(NH)-Phosphanylamido- and (PH)-Phosphoraneiminato Transition-Metal Complexes: Syntheses, Structures, and Computational Studies[†]

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Reactions of aminobis(diorganylamino)phosphanes $(R_2N)_2PNH_2$ (R = *i*Pr (**a**), Cy (**b**)) with Cp_2MCl_2 (M = Ti, Zr, Hf), $CpTiCl_3$, and $TiCl_4$ lead to the formation of the transition-metal complexes $(R_2N)_2PN(H)MCp_2Cl$ (M = Ti (**1b**), Zr (**2a,b**), Hf (**3a,b**)) $(R_2N)_2P(H)NTiCpCl_2$ (**8a,b**), and $(R_2N)_2P(H)NTiCl_3$ (**10a,b**), respectively. The influence of electronic effects of the metal fragment on the resulting equilibrium between the (NH)-phosphanylamido and the tautomeric (PH)-iminophosphorane form is presented in detail. Computational studies unambiguously confirm the experimental results. The molecular structures of **2a**, **3a**, and **8b** have been determined by single-crystal X-ray diffraction.

1. Introduction

Substituted-cyclopentadienyl early-transition-metal complexes have been investigated intensively due to their potential as alkene polymerization catalysts.[1] In attempts to develop comparable systems with accessible catalytic activity, several research groups have developed alternative ligands for early-metal systems with similar reactivities such as carbolyl, $C_2B_9H_{11}$,[2] or the phosphoraneiminato group, R_3PN^-, which have been described as isolobal with the cyclopentadienyl ligand.[3] In particular, early-transition-metal complexes, which stabilize the phosphorane ligand, have been the subject of a variety of experimental and theoretical studies.[4]

Furthermore, efforts to substitute the transition-metal center by main-group-metal fragments have drawn considerable attention.[5] Within our own studies, we have reported the reactions of aminobis(dicyclohexylamino)phosphane, $(Cy_2N)_2PNH_2$, with trialkylalanes and dialkylaluminum hydrides. The strong acidic character of the Al center led to the formation of bis(dicyclohexylamino)iminophosphorane−trialkylalane Lewis acid base adducts $(Cy_2N)_2P(H)N(H)AlR_3$ (R = Me, Et, *t*Bu) and dimeric bis(dicyclohexylamino)iminophosphorane−dialkylalane heterocycles $[(Cy_2N)_2P(H)NAlR_2]_2$ (R = Me, Et), respectively.[6] This corresponds to the results of previous experimental and theoretical investigations on the isomerization of (NH)-aminophosphanes $R_2P(NH)R'$ to (PH)-iminophosphoranes.[7]

In this context, we have recently published the reactions of aminobis(diorganylamino)phosphanes with group 4 bis(cyclopentadienyl)-substituted complexes,[8,9] leading to the formation of an equilibrium between the (NH)-phosphanylamido species **A** and the tautomeric (PH)-iminophosphorane form **B** (Scheme 1).

In the present paper, we report on experimental and computational studies of ligand effects on the NH/PH-tautomerization in (NH)-phosphanylamido and (PH)-phosphoraneiminato group 4 transition-metal complexes.

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Scheme 1

{M} = group 4 metal fragment
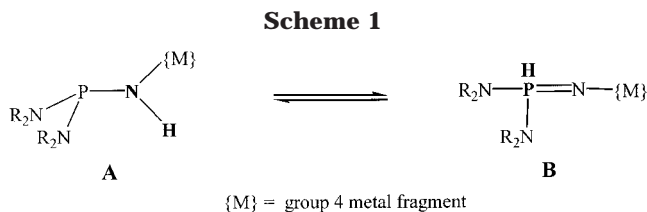
2. Experimental Section

2.1. General Considerations. All manipulations were performed with the exclusion of air and moisture under argon employing standard Schlenk techniques. Solvents were dried by using standard procedures. Cp$_2$TiCl$_2$, Cp$_2$ZrCl$_2$, Cp$_2$HfCl$_2$, and TiCl$_4$ were used as received. CpTiCl$_3$[10] and (R$_2$N)$_2$PNH$_2$ (R = *i*Pr, Cy)[8] were prepared by literature methods. A Bruker AMX 300 spectrometer was used for NMR spectroscopy. ^{1}H and ^{13}C{^{1}H} spectra were referenced to internal C$_6$D$_5$H (δ(^{1}H) 7.154, δ(^{13}C) 128.0) and ^{31}P to external H$_3$PO$_4$. Mass spectra were recorded on a VG Masslab 12-250 spectrometer in the electron impact mode (EI). Melting points were observed in sealed capillaries and were not corrected. Elemental analyses were performed at the Mikroanalytisches Labor der Universität Bonn.

2.2. General Synthesis of (*i*Pr$_2$N)$_2$PN(H)ZrCp$_2$Cl (2a) and (*i*Pr$_2$N)$_2$PN(H)HfCp$_2$Cl (3a). To a solution of aminobis-(diisopropylamino)phosphane (0.48 g, 2 mmol) in THF (20 mL) was added *n*-butyllithium (1.43 mL, 2.3 mmol, 1.6 M in hexane) at −30 °C. The mixture was stirred and warmed to −10 °C within 1 h. Then, a solution of dicyclopentadienyl-metallocene dichloride (**2a**, 0.58 g; **3a**, 0.76 g; 2 mmol for each) in THF (20 mL) was added dropwise at −78 °C. The mixture was warmed to room temperature. After the solvent was removed under reduced pressure, a mixture of pentane and diethyl ether (1:1) was added to the residue. The precipitated LiCl was filtered off and the solvent removed under vacuum. Both compounds were recrystallized from a 2:1 mixture of diethyl ether and toluene (**2a**, −30 °C; **3a**, −78 °C). **2a**: yield 0.88 g (88%); mp 132 °C. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 90.4 (s). ^{1}H NMR (CDCl$_3$): δ 6.19 (s, 10H, Cp), 3.30 (d, $^3J_{HP}$ = 14.2 Hz, $^3J_{HH}$ = 6.7 Hz, 4H, NCH), 1.41 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH$_3$), 1.36 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 114.5 (s, Cp), 44.8 (d, $^2J_{CP}$ = 11.4 Hz, PNC), 24.7 (s, PNCC). MS (180 °C/70 eV): *m/z* 502 (3) [M$^+$], 467 (4) [M$^+$ − Cl], 437 (1) [M$^+$ − Cp], 402 (5) [M$^+$ − N(*i*Pr)$_2$], 367 (3) [M$^+$ − N(*i*Pr)$_2$ − Cl], 255 (22) [ClZrCp$_2$$^+$], 100 (100) [N(*i*Pr)$_2$$^+$]. Anal. Calcd (found) for C$_{22}$H$_{39}$ClN$_3$PZr: C, 52.51 (52.45); H, 7.81 (7.75); N, 8.35 (8.28). **3a**: yield 0.98 g (83%); mp 123 °C. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 92.8 (s). ^{1}H NMR (CDCl$_3$): δ 6.04 (s, 10H, Cp), 3.46 (m, 4H, NCH), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH$_3$), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 110.1 (s, Cp), 46.5 (d, $^2J_{CP}$ = 5.4 Hz, PNC), 25.7 (s, PNCC), 23.1 (s, PNCC). MS (180 °C/70 eV): *m/z* 590 (2) [M$^+$], 547 (6) [M$^+$ − N(*i*Pr)], 513 (2) [M$^+$ − Cl − *i*Pr], 490 (45) [M$^+$ − N(*i*Pr)$_2$], 390 (25) [M$^+$ − (N(*i*Pr)$_2$)$_2$], 343 (52) [HfCp$_2$Cl$^+$], 247 (5) [M$^+$ − Cp$_2$HfCl], 100 (100) [N(*i*Pr)$_2$$^+$]. Anal. Calcd (found) for C$_{22}$H$_{39}$ClHfN$_3$P: C, 44.75 (44.66); H, 6.66 (6.61); N, 7.12 (7.08).

General Synthesis of (Cy$_2$N)$_2$PN(H)TiCp$_2$Cl (1b), (Cy$_2$N)$_2$PN(H)ZrCp$_2$Cl (2b), and (Cy$_2$N)$_2$PN(H)HfCp$_2$Cl (3b). To a solution of aminobis(dicyclohexylamino)phosphane (0.41 g, 1 mmol) in THF (15 mL) was added *n*-butyllithium (0.63 mL, 1.1 mmol, 1.6 M in hexane) at −10 °C. The mixture was stirred at this temperature for 1 h, and then a solution of dicyclopentadienylmetallocene dichloride (**1b**, 0.25 g; **2b**, 0.29 g; **3b**, 0.38 g; 1 mmol of each) in THF (15 mL) was added dropwise at −40 °C. The mixture was warmed to room temperature within 2 h, and the solvent was removed under reduced pressure. Mixtures of pentane and toluene (**1b**),

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pentane and diethyl ether (**2b**), and pentane (**3b**) were added to the residue. The precipitated LiCl was filtered off and the solvent removed under vacuum. **1b** and **3b** were crystallized from diethyl ether and **2b** from diethyl ether/toluene (2:1) at −30 °C. **1b**: yield 0.83 g (67%); mp 139 °C. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 100.6 (s). ^{1}H NMR (C$_6$D$_6$): δ 6.22 (s, 10H, Cp), 2.73 (m, 4H, NCH), 1.9−0.9 (m, 40H, CH$_2$). ^{13}C NMR (C$_6$D$_6$): δ 114.4 (s, Cp), 55.7 (d, $^2J_{CP}$ = 9.3 Hz, PNC), 36.1 (d, $^3J_{CP}$ = 8.2 Hz, PNCC), 35.5 (d, $^3J_{CP}$ = 5.6 Hz, PNCC), 34.8 (s, PNCCC), 27.6 (s, PNCCCC). Anal. Calcd (found) for C$_{34}$H$_{55}$ClN$_3$PTi: C, 65.85 (65.79); H, 8.94 (8.85); N, 6.78 (6.70). **2b**: yield 1.20 g (91%); mp 135 °C. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 94.0 (s). ^{1}H NMR (C$_6$D$_6$): δ 6.20 (s, 10H, Cp), 3.40 (m, 4H, NCH), 1.6−0.9 (m, 40H, CH$_2$). ^{13}C NMR (C$_6$D$_6$): δ 114.5 (s, Cp), 55.6 (d, $^2J_{CP}$ = 9.2 Hz, PNC), 35.9 (d, $^3J_{CP}$ = 5.3 Hz, PNCC), 35.3 (d, $^3J_{CP}$ = 6.9 Hz, PNCC), 27.9 (s, PNCCC), 25.8 (s, PNCCCC). Anal. Calcd (found) for C$_{34}$H$_{55}$ClN$_3$PZr: C, 61.55 (61.44); H, 8.35 (8.28); N, 6.33 (6.29). **3b**: yield 0.45 g (61%); mp 103 °C. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 95.4 (s). ^{1}H NMR (C$_6$D$_6$): δ 6.19 (s, 10H, Cp), 2.60 (m, 4H, NCH), 2.0−0.9 (m, 40H, CH$_2$). ^{13}C NMR (C$_6$D$_6$): δ 112.5 (s, Cp), 53.6 (d, $^2J_{CP}$ = 8.9 Hz, PNC), 34.4 (d, $^3J_{CP}$ = 4.1 Hz, PNCC), 33.6 (d, $^3J_{CP}$ = 4.1 Hz, PNCC), 27.2 (s, PNCCC), 26.2 (s, PNCCCC). Anal. Calcd (found) for C$_{34}$H$_{55}$ClHfN$_3$P: C, 54.40 (54.36); H, 7.38 (7.31); N, 5.60 (5.49).

General Synthesis of (*i*Pr$_2$N)$_2$P(H)NTiCpCl$_2$ (8a) and (Cy$_2$N)$_2$P(H)NTiCpCl$_2$ (8b). To a solution of aminobis(di-organylamino)phosphane (**a**, 0.48 g; **b**, 0.82 g; 2 mmol of each) in THF (20 mL) was added *n*-butyllithium (1.43 mL, 2.3 mmol, 1.6 M in hexane) at −40 °C (**8a**) and −10 °C (**8b**), respectively, and the mixture was stirred for 15 min (**8b**, 45 min). Then, a solution of cyclopentadienyltitanium trichloride (0.44 g, 2 mmol) in THF (20 mL) was added dropwise at −78 °C (**8b**, −40 °C). The mixture was slowly warmed to room temperature. The solvent was removed under reduced pressure. A mixture of pentane and toluene (**8b**, pentane and diethyl ether) was added to the residue. The precipitated LiCl was filtered off and the solvent removed under vacuum. **8a,b** were crystallized from toluene and diethyl ether (2:1) at −30 °C. **8a**: yield, 0.68 g (79%); mp 114 °C. ^{31}P NMR (C$_6$D$_6$): δ −16.1 (dquin, $^1J_{PH}$ = 549 Hz, $^3J_{PH}$ = 19.1 Hz). ^{1}H NMR (C$_6$D$_6$): δ 7.27 (d, $^1J_{PH}$ = 549 Hz, 1H, PH), 6.41 (s, 5H, Cp), 3.40−3.25 (m, $^3J_{HH}$ = 6.8 Hz, 4H, NCH), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CCH$_3$), 0.99 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CCH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 115.4 (s, Cp), 45.6 (d, $^2J_{CP}$ = 5.8 Hz, PNC), 23.8 (d, $^3J_{CP}$ = 3.0 Hz, PNCC), 22.9 (d, $^3J_{CP}$ = 3.0 Hz, PNCC). MS (200 °C/70 eV): *m/z* 430 (3) [M$^+$], 395 (2) [M$^+$ − Cl], 330 (7) [M$^+$ − N(*i*Pr)$_2$], 247 (6) [M$^+$ − CpTiCl$_2$], 183 (4) [CpTiCl$_2$$^+$],100 (100) [N(*i*Pr)$_2$]. Anal. Calcd (found) for C$_{17}$H$_{34}$Cl$_2$N$_3$PTi: C, 47.46 (47.35); H, 7.97 (7.91); N, 9.77 (9.70). **8b**: yield 0.98 g (83%); mp 125 °C. ^{31}P NMR (C$_6$D$_6$): δ −15.2 (dquin, $^1J_{PH}$ = 550 Hz, $^3J_{PH}$ = 16.5 Hz). ^{1}H NMR (C$_6$D$_6$): δ 7.26 (d, $^1J_{PH}$ = 550 Hz, 1H, PH), 6.58 (s, 5H, Cp), 3.20 (m, 4H, PNCH), 1.9−0.9 (m, 40H, CH$_2$). ^{13}C NMR (CDCl$_3$): δ 115.4 (s, Cp), 54.7 (d, $^2J_{CP}$ = 4.9 Hz, PNC), 34.8 (d, $^3J_{CP}$ = 2.7 Hz, PNCC), 34.1 (d, $^3J_{CP}$ = 1.9 Hz, PNCC), 27.3 (s, NCCC), 26.0 (s, NCCCC). Anal. Calcd (found) for C$_{29}$H$_{50}$Cl$_2$N$_3$PTi: C, 58.99 (58.87); H, 8.54 (8.47); N, 7.12 (7.01).

Synthesis of (*i*Pr$_2$N)$_2$P(H)NTiCl$_3$ (10a) and (Cy$_2$N)$_2$P-(H)NTiCl$_3$ (10b). To a solution of aminobis(diorganylamino)-phosphane (**a**, 0.36 g; **b**, 0.62 g; 1.5 mmol of each) in THF (20 mL) was added triethylamine (0.16 mL, 1.5 mmol) at −30 °C. This mixture was added dropwise to a solution of titanium tetrachloride (0.28 g, 1.5 mmol) in THF at −78 °C and warmed to room temperature within 2 h. After the solvent was removed under reduced pressure, hexane (20 mL) was added to the residue. The precipitated ammonium chloride was filtered off, and **10a,b** were crystallized from this solution at −60 °C. **10a**: yield 0.38 g (61%); mp 92 °C. ^{31}P NMR (CDCl$_3$): δ −11.6 (dquin, $^1J_{PH}$ = 582 Hz, $^3J_{PH}$ = 15.9 Hz). ^{1}H NMR (CDCl$_3$): δ 7.88 (d, $^1J_{PH}$ = 582 Hz, 1H, PH), 3.72 (m, 4H, NCH), 1.64 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CCH$_3$), 1.56 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CCH$_3$), 1.44 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CCH$_3$), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 6H,

Table 1. Crystallographic Data and Measurements for (iPr$_2$N)$_2$PN(H)ZrCp$_2$Cl (2a), (iPr$_2$N)$_2$PN(H)HfCp$_2$Cl (3a), and (Cy$_2$N)$_2$P(H)NTiCpCl$_2$ (8b)

	2a	3a	8b
mol formula	C$_{22}$H$_{39}$ClN$_3$PZr	C$_{22}$H$_{39}$ClHfN$_3$P	C$_{29}$H$_{50}$Cl$_2$N$_3$PTi·0.5(toluene)
fw	503.20	590.47	636.56
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	15.4818(4)	15.4475(3)	8.9411(3)
b, Å	10.2902(3)	10.2903(2)	10.5678(3)
c, Å	16.2080(5)	16.2122(4)	19.6517(4)
α, deg			102.374(2)
β, deg	106.785(2)	106.945(1)	93.787(2)
γ, deg			108.596(2)
V, Å^3	2472.10(12)	2456.20(9)	1700.81(8)
Z	4	4	2
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	0.630	4.417	0.481
temp, K	123(2)	123(2)	123(2)
D_{calcd}, g cm^{-3}	1.352	1.591	1.243
cryst dimens (mm)	0.20 × 0.07 × 0.04	0.25 × 0.15 × 0.10	0.25 × 0.15 × 0.10
$2\theta_{max}$, deg	50.0	56.66	56.6
min/max transmissn	0.8697, 0.9037	0.4038, 0.6781	
no. of rflns recorded	27 880	49 761	22 855
no. of nonequiv rflns recorded	4348	6116	6061
R_{int}	0.052	0.059	0.027
no. of params/restraints	256/1	256/1	400/403
R1,^{a} wR2^b	0.0328, 0.0741	0.0211, 0.0480	0.0353, 0.1046
goodness of fit^c	1.08	0.99	1.08
final max, min $\Delta\rho$, e Å^{-3}	0.690, −0.328	0.914, −1.086	0.413, −0.322

^{a} R1 = $\sum(||F_o| - |F_c||)/\sum|F_o|$ (for $I > 2\sigma(I)$). ^{b} wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. ^{c} Goodness of fit = $\{\sum[w(|F_o^2| - |F_c^2|)^2]/(N_{observns} - N_{params})\}^{1/2}$.

CCH$_3$). ^{13}C NMR (CDCl$_3$): δ 46.1 (d, $^2J_{CP}$ = 5.7 Hz, PNC), 23.8 (d, $^3J_{CP}$ = 3.0 Hz, PNCC), 22.7 (d, $^3J_{CP}$ = 2.3 Hz, PNCC). MS (180 °C/70 eV): m/z 400 (18) [M$^+$], 365 (15) [M$^+$ − Cl], 300 (20) [M$^+$ − N(iPr)$_2$], 246 (5) [M$^+$ − TiCl$_3$], 147 (9) [M$^+$ − TiCl$_3$ − N(iPr)$_2$], 100 (100) [N(iPr)$_2^+$]. Anal. Calcd (found) for C$_{12}$H$_{29}$Cl$_3$N$_3$PTi: C, 35.98 (35.84); H, 7.30 (7.19); N, 10.49 (10.36). **10b**: yield 0.67 g (79%); mp 105 °C. ^{31}P NMR (C$_6$D$_6$): δ −16.4 (dquin, $^1J_{PH}$ = 587 Hz, $^3J_{PH}$ = 15.8 Hz). ^{1}H NMR (C$_6$D$_6$): δ 7.00 (d, $^1J_{PH}$ = 587 Hz, 1H, PH), 3.00 (m, 4H, NCH), 1.9−1.3 (m, 40H, CH$_2$). ^{13}C NMR (C$_6$D$_6$): δ = 55.2 (d, $^2J_{CP}$ = 5.0 Hz, PNC), 34.8 (d, $^3J_{CP}$ = 2.7 Hz, PNCC), 33.6 (d, $^3J_{CP}$ = 1.9 Hz, PNCC), 27.0 (s, NCCC), 25.6 (s, NCCCC). MS (300 °C/16 eV): m/z 559 (2) [M$^+$], 524 (4) [M$^+$ − Cl], 476 (4) [M$^+$ − Cy], 406 (35) [M$^+$ − TiCl$_3$], 180 (75) [NCy$_2^+$]. Anal. Calcd (found) for C$_{24}$H$_{45}$Cl$_3$N$_3$PTi: C, 51.40 (51.32); H, 8.09 (8.00); N, 7.49 (7.36).

X-ray Structure Solution and Refinement. Crystallographic data for **2a**, **3a**, and **8b** are summarized in Table 1, and selected bond lengths and angles are given in Table 2. Figures 1−3 show the ORTEP diagrams of the solid-state structures of **2a**, **3a**, and **8b**. Data were collected on a Nonius Kappa-CCD diffractometer. Structures were solved by direct methods (SHELXS-97)[11] and refined by full-matrix least squares on F^2 (SHELXL-97).[12] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms, localized by difference electron density determination, used a riding model (coordinates of H(N) and H(P) free). An empirical absorption correction was applied for **2a** and **3a**; in **8b** one solvent molecule (toluene) and a cyclohexyl group are disordered.

3. Results and Discussion

The addition of Cp$_2$MCl$_2$ (M = group 4 metal) to a solution of aminobis(dialkylamino)phosphane, (R$_2$N)$_2$PNH$_2$ (R = iPr (**a**), Cy (**b**)), and n-butyllithium in THF afford the (NH)-phosphanylamido-substituted transition-metal complexes **1**−**3** (Scheme 2).

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**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2a, 3a, and 8b**

Compound 2a			
P1−N1	1.722(2)	Zr1−N1	2.067(2)
P1−N2	1.699(2)	Zr1−Cl1	2.497(1)
P1−N3	1.701(2)	Zr1−Cp(centroid)	2.226^a
N1−P1−N2	103.5(1)	P1−N1−Zr1	137.6(1)
N1−P1−N3	101.3(1)	N1−Zr1−Cl1	100.8(1)
N2−P1−N3	105.9(1)		

Compound 3a			
P1−N1	1.718(2)	Hf1−N1	2.052(2)
P1−N2	1.696(2)	Hf1−Cl1	2.467(1)
P1−N3	1.704(2)	Hf1−Cp(centroid)	2.209^a
N1−P1−N2	103.4(1)	P1−N1−Hf1	137.4(1)
N1−P1−N3	101.7(1)	N1−Hf1−Cl1	99.8(1)
N2−P1−N3	105.9(1)		

Compound 8b			
P1−N1	1.592(2)	Ti1−Cp(centroid)	2.061(1)
P1−N2	1.643(2)	Ti1−Cl1	2.306(1)
P1−N3	1.649(2)	Ti1−Cl2	2.314(1)
Ti1−N1	1.781(2)		
N1−P1−N2	115.4(1)	N1−Ti1−Cl1	102.8(1)
N1−P1−N3	111.6(1)	N1−Ti1−Cl2	104.4(1)
N2−P1−N3	109.6(1)	Cl1−Ti1−Cl2	103.0(1)
P1−N1−Ti1	152.0(1)		

^{a} Average M1−Cp(centroid) distance.

Compounds **1a,b**−**3a,b** can be stored at −30 °C for weeks without decomposition, and no rearrangement to the (PH)-phosphoraneiminato-substituted tautomers **4a,b**−**6a,b** is detected at this temperature.

The constitution of **1a,b**−**3a,b** follows from the high-resolution mass spectra and the ^{31}P, ^{1}H, and ^{13}C NMR spectra. Compared to the ^{31}P NMR resonances of the starting materials,[8] the observed phosphanylamido-complexes **1b**, **2a,b**, and **3a,b** show a downfield shift of the P(III) atoms (**1b**, 100.6 ppm; **2a**, 90.4 ppm; **2b**, 94.0 ppm; **3a**, 92.8 ppm; **3b**, 95.4 ppm).
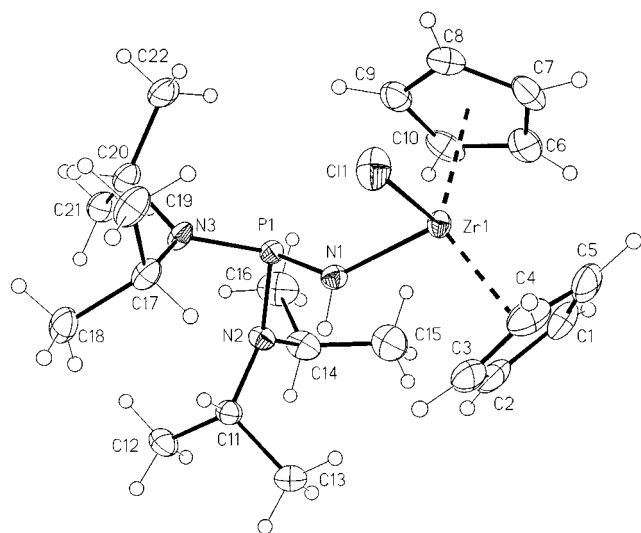
Figure 1. ORTEP plot (50% probability level) showing the solid-state structure and atom-numbering scheme for **2a**.
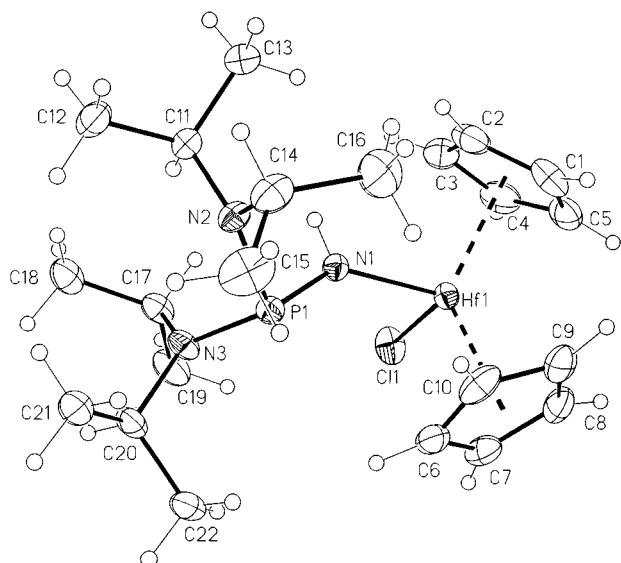
Figure 2. ORTEP plot (50% probability level) showing the solid-state structure and atom-numbering scheme for **3a**.
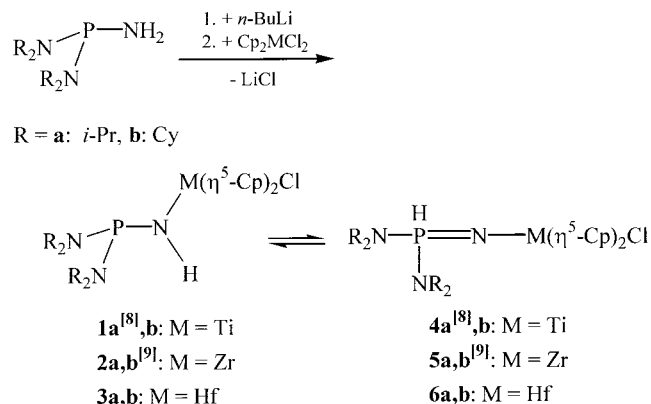
Scheme 2

R = **a**: *i*-Pr, **b**: Cy

1a[8],**b**: M = Ti   **4a**[8],**b**: M = Ti
2a,b[9]: M = Zr   **5a,b**[9]: M = Zr
3a,b: M = Hf   **6a,b**: M = Hf

The molecular structures of **2a** and **3a** are further proven by crystal structure analysis (Figures 1 and 2, Table 1). The transition metals feature a distorted-tetrahedral coordination by two η^5-coordinated cyclopentadienyl ligands, a chlorine atom, and the amido nitrogen atom. The P1–N1 bond lengths (**2a**, 1.722 Å;

Scheme 3

R = **a**: *i*-Pr, **b**: Cy
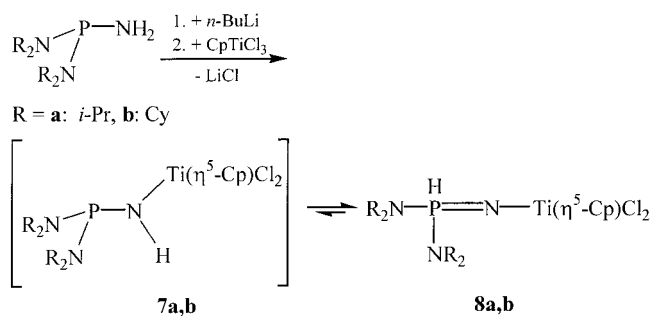
3a, 1.718 Å) differ only slightly from those observed for $(i\text{Pr}_2\text{N})_2\text{PN(H)TiCpCl}_2$ (P1–N1 = 1.723 Å), previously obtained in our group,[8] and fall in the typical range of P^{III}–N single-bond lengths.[13] The M1–N1–P1 bond angles (**2a**, 137.6°; **3a**, 137.4°), the planarity of N1, and the M1–N1 distance (**2a**, 2.067 Å; **3a**, 2.052 Å) suggest some kind of π-interaction between the nitrogen and the transition metal.

Heating **1**–**3** gently to 50 °C in polar solvents leads to the formation of the PH tautomers **4**–**6**, indicated by the occurrence of ^{31}P NMR resonances significantly shifted upfield (**4b**, −3.9 ppm; **5a**, −7.4 ppm; **5b**, −4.7 ppm; **6a**, 0.1 ppm; **6b**, 1.7 ppm) and characteristic P,H coupling constants ($^1J_{\text{HP}} \cong$ 550 Hz).[14] The reactions afford mixtures of the "NH" and the "PH" isomers, and **4**–**6** cannot be isolated in a pure form, indicating a slow establishment of the equilibrium. Heating the mixture up to higher temperatures or for a longer period leads to decomposition.

Metalation of aminobis(diorganylamino)phosphanes $(\text{R}_2\text{N})_2\text{PNH}_2$ (R = *i*Pr, Cy) with *n*-butyllithium and subsequent reaction with CpTiCl$_3$ gives the (PH)-phosphoraneiminato-substituted complexes **8a,b** (Scheme 3), proven by the significant shielding of the phosphorus atoms (**8a**, −16.1 ppm; **8b**, −15.2 ppm) in the ^{31}P NMR spectra and typical P,H coupling constants (**8a**, 549 Hz; **8b**, 550 Hz). The formation of the NH tautomers **7a,b** is not detected, even at low temperatures. This corresponds well with the stronger Lewis acidity of the mono- compared to the bis(cyclopentadienyl) fragment.

Single crystals of **8b**, suitable for X-ray structure determination, were obtained from a diethyl ether/toluene solution. The structure (Figure 3, Table 1) undoubtedly proves the presence of the (PH)-iminophosphorane form in the solid state, as expected from the multinuclear NMR studies.

The P1–N1 bond lengths of 1.592 Å lies in the upper range for PN double bonds.[15] Compared to the single bond covalent distances, the Ti1–N1 distance (1.781 Å) is significantly shortened. This corresponds well with the data found for the similar Ph$_3$PNTiCpCl$_2$ complex.[16] The M1–N1–P1 bond angle of 152.0° is not consistent with most common descriptions of the bonding situation in phosphoraneiminato complexes with linear M–N–P arrangements (161–177°) or a bent M–N–P moiety

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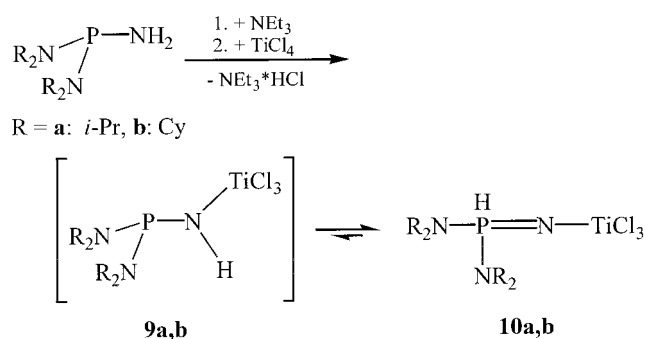(15) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, U.K., 1984.
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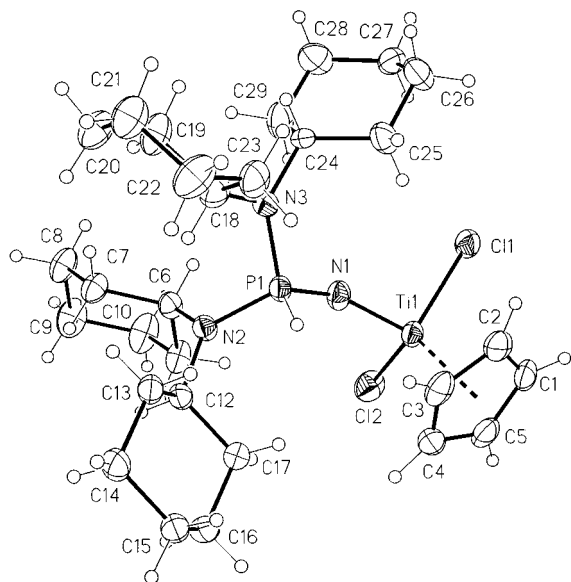
Figure 3. ORTEP plot (50% probability level; disordered parts omitted for clarity) showing the solid-state structure and atom-numbering scheme for **8b**.

Scheme 4

9a,b   **10a,b**

(130–140°).[4a] But, as recently demonstrated by Bickelhaupt, the variation of the bond angle over 50° is associated with a change on the potential energy surface of less than 2 kcal/mol.[4h] This indicates a great influence of the different substituents in the R_3PN^- fragment and the surroundings in the solid state on the observed M–N–P angle and explains the unusual situation in **8b**.

At least, $(R_2N)_2PNH_2$ species (R = *i*Pr, Cy) are reacted with titanium tetrachloride and triethylamine in THF (Scheme 4). As expected, no NH tautomers **9a,b** are accessible and only the PH compounds **10a,b** are formed, due to the increasing electrophilicity at the metal center compared to the cyclopentadienyl-substituted fragments $CpMCl_2$ and Cp_2MCl.

In the ^{31}P NMR spectra, the presence of the PH form is again confirmed by the observation of the typical shielding of the phosphorus atoms (**10a**, −11.6 ppm; **10b**, −16.4 ppm) and the occurrence of characteristic P,H coupling constants (**10a**, 582 Hz; **10b**, 587 Hz). The proposed constitution and the high thermal stability of **10a,b** are further proven by the results of mass spectroscopy. In both cases, the highest observed peaks correspond with the molecular ions.

4. Computational Studies

4.1. Computational Methods. All molecules were fully optimized at the B3LYP level. This method is

Table 3. Relative Energies (ΔE in kJ mol^{-1}) of the Two Tautomers According to Eq 1 for [RR′PHN]$^-$ Ions[a]

R	R′	ΔE	R	R′	ΔE
H	H	130.9	NH_2	NH_2	99.0
H	NH_2	109.4	$N(CH_3)_2$	$N(CH_3)_2$	98.7

[a] Values for ΔE + zero point vibrational energy correction are given in parentheses.

developed with Becke's three-parameter exchange functional[17] and the Lee–Young–Parr correlation functional.[18] As basis sets the relativistically corrected effective core potentials of Stevens, Basch, and Krauss[19] with a double-ζ basis expansion for the valence space were used, augmented by one set of polarization functions (of d type) for the heavy (non-hydrogen) main-group elements (SBK(d) basis). The use of polarization functions is imperative to get a correct description of the strongly polar P–N bond. For all anions this basis set was augmented by a set of diffuse s and p functions (SBK(d+diff)) to account for the larger extent of the MOs in these molecules. All stationary points were verified as local minima by inspection of the eigenvalues of the corresponding Hessian matrices (calculated at the DFT level as well). All calculations were performed using the Gaussian 98 package of programs.[20]

4.2. Computational Results. To give support to the experimental results, DFT calculations have been performed on several model compounds. Within these models the organic residues of the amino groups have been replaced by hydrogen atoms. The determination of the relative energy ΔE of the tautomers (as given by eq 1) was the main objective of our calculations, because an experimental measurement of ΔE is difficult.

$$(R_2P)NH^- \rightleftharpoons (R_2HP)N^- + \Delta E \qquad (1)$$

For the uncoordinated anion RR′PHN$^-$, the NH tautomer in equilibrium 1 is clearly favored. The size of ΔE depends on the number of amino groups at the phosphorus atom. This is demonstrated in Table 3. To mimic the experimental situation more closely, also the effect of dimethylamino substitution was considered. Accordingly, the electronegative groups such as NRR′ (R,R′ = H, CH$_3$) decrease the energy difference between the tautomers, though the sign of ΔE is not altered. The replacement of the hydrogens by methyl groups does not affect the equilibrium between both anionic structural isomers.

It is different if the anion is coordinated to a transition metal complex fragment. Because of the coordination

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Table 4. Relative Energies (ΔE in kJ mol^{-1}) for $MCl_xCp_{3-x}(NPH(NH_2)_2)$ vs $MCl_xCp_{3-x}(NHP(NH_2)_2)^a$

M	x	ΔE
Ti	3	-24.9 (-22.4)/31.0 (24.9)^b
	2	-9.7 (-10.6)
	1	33.3 (29.5)
Zr	3	-32.9 (-31.2)/51.8 (45.5)^b
	2	-9.7 (-11.0)
	1	28.2 (24.5)
Hf	3	-35.0 (-33.4)/56.9 (50.1)^b
	2	-12.9 (-14.5)
	1	26.4 (22.4)

^{a} Values for ΔE + zero point vibrational energy correction are given in parentheses. ^{b} The first entry is the relative energy of the NH transition state, and the second entry is the relative energy of the corresponding minimum. For molecular structures, see Figure 4.
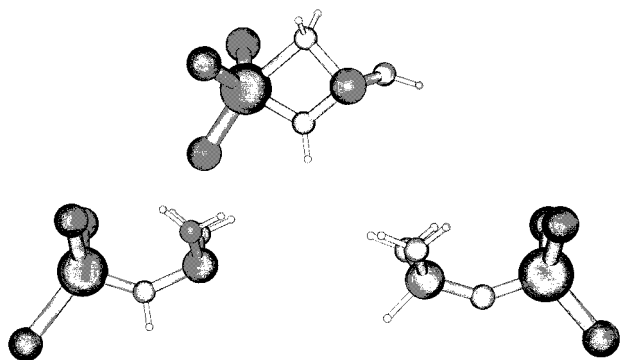
Figure 4. Molecular structure of complexes $MCl_3NHP(NH_2)_2$: (left) NH tautomer; (right) PH tautomer, transition state; (top) NH tautomer, minimum. The NH tautomer is the most favorable configuration for this complex.

the relative stability of the phosphoraneiminato form (eq 1, right) is promoted. If the anion $NPH(NH_2)_2^-$ is coordinated to a complex fragment of sufficient π-acidity, the equilibrium is shifted to the right-hand side, the outcome increasing with the Lewis acidity of the transition metal fragment. This is shown in Table 4 for several complexes with elements of group 4.

The calculated relative energies show that the π-acidity of the complex fragment and therefore the stability of the PH form depends on the number of π-donor ligands coordinated to the transition-metal atom. As a consequence, the stability of the PH tautomer increases in the order $MCp_2Cl < MCpCl_2 < MCl_3$. Here, one has to take into account that the expected structure of the complex $Cl_3M(NH)P(NH_2)_2$ is only a transition state on the energy hypersurface. In the corresponding minimum structure $NHP(NH_2)_2^-$ acts as a bidentate ligand. As shown in Figure 4, also one of the amino groups coordinates to the highly Lewis acidic transition metal center. This intramolecular stabilization is the only possibility for the isolated complex; in condensed matter, we expect intermolecular reactions (e.g., dimer formation) to be more important for the saturation of the coordination sphere of the transition metal center.

The relative stability of the "NH" vs the "PH" form also depends on the choice of the transition metal. Therefore, we explored complexes of all elements of group 4. According to our calculations, Hafnium is the best choice to stabilize the PH form, though the differences between the transition metals are rather small. Selected structural parameters from the optimization are given in Table 5.

Table 5. Calculated Bond Lengths (Å) and Angles (deg) for $MCl_xCp_{3-x}(NPH(N'H_2)_2)$ and $MCl_xCp_{3-x}(NHP(N'H_2)_2)$ (TS = transition state)

M	x	M–N	P–N	P–N′ ^{a}	M–Cl	P–N–M
			NH Tautomer			
Ti	3	1.914	1.724	1.760	2.249^b	111.9
	3 (TS)	1.850	1.775	1.714	2.220^b	139.2
Zr	3	2.074	1.722	1.769	2.405^b	112.7
	3 (TS)	2.007	0.772	1.721	2.380^b	139.4
Hf	3	2.050	1.772	1.772	2.383^b	112.3
	3 (TS)	1.985	1.770	1.723	2.360^b	139.5
Ti	2	1.901	1.772	1.719	2.282^b	135.2
Zr	2	2.049	1.765	1.727	2.429^b	134.8
Hf	2	2.026	1.765	1.728	2.397^b	135.9
Ti	1	1.960	1.740	1.735	2.443	141.5
Zr	1	2.101	1.736	1.737	2.520	138.8
Hf	1	2.073	1.737	1.737	2.486	139.1
			PH Tautomer			
Ti	3	1.772	1.588	1.677	2.240^b	143.9
Zr	3	1.933	1.573	1.685	2.400^b	178.8
Hf	3	1.913	1.569	1.686	2.375^b	178.5
Ti	2	1.803	1.582	1.682	2.318^b	137.7
Zr	2	1.957	1.569	1.689	2.449^b	150.8
Hf	2	1.938	1.561	1.692	2.419^b	170.8
Ti	1	1.859	1.556	1.708	2.472	142.5
Zr	1	2.000	1.555	1.701	2.542	152.4
Hf	1	1.980	1.552	1.703	2.506	154.1

^{a} Average P–N′ distance. ^{b} Average M–Cl distance.

The calculated structures are in good agreement with the experimental findings and give support to the reliability of our results.

5. Conclusions

The syntheses and structures of different group 4 transition-metal complexes of the type $(R_2N)_2PN(H)MCp_nCl_{3-n}$ and the tautomeric $(R_2N)_2P(H)NMCp_nCl_{3-n}$ are presented. The formation of the (NH)-phosphanyl-amido or the (PH)-iminophosphorane form is dependent on the Lewis acidity of the transition-metal fragment. A stronger acidic character of the metal center stabilizes the PH form. This corresponds to the results previously obtained for similar reactions with several aluminum trialkyls and dialkylaluminum hydrides.

Computational studies ambiguously confirm the experimental results and can be summarized as follows: to stabilize the PH tautomer, a π-acceptor binding to the nitrogen atom is necessary. If this atom/fragment is only a σ-acceptor (e.g., a proton), the NH form is the energetically favored tautomer. Cyclopentadienyl ligands compete with the phosphoraneiminato ligand for the acceptor orbitals of the transition-metal atom. If the transition-metal complex fragment contains two Cp ligands, its acidity is not sufficient to stabilize the PH tautomer. For the NH–PH tautomerization, all elements of group 4 have similar acceptor strengths.

Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates for **2a**, **3a**, and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000967B