Zircona-phosphazine complexes: synthesis and X-ray determination

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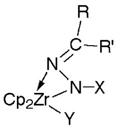
Addition of diazoalkane derivatives RCH(N_2) [R = CO_2Et (**a**), $SiMe_3$ (**b**)] on α-phosphino zirconocene complexes **1**, **4** and **6** affords stable *N*-metal phosphazine compounds **3a**,**b**, **5a**,**b** and **7a**,**b**, respectively. The single crystal X-ray structure of **3a** is reported and shows an *s-transoid* (*E*) geometry for the phosphazine substructure P1–N1–N2–C9 with a zirconium-to-nitrogen distance in the range of that of Cp_2Zr–N σ-bonds in zirconate complexes, which reveals a zwitterionic canonical form for **3a**.

Introduction

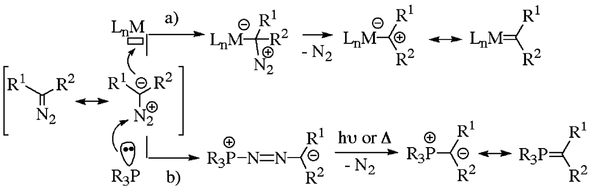
The reaction of diazoalkanes $R^1R^2CN_2$ with transition metals results either in the coordination through the nitrogen atoms[1] or in the formation of a carbon–metal bond.[2] It has also long been established that coordinatively unsaturated transition metal complexes [ML_n] (or their precursors [ML_nY] containing a readily displacable ligand Y) are efficient catalysts for the decomposition reaction of diazoalkanes $R^1R^2CN_2$ into the corresponding carbene derivatives RR′C: after evolution of dinitrogen N_2 (Scheme 1, path a) as in catalytic cyclopropanation and olefin metathesis reactions.[3] Treatment of zirconocene(IV) complexes with diazoalkanes resulted in the insertion product into zirconium–carbon,[4] –hydrogen,[4c] –phosphorus[5] and –metal[6] bonds to give the corresponding hydrazonato ligands **I** with an η^2-*N*,*N* coordination mode. We also recently described unprecedented α-metalated diazoalkanes L_nM–$C(N_2)R$ containing a zirconocene metal fragment.[7]



I

It has been known for some time that diazoalkanes react with phosphines R_3P to give the corresponding stable phosphazine moieties R_3PNNCR_2 (Scheme 1, path b).[8] Although the synthetic utility of phosphazines has been recognized for many years[9] the coordination chemistry of these classes of compounds has not yet been investigated.

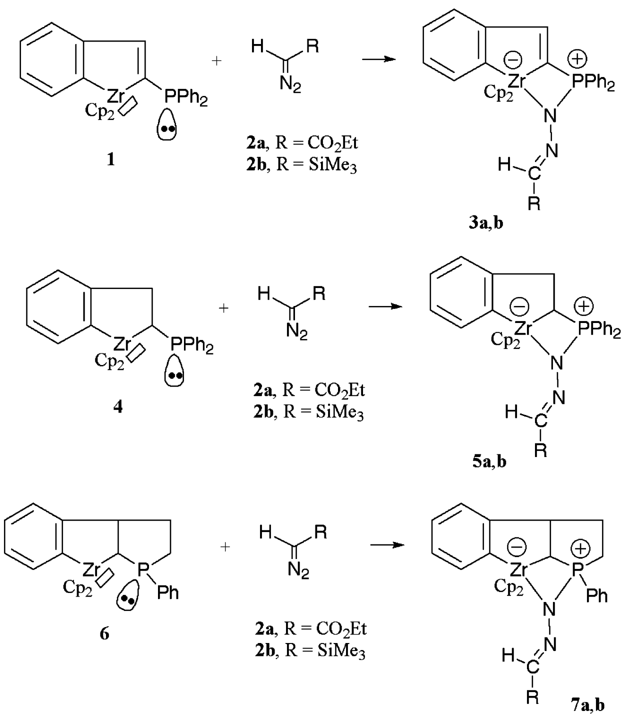
Lately, the first example of the formation of a phosphazine complex *via* formal insertion of a diazoalkane into an iron–phosphine bond was described by Grubbs and Louie.[10] We have investigated the reactivity of diazoalkanes with a variety of coordinatively unsaturated α-phosphino zirconocene complexes. Herein, we report the preparation of stable *N*-zirconated phosphazine complexes and the structural characterization of one of these compounds.



Scheme 1 Typical reactivity of diazoalkanes with (a) metal complexes L_nM and (b) phosphanes R_3P.

Results and discussion

Addition of ethyl diazoacetate **2a** to 2-phosphino-zirconainden **1** resulted in immediate formation of the dark red compound **3a** in 86% yield (Scheme 2). Similarly, addition of



Scheme 2 Synthesis of zwitterionic N-zirconated phosphazine complexes.

Table 1 Selected ^{31}P and ^{13}C NMR spectroscopic data[a] for *N*-zirconated phosphazine complexes **3a**,**b**, **5a**,**b** and **7a**,**b** and their precursor compounds **1**, **4** and **6**

	^{31}P	C1[b]	C6[b]	C7[b]	C8[b]	C9[b]
1	6.9	184.9	165.7	142.7	191.5	
				(13.0)	(49.0)	
3a	35.4	192.4	156.7	164.7	154.4	132.9
		(10.1)	(31.0)		(53.6)	(33.9)
3b	32.0	192.2	156.9	163.5	155.8	150.4
		(11.4)	(31.2)		(54.2)	(29.2)
4	−3.5	182.2	158.0	42.5	25.9	
		(6.5)	(27.3)		(32.3)	
5a	38.8	181.9	155.4	38.9	12.0	128.8
		(14.1)	(21.1)		(66.3)	(22.2)
5b	33.5	183.2	156.4	39.9	12.3	150.3
		(13.9)	(21.0)		(67.6)	(27.6)
6	−4.7	182.1	160.3	57.6	49.1	
		(5.1)	(15.3)		(37.0)	
7a	57.5	183.3	161.6	54.0	27.1	140.3
		(12.0)	(18.4)	(15.8)	(72.0)	(15.3)
7b	53.2	183.8	162.0	54.1	26.6	152.6
		(12.2)	(17.9)	(15.0)	(72.3)	(28.6)

[a] Chemical shifts in ppm and couplings (between parentheses) in Hz. [b] The numbering is as shown in Fig. 1.

trimethylsilyl diazo compound **2b** to **1** produced the dark yellow diazo adduct **3b** in 82% yield.

From their elemental analyses and mass spectra, compounds **3a**,**b** appear to have the correct composition for a formally 1:1 adduct of the starting reagents [$\mathbf{1}\cdot RCH(N_2)$]. These reactions proceed without loss of N_2. Complexes **3a**,**b** exhibit the characteristic spectroscopic features of five-coordinated zirconate species (Table 1).[11] ^{31}P NMR spectra showed the clean formation of a unique phosphorus product in the region expected for pentavalent α-phosphino zirconainden complexes. As already observed for these zwitterionic phosphonium zirconates,[11] in ^{13}C NMR the signals of the ZrCP fragment are significantly shifted to high field at 154–156 ppm, relative to that of the starting complex **1** (δ ^{13}C 191 ppm), with a $^{1}J_{CP}$ coupling constant around 54 Hz. Characteristic ^{13}C NMR chemical shifts at δ 192 ppm, which appeared as a doublet (J_{CP} = 10–11 Hz), were detected for the aryl sp^2 carbon atom directly linked to the zirconium atom. The most striking data of the terminal *N*-coordinated diazo group in **3a**,**b** are the ^{13}C NMR resonances of the $C(N_2)$ carbon atom, which were dramatically deshielded [δ ^{13}C 132.9 (**3a**) and 150.3 (**3b**) ppm] relative to the starting diazoalkane reagents[12] and compare well with the chemical shift of the $C(sp^2)$ carbon atom in hydrazone derivatives $>C{=}N{-}N<$. The NMR data are consistent with the dinitrogen function of the diazoalkane moiety bridged to the zirconium and phosphorus atoms. However, in order to gain a better insight into the structure of these novel phosphazine complexes, X-ray crystallography studies were undertaken on **3a** (Table 2). A view of the molecule is shown in Fig. 1 and reveals that the terminal nitrogen atom of the ethyl diazoacetate is connected to both the phosphorus and zirconium centers.

Table 2 Selected bond lengths (Å) and angles (°) for **3a**

P–N1	1.6446(16)	N1–N2	1.366(2)
N2–C9	1.2854(18)	N1–Zr	2.3708(16)
C1–Zr	2.383(2)	C8–Zr	2.3306(19)
C1–C6	1.414(2)	C6–C7	1.463(5)
C7–C8	1.332(7)	C9–C10	1.473(9)
C9–N2–N1	117.44(14)	N2–N1–P	116.04(12)
N2–N1–Zr	140.83(12)	N1–Zr–C1	131.70(6)
C1–Zr–C8	68.79(5)	N1–P–C8	93.30(6)
Zr–C8–P	101.13(4)	Zr–C8–C7	121.69(15)

Table 3 Selected crystallographic data for **3a**

Empirical formula	$C_{34}H_{31}N_2O_2PZr$
Formula weight	621.80
T/K	160(2)
Wavelength/	0.71073
Crystal system, space group	Monoclinic
Space group	$P2_1/n$
a/Å	19.125(2)
b/Å	7.8428(9)
c/Å	19.805(2)
β/°	107.921(12)
U/Å^3	2826.4(5)
Z	4
μ/mm^{-1}	0.480
Final $R1$ [$I > 2\sigma(I)$]	0.0237
Final $wR2$ [$I > 2\sigma(I)$]	0.0578
$R1$ (all data)	0.0305
$R2$ (all data)	0.0601

The X-ray structure shows an *s-transoid* (*E*) geometry for the phosphazine substructure P1–N1–N2–C9 with a torsion angle of 179.19(0.11)°. The C9–N2 bond presents a 1.285(3) Å length, which is in total accord with those found in $FeCl_2[N(PMe_2Ph)NC(H)CO_2Et]_2$ and $FeCl_2[N(PMe_2Ph)NCPh_2]$ phosphazine iron complexes[10] and the reference value for a double bond between $N(sp^2)$ and $C(sp^2)$ atoms.[13] The phosphazine shows the expected lengthening of the N–N distance from 1.126(4) Å in the free and in the end-on *N*-metallated diazoalkane[14] to 1.372 (3) Å with a corresponding change from linearity in the C–N–N diazo group to a bond angle of 117°, closer to the sp^2 standard. Distances and angles around the phosphorus atom are consistent with a four-coordinate cyclic phosphonium salt. Note that the P–N1 bond length at 1.644 (2) Å is halfway between a single P–N [1.701 (14) Å] and a typical P=N [1.597 (16) Å] bonds.[15] The atoms of the metallapolycycle skeleton are practically coplanar and lie roughly in the equatorial plane, which bisects the dihedral angle formed by the Cp ligands bonded to the zirconium atom in a nearly symmetric η^5-fashion. The Zr–N1 bond length [2.368(2) Å] is in good agreement with those found in five-valent zirconocene ate-complexes.[11,16] All these observations indicate a higher contribution of the zwitterionic form for **3a**.

In order to enhance the scope of our results, diazoalkanes **2a**,**b** were added on the 2-phosphino-1-zircoindan **4** to give the corresponding *N*-zirconated phosphazine complexes **5a**,**b**

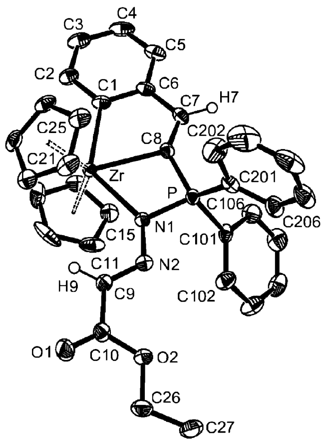
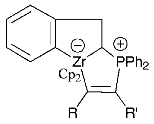


Fig. 1 X-Ray crystal structure of **3a** (CAMERON drawing with thermal ellipsoids at 50% probability). Hydrogen atoms are omitted for clarity except for H7 and H9.

in high yield. From their elemental analyses, compounds **5a**,**b** appear to have the correct composition for a formally 1:1 adduct of the starting reagents [**4**·$RC(N_2)H$]. Complexes **5a**,**b** 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 $\delta = 39$ (**5a**) and 33 (**5b**) ppm expected for pentavalent phosphonium zircona-indene complexes. As already observed for the phosphonium zirconates **A**,[17] in ^{13}C NMR the signals of the ZrCH and CH_2 fragments are shifted to high field. Moreover, the signal in ^{13}C NMR of the CHR (R = CO_2Et, $SiMe_3$) moiety appeared at 140–150 ppm as a doublet with a $^3J_{CP}$ coupling constant in the range of 30 Hz, which is in agreement with the corresponding fragment found in complexes **3a**,**b**. Therefore, it is reasonable to postulate that the NMR data of compounds **5a**,**b** are consistent with a structure in which the terminal nitrogen atom of the diazo function bridges the zirconium and phosphorus atoms.



A

The *N*-zirconated phosphazines complexes **7a**,**b** were obtained in an identical manner as for compounds **3a**,**b** and **5a**,**b**. In ^{31}P NMR, the chemical shifts at 53 and 57 ppm for **7a** and **7b** (to be compared with $\delta = -4.7$ ppm for **6**) is typical for analogous phosphorus five-valent zirconocenes. The shielded chemical shift at 27 ppm observed in ^{13}C NMR with the low field resonance at 3.60–3.70 ppm in ^1H NMR are indicative of the central Zr–CH bond in the corresponding five-valent zirconocene complexes.[11b,e] The chemical shift and the J_{HP} coupling constant of the RCH moiety of the diazo fragment for **7a**,**b** compare well with those reported for **3a**,**b** and **5a**,**b** (see Table 1).

Conclusions

Metal phosphazine complexes are still rather scarce. We showed that addition of diazoalkanes on α-phosphino-Zr(IV) complexes led to the formation of phosphazine compounds with an end-on η^1-*N* coordination mode of the zirconocene metal fragment. The reactivity of such phosphazine complexes is under active investigations.

Experimental

All manipulations were performed under an argon atmosphere, either on a vacuum line using standard Schlenk techniques or in a Braun MB 200-G drybox. Solvents were freshly distilled from dark purple solutions of sodium/benzophenone ketyl (THF, toluene) or lithium aluminium hydride (pentane). Deuterated NMR solvents were treated with $LiAlH_4(C_6D_6)$, distilled, and stored under argon.

Nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on Bruker MSL-400, AM-250, AC-200, and AC-80 Fourier transform spectrometers. Chemical shifts are given downfield relative to Me_4Si (^1H, ^{13}C, ^{29}Si) or H_3PO_4 (^{31}P), respectively.[13] C NMR assignments were confirmed by inverse gradient δ ^1H-δ $^{13}C\{^{31}P\}$ HMQC and ^{31}P-^1H INEPT NMR experiments. For the NMR data of compounds **3a**,**b**, **5a**,**b**, and **7a**,**b** the numbering system is as given in Table 1. Elemental and mass spectral analyses obtained on a Nermag R10–10H were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS.

Complexes **1**,[18] **4**,[17] and **6**[19] were prepared according to literature procedures. Diazoalkane reagents $RCH(N_2)$ with R = CO_2Et, $SiMe_3$ were purchased from Aldrich and used without further purification.

Syntheses

Preparation of μ^1-*N*-zirconated phosphazide complex 3a. To a solution of **1** (0.363 g, 0.716 mmol) in toluene (5 mL) ethyl diazoacetate **2a** (0.075 mL, 0.716 mmol) was added at room temperature. The mixture was stirred at room temperature for 1 h and then evaporated to dryness. The resulting solid residue was extracted with a mixture THF–pentane (10 mL:40 mL) and filtered. The volatiles were removed from the solution to give **3a** as a red solid in 86% yield (0.382 g). MS (FAB): *m*/*z* 621 $[M^+ + 1]$. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 35.4 (s) ppm. ^1H NMR (C_6D_6): δ 1.07 (t, 3H, $J_{HH} = 7.1$ Hz, CH_3), 4.21 (q, 2H, $J_{HH} = 7.1$ Hz, CH_2), 5.72 (s, 10H, Cp), 6.96–7.43 (m, 8H, CH_{arom}), 7.52 (d, 1H, $J_{HP} = 1.5$ Hz, =CH), 7.72–7.82 (m, 6H, CH_{arom}), 8.16 (d, 1H, $J_{HP} = 24.3$ Hz, PC=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 15.0 (s, CH_3), 60.7 (s, CH_2), 108.4 (s, Cp), 123.7, 126.2, 126.8 and 141.6 (s, CH_{arom}), 129.4 (d, $J_{CP} = 11.0$ Hz, *o*-PPh_2), 132.2 (d, $J_{CP} = 10.1$ Hz, *m*-PPh_2), 132.3 (d, $J_{CP} = 68.3$ Hz, *i*-PPh_2), 132.4 (s, *p*-PPh_2), 132.9 (d, $J_{CP} = 33.9$ Hz, =CH), 154.4 (d, $J_{CP} = 53.6$ Hz, ZrCP), 156.7 (d, $J_{CP} = 31.0$ Hz, ZrC*C*), 164.7 (s, PC=*C*H), 164.9 (s, C=O), 192.4 (d, $J_{CP} = 10.1$ Hz, ZrC) ppm. Anal. calcd. for $C_{34}H_{31}N_2O_2PZr$ (621.82): C, 65.67; H, 5.02; N, 4.50; found: C, 65.62; H, 4.97; N, 4.58.

Preparation of the *N*-zirconated phosphazide complex 3b. To a solution of **1** (0.413 g, 0.814 mmol) in toluene (8 mL) (trimethylsilyl)diazomethane **2b** (2.0 M solution in hexanes; 0.407 mL, 0.814 mmol) was added 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 a mixture THF–pentane (10 mL:50 mL) and filtered. The volatiles were removed from the solution to give **3b** as a yellow solid in 82% yield (0.415 g). MS (FAB): *m*/*z* 621 $[M^+ + 1]$. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 32.0 (s) ppm. ^1H NMR (C_6D_6): δ 0.27 (s, 9H, $SiMe_3$), 5.83 (s, 10H, Cp), 7.04–7.47 (m, 8H, CH_{arom}), 7.64 (d, 1H, $J_{HP} = 2.0$ Hz, =CH), 7.70–7.78 (m, 6H, CH_{arom}), 8.26 (d, 1H, $J_{HP} = 24.3$ Hz, PC=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ −0.9 (s, $SiMe_3$), 108.2 (s, Cp), 123.6, 126.0, 126.3 and 141.7 (s, CH_{arom}), 129.1 (d, $J_{CP} = 11.2$ Hz, *o*-PPh_2), 131.9 (s, *p*-PPh_2), 132.1 (d, $J_{CP} = 9.8$ 9.8 Hz, *m*-PPh_2), 133.9 (d, $J_{CP} = 65.0$ Hz, *i*-PPh_2), 150.4 (d, $J_{CP} = 29.2$ Hz, =CH), 155.8 (d, $J_{CP} = 54.2$ Hz, ZrCP), 156.9 (d, $J_{CP} = 31.2$ Hz, ZrC*C*), 163.5 (s, PC=*C*H), 192.2 (d, $J_{CP} = 11.4$ Hz, ZrC) ppm. Anal. calcd. for $C_{34}H_{35}N_2PSiZr$ (621.94): C, 65.66; H, 5.67; N, 4.50; found: C, 65.42; H, 5.58; N, 4.57.

Preparation of the *N*-zirconated phosphazide complex 5a. To a solution of **4** (0.360 g, 0.708 mmol) in toluene (6 mL) ethyl diazoacetate **2a** (0.074 mL, “ 0.708 mmol) was added 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 a mixture THF–pentane (10 mL:40 mL) and filtered. The volatiles were removed from the solution to give **5a** as a yellow solid in 77% yield (0.340 g). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 38.8 (s) ppm. ^1H NMR (C_6D_6): δ 1.44 (t, 3H, $J_{HH} = 7.1$ Hz, CH_3), 2.72 (m, 1H, CH), 3.08 (m, 1H, CH_2), 3.48 (m, 1H, CH_2), 4.37 (m, 2H, OCH_2), 5.79 (s, 5H, Cp), 6.06 (s, 5H, Cp), 6.91–7.87 (m, 15H, CH_{arom} and =CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.0 (d, $J_{CP} = 66.3$ 66.3 Hz, ZrCH), 14.6 (s, CH_3), 38.9 (s, CH_2), 60.5 (s, OCH_2), 108.5 (s, Cp), 123.0, 123.8, 123.9 and 140.3 (s, CH_{arom}), 128.7 (d, $J_{CP} = 10.6$ Hz, *o*-PPh_2), 128.8 (d, $J_{CP} = 22.2$ Hz, =CH), 128.9 (d, $J_{CP} = 11.6$ Hz, *o*-PPh_2), 130.1 (d, $J_{CP} = 73.4$ Hz, *i*-PPh_2), 131.2 (d, $J_{CP} = 9.3$ Hz, *m*-PPh_2), 131.8 (s, *p*-PPh_2), 132.2 (d, $J_{CP} = 9.1$ Hz, *m*-PPh_2), 132.5 (s, *p*-PPh_2), 133.8

(d, J_{CP} = 63.7 Hz, *i*-PPh$_2$), 155.4 (d, J_{CP} = 21.1 Hz, ZrC*C*), 165.0 (s, C=O), 181.9 (d, J_{CP} = 14.1 Hz, ZrC) ppm. Anal. calcd. for $C_{34}H_{33}N_2O_2PZr$ (623.84): C, 65.46; H, 5.33; N, 4.49; found: C, 65.50; H, 5.27; N, 4.38.

Preparation of μ^1-*N*-zirconated phosphazide complex 5b. To a solution of **4** (0.317 g, 0.622 mmol) in toluene (5 mL) (trimethylsilyl)diazomethane **2b** (2.0 M solution in hexanes; 0.311 mL, 0.622 mmol) was added 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 a mixture THF–pentane (10 mL:40 mL) and filtered. The volatiles were removed from the solution to give **5b** as a yellow solid in 79% yield (0.306 g). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 33.5 (s) ppm. ^1H NMR (C_6D_6): δ 0.25 (s, 9H, SiCH$_3$), 2.53 (m, 1H, CH), 3.13 (m, 1H, CH$_2$), 3.49 (m, 1H, CH$_2$), 5.70 (s, 5H, Cp), 5.88 (s, 5H, Cp), 7.01–7.35 (m, 11H, CH$_{arom}$), 7.52 (d, 1H, J_{HH} = 1.8 Hz, =CH), 7.55–7.69 (m, 3H, CH$_{arom}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ–1.0 (s, SiCH$_3$), 12.3 (d, J_{CP} = 67.6 Hz, ZrCH), 39.9 (s, CH$_2$), 108.9 (s, Cp), 123.6, 124.6, 124.7 and 141.0 (s, CH$_{arom}$), 128.8 (d, J_{CP} = 10.5 Hz, *o*-PPh$_2$), 129.0 (d, J_{CP} = 11.1 Hz, *o*-PPh$_2$), 131.5 (d, J_{CP} = 12.7 Hz, *m*-PPh$_2$), 131.8 (s, *p*-PPh$_2$), 132.4 (d, J_{CP} = 9.0 9.0 Hz, *m*-PPh$_2$), 136.2 (d, J_{CP} = 63.8 Hz, *i*-PPh$_2$), 150.3 (d, J_{CP} = 27.6 Hz, =CH), 156.4 (d, J_{CP} = 21.0 Hz, ZrC*C*), 183.2 (d, J_{CP} = 13.9 Hz, ZrC) ppm. Anal. calcd. for $C_{34}H_{37}N_2PSiZr$ (623.96): C, 65.44; H, 5.97; N, 4.48; found: C, 65.30; H, 5.92; N, 4.60.

Preparation of the *N*-zirconated phosphazide complex 7a. To a solution of **6** (0.240 g, 0.523 mmol) in toluene (6 mL) ethyl diazoacetate **2a** (0.072 μL, 0.523 mmol) was added at room temperature. The mixture was stirred at room temperature for 1 h and then evaporated to dryness. The resulting solid residue was extracted with a mixture THF–pentane (10 mL:40 mL) and filtered. The volatiles were removed from the solution to give **7a** as a yellow solid in 70% yield (0.210 g). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 57.5 (s) ppm. ^1H NMR (C_6D_6): δ 1.05 (t, 3H, J_{HH} = 7.1 Hz, CH$_3$), 1.48–1.63 (m, 1H, CH$_2$), 1.86–2.19 (m, 3H, CH$_2$), 2.69–2.74 (m, 1H, CH), 3.54–3.65 (m, 1H, CH), 4.14 (q, 2H, J_{HH} = 7.1, OCH$_2$), 5.62 (s, 5H, Cp), 5.69 (s, 5H, Cp), 6.86–7.19 (m, 7H, CH$_{arom}$), 7.5 (d, J_{HH} = 2.0 Hz, 1H, =CH), 7.64–7.77 (m, 2H, CH$_{arom}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 14.6 (s, CH$_3$), 27.1 (d, J_{CP} = 72.0 Hz, ZrCHP), 30.8 (d, J_{CP} = 49.0 Hz, CH$_2$P), 33.5 (d, J_{CP} = 6.3 Hz, PCH$_2$*C*H$_2$), 54.0 (d, J_{CP} = 15.8 Hz, PCH*C*H), 60.7 (s, OCH$_2$), 109.3 (s, Cp), 110.3 (s, Cp), 124.8, 124.9, 129.2 and 131.9 (s, CH$_{arom}$), 129.1 (d, J_{CP} = 10.5 Hz, *o*-PPh), 131.3 (d, J_{CP} = 9.2 Hz, *m*-PPh), 134.5 (d, J_{CP} = 57.5 Hz, *i*-PPh), 140.3 (d, J_{CP} = 15.4 Hz, HCN), 161.6 (d, J_{CP} = 18.4 Hz, ZrC*C*), 165.0 (s, CO), 183.3 (d, J_{CP} = 12.0 Hz, ZrC) ppm. Anal. calcd. for $C_{30}H_{31}N_2O_2PZr$ (573.80): C, 62.82; H, 5.40; N, 4.89; found: C, 62.31; H, 5.28; N, 4.45.

Preparation of the *N*-zirconated phosphazide complex 7b. To a solution of **6** (0.265 g, 0.577 mmol) in toluene (6 mL) (trimethylsilyl)diazomethane **2b** (2.0 M solution in hexane, 0.289 g, 0.577 mmol) was added at room temperature. The mixture was stirred at room temperature for 30 mn and then evaporated to dryness. The resulting solid residue was extracted with a mixture THF–pentane (10 mL:40 mL) and filtered. The volatiles were removed from the solution to give **7b** as a yellow solid in 83% yield (0.275 g). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 53.2 (s) ppm. ^1H NMR (C_6D_6): δ 0.22 (s, 9H, SiCH$_3$), 1.59 (m, 1H, CH$_2$), 2.11–2.40 (m, 3H, CH$_2$), 2.63 (m, 1H, CH), 3.68 (m, 1H, PCHZr), 5.77 (s, 5H, Cp), 5.79 (s, 5H, Cp), 7.03–7.30 (m, 7H, CH$_{arom}$), 7.46 (d, J_{HH} = 2.0 Hz, 1H, =CH), 7.52–7.58 (m, 2H, CH$_{arom}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.0 (s, SiCH$_3$), 26.6 (d, J_{CP} = 72.3 Hz, ZrCHP), 29.8 (d, J_{CP} = 47.9 Hz, CH$_2$P), 33.8 (d, J_{CP} = 6.4 Hz, PCH$_2$*C*H$_2$), 54.1 (d, J_{CP} = 15.0 Hz, PCH*C*H), 109.2 (s, Cp), 110.2 (s, Cp), 123.8, 124.7, 124.8, 129.7 and 131.3 (s, CH$_{arom}$), 131.1 (d, J_{CP} = 9.2 Hz, *o*-PPh), 136.1 (d, J_{CP} = 57.3 Hz, *i*-PPh), 152.6 (d, J_{CP} = 28.6 Hz, HCN), 162.0 (d, J_{CP} = 17.9 Hz, ZrC*C*), 183.8 (d, J_{CP} = 12.2 Hz, ZrC) ppm. Anal. calcd. for $C_{30}H_{35}N_2PSiZr$ (573.90): C, 62.78; H, 6.14; N, 4.88; found: C, 62.90; H, 6.35; N, 4.95.

X-Ray analysis of 3a

Single crystals of **3a** were obtained by layering pentane on top of a saturated dichloromethane solution of the corresponding complex. 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. Crystal decay was monitored during data collection and no significant intensity fluctuations have been observed. The structure has been solved by direct methods using SIR92[20] and refined by least-squares procedures on F^2 with the aid of SHELXL97,[21] which is included in the software WinGX, version 1.63.[22] All hydrogens atoms were located on a difference Fourier map but refined by using a riding model with an isotropic thermal parameter fixed at 20% higher than those of the carbons atoms to which they were connected, except for hydrogens atoms H(2) and H(9), which were isotropically refined. All non-hydrogens atoms were anisotropically refined and in the last cycles of refinement a weighting scheme was used. The drawing of molecule was obtained with the program ORTEP32[23] with 50% probability displacement ellipsoids for the non-hydrogen atoms.

CCDC reference number 203942. See http://www.rsc.org/suppdata/nj/b2/b210773m/ for crystallographic files in CIF or other electronic format.

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