (s) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.22 (m, 24H, CH$_3$), 3.10 (d, 3H, J_{HP} = 2.7 Hz, NCH$_3$), 3.79 (m, 4H, NCH), 5.82 (s, 10H, CH$_{\mathrm{Cp}}$), 7.10−7.14 (m, 2H, CH$_{\mathrm{arom}}$), 7.48 (m, 1H, CH$_{\mathrm{arom}}$), 8.40 (d, 1H, J_{HH} = 7.4 Hz, CH$_{\mathrm{arom}}$) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 23.9 (d, J_{CP} = 6.8 Hz, CH$_3$), 39.2 (s, NCH$_3$), 49.7 (d, J_{CP} = 15.1 Hz, NCH), 108.9 (s, CH$_{\mathrm{Cp}}$), 123.1, 127.8, 132.6, and 140.7 (s, CH$_{\mathrm{arom}}$), 150.4 (s, ZrCC), 186.5 (d, J_{CP} = 5.9 Hz, C=S), 194.6 (s, ZrC), 199.7 (d, J_{CP} = 86.3 Hz, PC=N) ppm. Anal. Calcd for $C_{31}H_{45}N_4PSZr$ (627.98): C, 59.29; H, 7.22; N, 8.92. Found: C, 59.18; H, 7.30; N, 8.85.

Preparation of Complex 8. To a solution of **1a** (0.404 g, 0.729 mmol) in toluene (8 mL) was added *N*,*N'*-dicyclohexylcarbodiimide (0.150 g, 0.729 mmol) at room temperature. The mixture was stirred at room temperature for 45 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (40 mL) and filtered. The volatiles were removed from the solution to give **8** as a red solid in 64% yield (0.355 g). IR (KBr): 1556 cm^{-1} ν(C=N), 1631 cm^{-1} ν(C=N). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 69.6 (s) ppm. ^{1}H NMR (C$_6$D$_6$): δ 0.96−1.86 (m, 20H, CH$_2$), 1.17 (d, 12H, J_{HH} = 6.6 Hz, CH$_3$), 1.28 (d, 12H, J_{HH} = 6.5 Hz, CH$_3$), 2.01 (m, 1H, CH$_2$CHN), 2.07 (m, 1H, CH$_2$CHN), 3.55 (m, 4H, NCH), 5.76 (s, 10H, CH$_{\mathrm{Cp}}$), 6.99−7.46 (m, 3H, CH$_{\mathrm{arom}}$), 8.82 (m, 1H, CH$_{\mathrm{arom}}$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 24.5 (d, J_{CP} = 7.2 Hz, CH$_3$), 25.3, 26.2, 27.1, 27.5, 35.8, and 37.7 (s, CH$_2$), 25.8 (d, J_{CP} = 6.3 Hz, CH$_3$), 49.5 (d, J_{CP} = 13.4 Hz, NCH), 56.7 (br, CH$_2$*CH*N), 59.1 (br, CH$_2$*CH*N), 109.3 (s, CH$_{\mathrm{Cp}}$), 123.1, 127.6, and 142.1 (s, CH$_{\mathrm{arom}}$), 130.7 (d, J_{CP} = 2.5 Hz, CH$_{\mathrm{arom}}$), 152.6 (s, ZrC*C*), 153.5 (d, J_{CP} = 35.0 Hz, NC=N), 193.1 (d, J_{CP} = 4.5 Hz, ZrC), 200.9 (d, J_{CP} = 30.0 Hz, PC=N) ppm. Anal. Calcd for $C_{42}H_{64}N_5PZr$ (761.19): C, 66.27; H, 8.47; N, 9.20. Found: C, 66.32; H, 8.39; N, 9.17.

Preparation of Complex 9a. To a solution of **1a** (0.320 g, 0.577 mmol) in toluene (6 mL) was added diphenylphosphoryl azide (0.124 mL, 0.577 mmol) at room temperature. The mixture was stirred at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatiles were removed from the solution to give **9a** as a red solid in 91% yield (0.435 g). IR (KBr): 1606 cm^{-1} ν(C=N), 2000 cm^{-1} ν(N=N). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 1.3 (s, P=O), 54.1 (s, (^{i}Pr$_2$N)$_2$P) ppm. ^{1}H NMR (C$_6$D$_6$): δ 1.11 (d, 12H, J_{HH} = 6.5 Hz, CH$_3$), 1.25 (d, 12H, J_{HH} = 6.6 Hz, CH$_3$), 3.72 (m, 4H, NCH), 5.89 (s, 10H, CH$_{\mathrm{Cp}}$), 6.78−7.62 (m, 13H, CH$_{\mathrm{arom}}$), 8.93 (m, 1H, CH$_{\mathrm{arom}}$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 24.3 (d, J_{CP} = 7.3 Hz, CH$_3$), 25.3 (d, J_{CP} = 7.0 Hz, CH$_3$), 49.8 (d, J_{CP} = 14.1 Hz, NCH), 111.2 (s, CH$_{\mathrm{Cp}}$), 122.5 (d, J_{CP} = 3.3 Hz, CH$_{\mathrm{arom}}$), 123.8, 125.5, 129.6, 130.1, and 142.1 (s, CH$_{\mathrm{arom}}$), 128.6 (d, J_{CP} = 24.3 Hz, CH$_{\mathrm{arom}}$), 149.3 (d, J_{CP} = 32.7 Hz, ZrC*C*), 152.3 (d, J_{CP} = 7.4 Hz, *i*-OPh), 196.6 (d, J_{CP} = 7.4 Hz, ZrC), 198.0 (d, J_{CP} = 81.9 Hz, PC=N) ppm. Anal. Calcd for $C_{41}H_{52}N_6O_3P_2Zr$ (830.07): C, 59.32; H, 6.31; N, 10.12. Found: C, 59.41; H, 6.29; N, 10.20. MS (FAB/MNBA): *m*/*z* 829 [M + H]$^{+}$.

Preparation of Complex 9b. To a solution of **1b** (0.271 g, 0.380 mmol) in toluene (5 mL) was added diphenylphosphoryl azide (0.082 mL, 0.380 mmol) at room temperature. The mixture was stirred at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (25 mL) and filtered. The volatiles were removed from the solution to give **9b** as a red solid in 77% yield (0.290 g). IR (KBr): 1596 cm^{-1} ν(C=N), 2079 cm^{-1} ν(N=N). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 2.0 (s, P=O), 58.3 (s, (Cy$_2$N)$_2$P) ppm. ^{1}H NMR (C$_6$D$_6$): δ 0.83−2.11 (m, 40H, CH$_2$), 3.45 (m, 4H, NCH), 5.93 (s, 10H, CH$_{\mathrm{Cp}}$), 6.81−7.69 (m, 13H, CH$_{\mathrm{arom}}$), 9.07 (m, 1H, CH$_{\mathrm{arom}}$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 26.6 and 27.7 (s, CH$_2$), 35.6 (d, J_{CP} = 6.6 Hz, CH$_2$), 36.5 (d, J_{CP} = 6.6 Hz, CH$_2$), 59.6 (d, J_{CP} = 6.6 Hz, NCH), 111.3 (s, CH$_{\mathrm{Cp}}$), 122.5 (d, J_{CP} = 3.4 Hz, CH$_{\mathrm{arom}}$), 123.9, 125.4, 129.5, 130.1, and 142.3 (s, CH$_{\mathrm{arom}}$), 132.6 (d, J_{CP} = 40.7 Hz, CH$_{\mathrm{arom}}$), 149.8 (d, J_{CP} = 35.0 Hz, ZrC*C*), 152.4 (d, J_{CP} = 7.3 Hz, *i*-OPh), 196.5 (d, J_{CP} = 6.8 Hz, ZrC), 198.0 (d, J_{CP} = 85.0 Hz, PC=N) ppm. Anal. Calcd for $C_{53}H_{68}N_6O_3P_2Zr$ (990.33): C, 64.28; H, 6.92; N, 8.48. Found: C, 64.17; H, 6.71; N, 8.52.

X-ray Analyses of 4. Data were collected at low temperature (T = 160 K) on a IPDS STOE diffractometer equipped with an Oxford Cryosystems Cryostream Cooler Device and using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Final unit cell parameters were obtained by means of a least-squares refinement of a set of well-measured reflections, and crystal decay was monitored during the data collection; no significant fluctuations of intensities have been observed. Structures have been solved by direct methods using SIR92[20] and refined by least-squares procedures on F^2 with the aid of SHELXL97[21] included in the program package WinGX version 1.63,[22] and atomic scattering factors were taken from *International Tables for X-Ray Crystallography*.[23] All hydrogens

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[20] SIR92−A program for crystal structure solution: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guargliardi, A *J. Appl. Crystallogr.* **1993**, *26*, 343. SIR97: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guargliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

[21] Sheldrick, G. M. *SHELX97* [includes *SHELXS97*, *SHELXL97*, *CIFTAB*]−Programs for Crystal Structure Analysis (Release 97−2); Institüt für Anorganische Chemie der Universität: Göttingen, Germany, 1998.

[22] WINGX−1.63 Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-Crystal X-Ray Diffraction Data. Farrugia, L. *J. Appl. Crystallogr.* **1999**, *32*, 837.

atoms were located on difference Fourier maps refined by using a riding model, except the hydrogen H(1) connected to the C(1) atom. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. A drawing of the molecule is performed with the program ORTEP32[24] with 50% probability displacement ellipsoids for non-hydrogens.

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

OM0200508

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(23) *International tables for X-ray crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV.

(24) ORTEP3 for Windows: Farrugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565.