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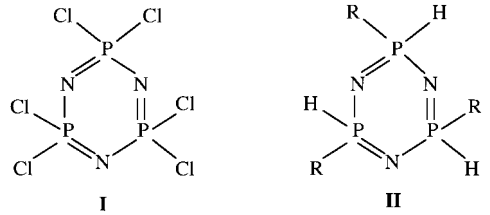
Synthesis and Crystal Structure of a *P*-Hydridophosphoraniminato–Zirconium Complex and Reaction to the First Tris(hydrido)cyclotriphosphazene**

Gerold Schick, Michael Raab, Dietrich Gudat, Martin Nieger, and Edgar Niecke*

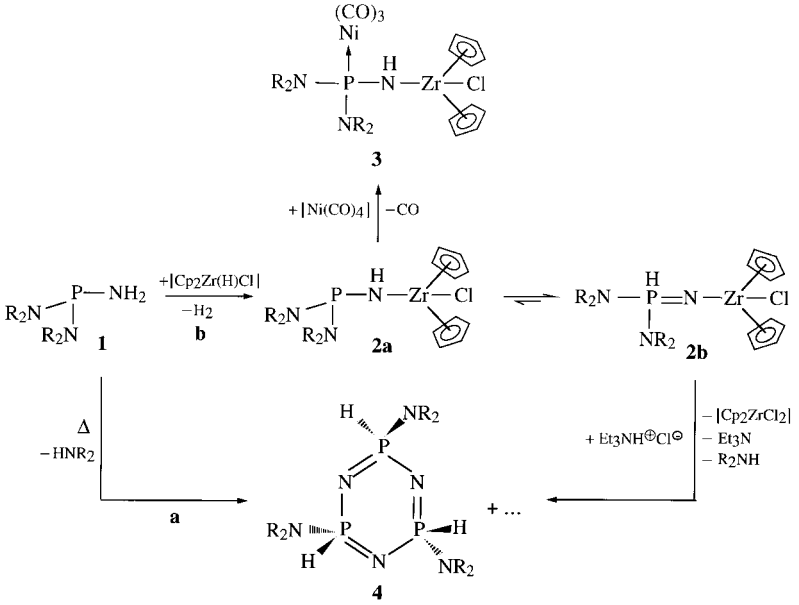
Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday

Cyclophosphazenes belong to the best characterized compounds of main group elements and play a key role in the construction of inorganic polymers.[1] In particular, ring-opening polymerization (ROP) of hexachlorocyclotriphosphazene ($Cl_2PN)_3$ (**I**) and subsequent substitution reactions give way to specifically substituted polymers whose high thermal stability and elastomeric and/or thermoplastic properties have been utilized for various special applications. In contrast, attempts to synthesize hydridocyclophosphazenes and study their reactivity are rare and have been confined to a limited number of compounds containing only a single PH functionality.[2] Here we report on the synthesis of the first representative of a tris(hydrido)cyclotriphosphazene of type **II** (according to our investigations, the previously described[3] compound $[(Me_2N)(H)PN]_3$ is actually not a cyclophosphazene, but a hydridophosphazene polymer; the synthesis and characterization of this and further poly(hydrido)phosphazenes of the type $[(R_2N)(H)PN]_n$ will be reported elsewhere[4]).



I **II**

In solution the aminophosphane **1**, which is accessible by ammonolysis of the corresponding diaminochlorophosphane,[5] decomposes at ambient temperature under cleavage of dicyclohexylamine to give mixtures of oligomeric and polymeric amino(hydrido)phosphazenes (Scheme 1, path a).[4] Chromatographic separation affords the *cis,trans,trans*-configurated cyclic trimer **4** in low yields (ca. 10%).[6] The tris(hydrido)cyclophosphazenes are obtained in higher yields by controlled cleavage of the *P*-hydridophosphoraniminato–zirconium complex **2b** with triethylammonium chloride (Scheme 1, path b).



Scheme 1. R = *cyclo*-Hexyl.

Complex **2b** is easily accessible by treatment of **1** with [Cp_2Zr(H)Cl]. The reaction proceeds by elimination of H_2 and formation of a Zr–N bond, and affords primarily a mixture of the two tautomers **2a** and **2b** in a ratio of 1:20. Compound **2b** can be isolated in pure form by crystallization at low temperature. Its reaction with tetracarbonylnickel affords in quantitative yield the phosphanylamido–$Ni(CO)_3$ complex **3**, whose formation is presumably preceeded by conversion of **2b** into the thermodynamically less favored tautomer **2a**. An intramolecular cyclization of **2a** under formation of a zirconaazaphosphirane as was recently reported by Majoral et al.[7] is not observed in this case.

The composition and constitution of **2b** and **3** follow from high-resolution mass spectra and ^{31}P, ^{1}H, and ^{13}C NMR spectra. The presence of a hydridophosphorane moiety in **2b** is proven in the ^{31}P NMR spectrum by the significant shielding of the phosphorus atom with respect to that in **1**, and by the

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occurrence of a characteristic P,H coupling (^1J(P,H) = 529 Hz).[2b, 8] The phosphanylamido configuration of the tautomer **2a** and the nickel complex **3** is suggested by the downfield shift of the ^{31}P NMR signals ($\delta = 94.0$ (**2a**), 128.1 (**3**)) and the absence of ^1J(P,H) coupling. In the case of **3**, the proposed constitution is further confirmed by observation of coupling between phosphorus and the carbonyl carbon atoms (^2J(P,C) = 2.9 Hz) and the occurrence of ν_{CO} absorptions whose frequencies (2041, 1980 cm^{-1}) and intensities are characteristic for a phosphane–Ni(CO)$_3$ complex.

The molecular structure of the zirconium complex **2b** is further proven by a crystal structure analysis (Figure 1).[9] The transition metal features a distorted tetrahedral coordination

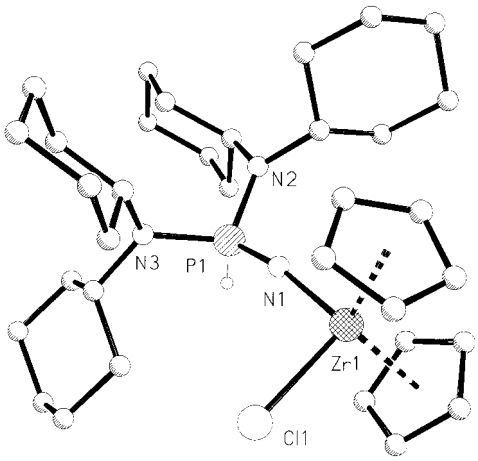

Figure 1. Structure of **2b** in the crystal. Selected bond lengths [pm] and angles [°]: Zr1–N1 195.1(3), Zr1–Cl1 247.9(1), Zr1–Cp(centroid) 224.9(2), 227.0(2), P1–N1 156.0(3), P1–N2 165.8(3), P1–N3 166.0(2); Zr1-N1-P1 165.5(2), Cl1-Zr1-N1 100.8(1), Cp1-Zr1-N1 108.2(1), Cp$_2$-Zr1-N1 107.4(1), Cp1-Zr1-Cp2 127.5(1), Cp1-Zr1-Cl 104.4(1), Cp2-Zr1-Cl 105.2(1), N1-P1-N2 110.9(1), N1-P1-N3 114.7(1), N2-P1-N3 110.3(1).

by two η^5-coordinated cyclopentadienyl ligands, a chlorine atom, and the iminato N atom. The large bond angle in the Zr1-N1-P1 fragment (165.5(2)°) and the short Zr1–N1 distance (195.1(3) pm) suggest, in accord with analogous findings in phosphoraniminato–transition metal complexes[10] as well as related alkylideneamido[11] and imido metallocenes,[12] a high share of p character in the Zr–N bond. The P1–N1 distance of 156.0(3) pm falls into the typical range for P–N double bonds[13] and thus mirrors the invariance of the P–N bond distance with respect to alterations of the metal–nitrogen bond, which is characteristic of phosphoraniminato complexes.[10] The remaining bond distances and angles display no peculiarities.

The constitution and configuration of the tris(hydrido)cyclophosphazene **4** are unequivocally proven by the results of NMR and MS studies. The observation of the ^{31}P NMR signals in the characteristic region for hydridophosphazenes[2, 8] and the occurrence of ^1J(P,H) couplings (^1J(P,H) = 589.4, 580.0 Hz) exclude a formulation as an isomeric cyclotriphosphazane. The observed A$_2$M-type splittings for the signals of the nuclei in the (PH)$_3$ moiety in both the ^{1}H{^{31}P} and ^{31}P{^{1}H} NMR spectra prove clearly a non-geminal *trans* attachment of the hydrogen atoms at the ring. Since the magnetic equivalence in the A$_2$ moieties is removed under the effect of the heteronuclear PH coupling, the ^{1}H NMR spectrum displays the more complicated splitting pattern of a [AK]$_2$NX spin system (A, N = ^{1}H; K, X = ^{31}P), whose simulation enables the determination of the magnitudes of the remaining homo- and heteronuclear coupling constants (Figure 2).

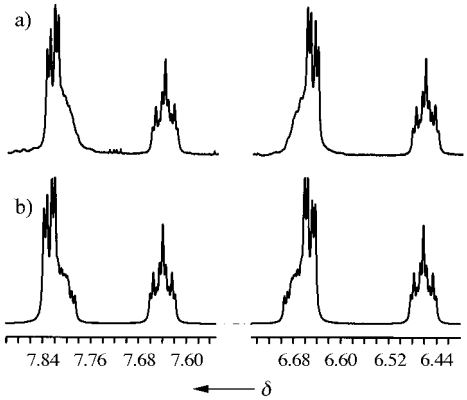

Figure 2. Experimental (a) and simulated ^{1}H NMR spectrum (b) of the P-bound protons of **4**. The parameters of the simulation are listed in the Experimental Section.

An inspection of the results of the simulation reveals remarkably large values for the ^4J(H,H) coupling constants (^4J(H,H) = −5.2 Hz (*cis*), +2.8 Hz (*trans*)); the P,H and P,P coupling constants (see the Experimental Section) are as expected.[2b, 8] The presence of chirality centers at the two isochronous phosphorus atoms leads further to a diastereotopy of the methine and methylene groups in the cyclohexyl substituents at these positions, and thus to a doubling of the corresponding ^{1}H and ^{13}C NMR signals.

Experimental Section

2b: To a solution of aminophosphane **1** (4.07 g, 10 mmol) in toluene (75 mL) is added [Cp$_2$Zr(H)Cl] (2.58 g, 10 mmol) under stirring at 25 °C, and the mixture is then stirred for 3 d under exclusion of light. Any remaining white solids are subsequently separated from the yellow solution by filtration. The filtrate is then evaporated in vacuo, and the remaining yellow air- and moisture-sensitive solid residue is recrystallized at −78 °C from pentane/diethyl ether; yield: 5.63 g (85 %). M.p. 43–46 °C (decomp); ^{31}P NMR (121.5 MHz, CDCl$_3$): $\delta = -4.7$ (dquint, ^1J(P,H) = 529, ^3J(P,H) = 16.5 Hz); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.2$ (d, ^1J(P,H) = 529 Hz, PH, 1 H), 6.1 (s, Cp, 10 H), 3.1 (m, NCH, 4 H), 1.9–0.9 (m, CH$_2$, 40 H); ^{13}C NMR (75.5 MHz, CDCl$_3$): $\delta = 112.3$ (s, Cp), 54.7 (d, ^2J(P,C) = 5.3 Hz, NCH), 35.1 (d, ^3J(P,C) = 3 Hz, NC*C*H$_2$), 35.0 (d, ^3J(P,C) = 1.7 Hz, NC*C*H$_2$), 27.7 (s, NCC*C*H$_2$), 26.4 (s, NCCC*C*H$_2$); MS (EI, 70 eV): *m*/*z* (%): 661(3) [*M*$^+$], 626 (1) [*M*$^+$ − Cl], 578 (21) [*M*$^+$ − *c*-Hex], 481 (53) [*M*$^+$ − N(*c*-Hex)$_2$], 255 (32) [Cp$_2$ZrCl$^+$], 180 (100) [N(*c*-Hex)$_2^+$].

3: To a solution of **2b** (0.63 g, 1 mmol) in toluene (10 mL) is added at 25 °C [Ni(CO)$_4$] (0.17 g, 1 mmol). After the evolution of CO has ceased, the mixture is further stirred for 12 h. The light brown solution is then evaporated in vacuo, and the colorless air- and moisture-sensitive residue recrystallized from diethyl ether at −78 °C; yield: 0.70 g (87 %). M.p. 137 °C (decomp); ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): $\delta = 128.1$ (s); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 6.3$ (s, Cp, 10 H), 3.4 (m, NCH, 4 H), 2.2 (d, ^2J(P,H) = 2.9 Hz, NH, 1 H) 1.9–1.0 (m, CH$_2$, 40 H); ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): $\delta = 197.4$ (d, ^2J(P,C) = 2.7 Hz, CO), 114.5 (s, Cp), 57.0 (d, ^2J(P,C) = 14.1 Hz, NCH), 37.1 (d, ^3J(P,C) = 1.5 Hz, NC*C*H$_2$), 34.8 (d, ^3J(P,C) = 1.5 Hz, NC*C*H$_2$), 27.9, 27,7 (s, NCC*C*H$_2$), 26.5 (s, NCCC*C*H$_2$); IR: $\tilde{\nu}_{CO}$ (cm^{-1}) = 2041, 1980.

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4: a) Aminophosphane **1** (5 g) is dissolved in a mixture of pentane (150 mL) and diethyl ether (50 mL), and the resulting solution is stirred for 2 d at ambient temperature. After all volatile components have been removed in vacuo, the obtained crude product mixture is subjected to chromatography on silica gel that has been pretreated with chlorotrimethylsilane. Elution with pentane furnishes **4** ($R_f = 0.9$) as a colorless solid; yield: 0.2 g (10.5 %). M.p. 80 °C. b) Alternatively, the zirconium complex **2b** (4 g, 6 mmol) is dissolved in diethyl ether (150 mL) and treated at ambient temperature under stirring with triethylammonium chloride (0.83 g, 6 mmol). After the mixture has been stirred for 4 h, all volatile components are removed in vacuo, and the remaining solid residue is extracted with pentane. The combined extracts are evaporated to dryness, and **4** is obtained after chromatographic workup as described above; yield: 0.29 g (23 %). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 4.7$ (t, $^2J(P,P) = 17.6$ Hz, P_X), -0.5 (d, $^2J(P,P) = 17.6$ Hz, P_K); $^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): $\delta = 7.23$ (d, $^4J(H,H) = 2.7$ Hz, 2H, H_A), 7.05 (t, $^4J(H,H) = 2.7$ Hz, 1H, H_N); ^1H NMR (500 and 300 MHz, $CDCl_3$): $\delta = 7.23$ (m, 2H, H_A), 7.05 (m, 1H, H_N), (iteration with WINDAISY gave the following coupling constants (the signs given are based on a positive sign for $^1J(P,H)$): $^1J(P_K,H_A) = +580.0$, $^3J(P_X,H_A) = +6.4$, $^3J(P_K,H_A) = +8.8$, $^4J(H_A,H_A) = -5.2$, $^4J(H_A,H_N) = +2.8$, $(^2J(P_K,P_K) = +10.6$, $^2J(P_K,P_X) = +16.9$, $^1J(P_X,H_N) = +589.4$, $^3J(P_K,H_N) = +7.8)$, 3.1 (m, $|^3J(P,H) + ^5J(P,H)| = 6$, $^3J(H,H) = 11.7$, 3.6 Hz, NC*H*, 4H), 3.0 (dtt, $^3J(P,H) = 8$, $^3J(H,H) = 11.7$, 3.5 Hz, NC*H*, 2H), 1.9 – 0.9 (m, CH_2, 60H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 54.9$ (d, $^2J(P,C) = 5.4$ Hz, NC*N*), 54.2 (pseudo t, $|^2J(P,C) + ^4J(P,C)| = 5.4$ Hz, NC*N*), 34.4 (pseudo t, $|^3J(P,C) + ^5J(P,C)| = 1.5$ Hz, NCCH_2), 34.3 (d, $^3J(P,C) = 3.2$ Hz, NCCH_2), 34.1 (pseudo t, $|^3J(P,C) + ^5J(P,C)| = 1.5$ Hz, NC*C*H_2), 27.25, 27.20, 27.15 (s, NCCCH_2), 26.3, 26.2 (s, NCCCCH_2); MS (EI, 70 eV): *m/z* (%): 678 (1) [M^+], 595 (2) [$M^+ - c$-Hex], 498 (7) [$M^+ - N(c\text{-Hex})_2$], 180 (100) [$N(c\text{-Hex})_2^+$]; HR-MS (EI, 70 eV): calcd for $C_{36}H_{69}N_6P_3$: 678.4797, found: 678.4797.

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Catalytic Asymmetric Allenylation: Regulation of the Equilibrium between Propargyl- and Allenylstannanes during the Catalytic Process**

Chan-Mo Yu,* Sook-Kyung Yoon, Kwangwoo Baek, and Jae-Young Lee

Dedicated to Professor Elias J. Corey on the occasion of his 70th birthday

The availability of efficient synthetic methods for achieving absolute stereoselectivity by catalytic processes in the production of enantiomerically pure compounds is of considerable current interest because such products can be used as chiral building blocks for the synthesis of valuable chiral substances.[1] In this regard, allyl-transfer reactions provide excellent stereoselective routes for converting aldehydes into the corresponding alcohols.[2] Subsequent to early studies by Hoffmann et al.[3] on the use of chirally modified allyl boranes to accomplish asymmetric induction, many research groups have made important contributions to the extension of this

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