# Syntheses and Reactivity of Aminobis(diorganylamino)phosphanes☆

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Aminobis(diorganylamino)phosphanes $(R_2N)_2PNH_2$ (R = *i*Pr, c-Hex, Ph) (**2a–c**), were obtained by treatment of the corresponding chlorobis(diorganylamino)phosphanes **1a–c** with lithium amide in liquid ammonia. The transition metal phosphane complex $(R_2N)_2(H_2N)PNi(CO)_3$ (**3**) was prepared by reaction of **2a** with tetracarbonylnickel. *N*-Complexation of **2a** with trimethylalane affords the iminophosphorane–alane adduct $(R_2N)_2HP{=}N(H)AlMe_3$ (**4**) by 1,2-H shift from the nitrogen to the phosphorus atom. The corresponding reaction with aluminium trichloride leads to the formation of the salt $[(R_2N)_2HP{=}N(H)]_2AlCl_2^+[AlCl_4]^-$ (**5**), in which two iminophosphorane moieties are linked by an $AlCl_2$ bridge. Lithiation of **2a** and subsequent reaction with titanocene dichloride result in nucleophilic replacement of one chlorine atom to give the phosphanylamido-substituted titanocene compound $(R_2N)_2P{-}N(H)Ti(Cl)Cp_2$ (**6a**), which rearranges to its *P*-hydroiminophosphorane tautomer $(R_2N)_2P(H){=}NTi(Cl)Cp_2$ (**6b**) on gentle heating. No isomerisation was observed in the case of *N*-borylated aminophosphane $(R_2N)_2P{-}NH{-}(9\text{-}BBN)$ (**7**), obtained by reaction of lithiated **2a** with *B*-Cl-9-BBN. The X-ray structure analyses of compounds **2b**, **c**, **3**, **4**, **5**, and **6a** are discussed.

In the past triaminophosphanes have been the subject of extensive studies[1]. The ready availability of substituted triaminophosphanes $(R_2N)_3P$ by reaction of $PCl_3$ with secondary amines[2], their versatile reactivity and their properties as complex ligands[3] characterise them as valuable synthons in organophosphorus chemistry. Amongst other reactions, oxidation to phosphoranes[4] and phosphonium salts[5], transesterification and transamination reactions[4] as well as displacement reactions with hydrogen halides and boron halides furnishing the corresponding aminohalophosphanes[6] have been described. In contrast, analogous triaminophosphanes derived from primary amines $(RHN)_3P$ lack thermal stability, due to facile amine elimination at ambient temperature, which leads to condensation reactions[7]. Parent triaminophosphane $(H_2N)_3P$ was postulated as an intermediate of the complete ammonolysis of phosphorus trichloride[8]. However, there is no spectroscopic evidence known for this species. Elimination of ammonia results in the formation of not well-defined solids of varying composition. Mention should be made that thermally stable transition metal complexes $(H_2N)_3PM(CO)_5$ (M = Cr, Mo, W) are well-known[9]. Mixed aminophosphanes of the type $(R_2N)_{3-x}P(NH_2)_x$ ($x$ = 1, 2) have not been described so far. Formation of polymeric not well-defined products was reported for the ammonolysis of $(Ph_2N)PCl_2$[10], whilst oligomeric hydridophosphazenes were obtained by treatment of ammonia with $(Me_2N)_2PCl$, which themselves easily undergo condensation reactions at ambient temperature[11].

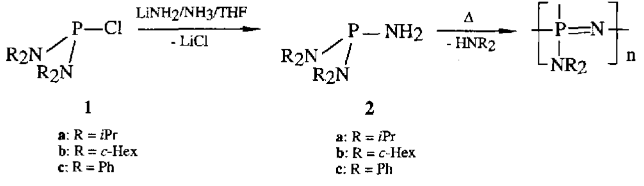
Recognizing the potential synthetic utilily of triaminophosphanes bearing $NH_2$ groups as substituents with respect to an additional reactive site, we have focussed our attention on the stabilisation of such species by introduction of sterically protecting diorganylamino groups[12] into the molecules.

In this paper we report on the synthesis, crystal structure, and reactivity of the first aminobis(diorganylamino)phosphanes $(R_2N)_2P{-}NH_2$.

## Results and Discussion

The reactions of the bis(diorganylamino)chlorophosphanes **1a–c** with lithium amide in liquid ammonia at −35 °C afforded the corresponding aminobis(diorganylamino)phosphanes **2a–c** which were isolated as an air- and moisture-sensitive, colourless oil (**2a**) or colourless crystals (**2b, c**) (Scheme 1). The compounds can be stored at low temperatures for weeks without decomposition. However, in solution at ambient temperature they slowly undergo condensation reactions to give oligomeric and polymeric hydridophosphazenes[13] by elimination of the corresponding diorganylamine. Elimination of ammonia and formation of diphosphanylamines $R_2P{-}NH{-}PR_2$ as reported for $Me_2PNH_2$[2c] or $Ph_2PNH_2$[14] were not detected in the case of compounds **2a–c**.

Scheme 1



Their constitution became evident from multinuclear NMR investigations. The replacement of the chlorine atom in the chlorophosphanes **1a**–**c** by the amido group causes a significant downfield shift of the phosphorus atom signal in the $^{31}$P-NMR spectrum (**2a**: $\Delta\delta = 62.0$, $\delta = 77.0$; **2b**: $\Delta\delta = 64.0$, $\delta = 80.4$; **2c**: $\Delta\delta = 52.0$, $\delta = 71.5$), as observed in the case of tris(diorganylamino)-substituted derivatives[15]. The presence of the $NH_2$ group in **2c** is evidenced by the coupling of the two amino protons with the phosphorus atom ($^2J_{PH} = 17.1$ Hz). This coupling was not observed in the case of compound **2a** or **2b**, which might be the result of a fast intermolecular proton exchange.

Suitable crystals of compounds **2b** and **c** for X-ray structure analyses were obtained from pentane/diethyl ether at −78 °C. Their structures are given in Figures 1 and 2 and selected structural parameters are listed in Table 1. The geometry around the phosphorus atom in **2b** and **c** is distorted trigonal-pyramidal (**2b**: Σ P1: 307°, **2c**: Σ P1: 306°), with typical P(III)−N[16] bond lengths. Whilst in **2b** the P−N bond lengths between the phosphorus atom and the two $R_2N$ groups [P1−N2: 169.1(2), P1−N3: 169.5(2)] are slightly shorter than the bond length between the phosphorus and the nitrogen atom of the $NH_2$ group [P1−N1: 172.2(2)], the situation is reversed in **2c** [P1−N1: 167.0(2), P1−N2: 173.4(2), P1−N3: 173.3(2)]. In contrast to the nitrogen atoms in the diorganylamino groups, which exhibit a planar geometry (**2b**: Σ N2: 360°, Σ N3: 360°; **2c**: Σ N2: 359°, Σ N3: 360°), the nitrogen atoms of the $NH_2$ groups show a distinct pyramidalisation (**2b**: Σ N1: 326°; **2c**: Σ N1: 347°). Two molecules of **2b** are connected by van der Waals contacts between the phosphorus atom and one of the hydrogen atoms of the $NH_2$ group (288 pm). In **2c** the intramolecular distances between one NH proton and the carbon atoms of one phenyl group (H1···C1−C6: 280−331 pm) lie in the range of the sum of the van der Waals radii.

Figure 1. Molecular structure of aminophosphane **2b** in the solid state. C−H hydrogen atoms are omitted for clarity, second molecule generated by transformation $-x$, $1 - y$, $-z$

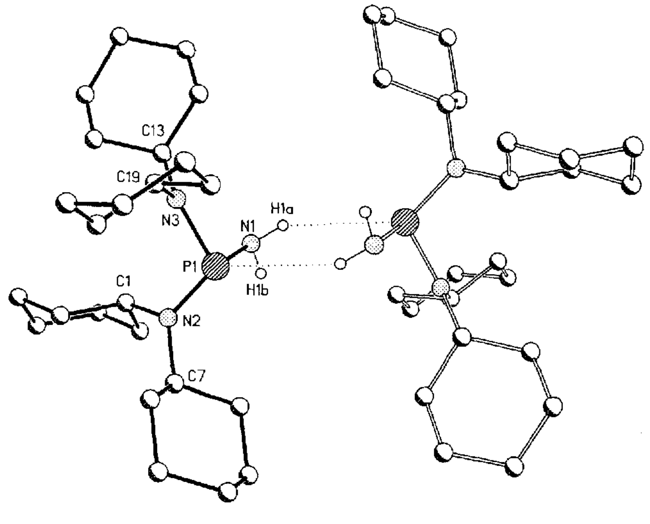


Figure 2. Molecular structure of aminophosphane **2c** in the solid state. C−H hydrogen atoms are omitted for clarity, second molecule generated by transformation $1 - x$, $1 - y$, $1 - z$

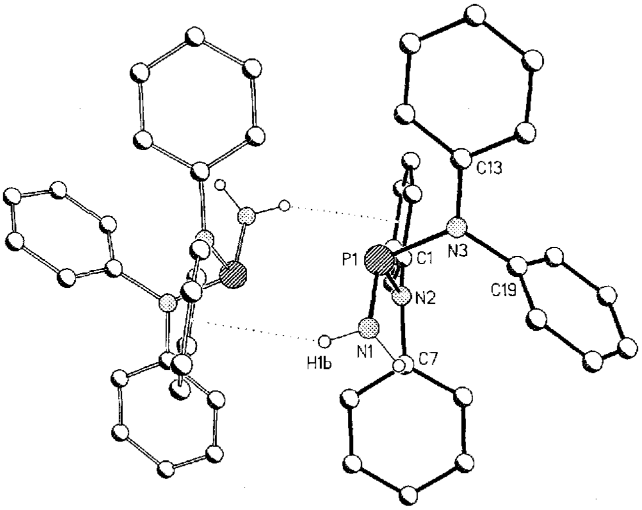


Table 1. Selected bond lengths [pm] and bond angles [°] of compounds **2b**, **2c**, **3**, and **6a**

| | **2b** | **2c** | **3** | **3′** | **6a** |
|---|---|---|---|---|---|
| P1-N1 | 172.2(2) | 167.0(2) | 168.3(2) | 168.1(3) | 172.3(3) |
| P1-N2 | 169.1(2) | 173.4(2) | 169.2(2) | 169.5(2) | 169.4(3) |
| P1-N3 | 169.5(2) | 173.3(2) | 168.4(3) | 168.6(2) | 169.7(3) |
| Σ° P1 | 307 | 306 | – | – | 312 |
| Σ° N1 | 326 | 347 | 324 | 330 | 359 |
| Σ° N2 | 360 | 359 | 356 | 356 | 359 |
| Σ° N3 | 360 | 360 | 360 | 360 | 360 |
| N1-P1-N2 | 98.7(1) | 102.5(1) | 101.7(1) | 98.7(1) | 102.7(2) |
| N1-P1-N3 | 97.4(1) | 102.4(1) | 106.3(1) | 109.5(1) | 101.6(1) |
| N2-P1-N3 | 110.6(1) | 100.7(1) | 103.0(1) | 102.5(1) | 107.2(2) |
| N-C[a] | 148 | 143 | 148 | 148 | 148 |
| Ni1-P1 | – | – | 224.4(1) | 223.8(1) | – |
| Ti1-N1 | – | – | – | – | 193.7(3) |
| Ti-Cp (centroid[b]) | – | – | – | – | 209 |
| T1-Cl1 | – | – | – | – | 242.1(1) |
| P1-N1-Ti1 | – | – | – | – | 141.5(2) |
| N1-Ti1-Cl1 | – | – | – | – | 96.8(1) |

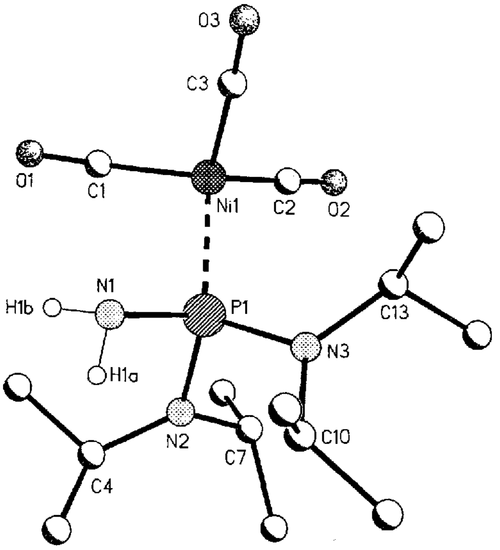
[a] Average N−C bond lengths are given. – [b] Average Ti−Cp(centroid) distance.

Due to facile elimination of amine all attempts to crystallise **2a** have failed so far. However, the corresponding phosphane complex **3**, obtained by treatment of **2a** with tetracarbonylnickel, was isolated by crystallisation from toluene as colourless crystals suitable for an X-ray analysis (Figure 3).

Two indepent, nearly identical molecules are found in the asymmetric unit of phosphane complex **3**. The phosphorus and the nickel atom exhibit a distorted tetrahedral environment, and the three P−N bond lengths vary only slightly around the average bond length of 169 pm (Table 1). The structural parameters of the P−Ni(CO)$_3$ moiety are consistent with those reported previously for (CO)$_3$Ni-phosphane complexes[17].

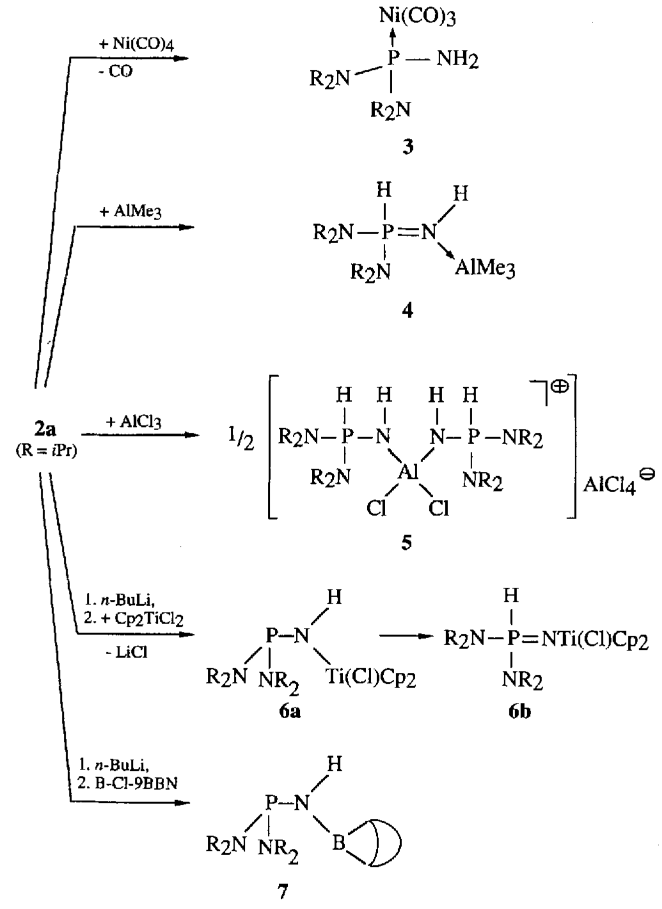
In contrast to the transition metal fragment, which attacks the phosphorus atom, a hard Lewis acid should prefer a complexation via the nitrogen atom of the amino group. This expectation was verified by reaction of **2a** with $AlMe_3$ in pentane at −78 °C and resulted in the formation of the *P*-hydrophosphoranimine-*N*−alane adduct **4** (Scheme 2).

Figure 3. Molecular structure of one of the crystallographically independent molecules of **3**. C–H hydrogen atoms are omitted for clarity



Coordination of the Lewis acid at the less sterically protected nitrogen atom of the $NH_2$ group with subsequent hydrogen shift from the nitrogen to the phosphorus atom was also observed in the reaction of **2a** with $AlCl_3$. However, here the salt $[(R_2N)_2HP{=}N(H)]_2AlCl_2^+$ $[AlCl_4]^-$ (**5**) was formed (Scheme 2).

Scheme 2

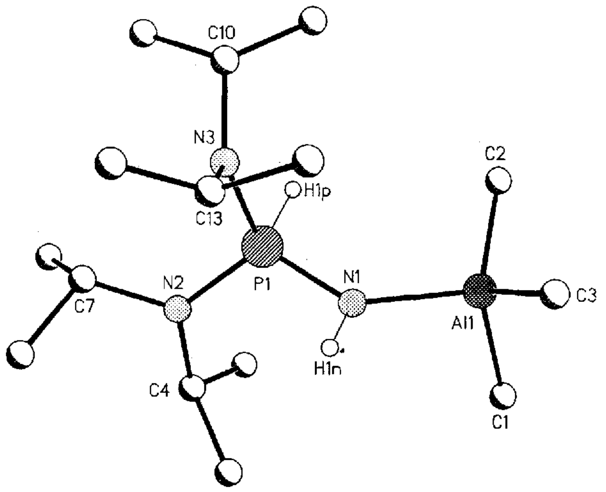


The isomerisation of N–H aminophosphanes $R_2PN(H)R'$ to the corresponding P–H iminophosphoranes $R_2P(H)NR'$ has been the subject of several theoretical and experimental investigations[18]. The relative stability of both isomers is known to be dependent on the steric as well as the electronic influences exerted by the substituents R and R′. Electron-withdrawing groups R′ such as $SO_2C_6H_4CH_3$ and $PS(OC_6H_5)_2$ as well as bulky substituents R and R′ are known to stabilize the P–H isomer. To the best of our knowledge, compounds **4** and **5** are the first examples in which the rearrangement of an aminophosphane to its phosphorane tautomer is induced by complexation by Lewis acids at the nitrogen lone pair[19].

Diagnostic of the 1,2-hydrogen shift from the nitrogen to the phosphorus atom in compound **4** are the high-field shift of the $^{31}$P-NMR signal ($\delta = 13.7$) and the characteristic PH coupling constant[20] ($^1J_{PH} = 563.3$ Hz). In the $^1$H-NMR spectrum the proton bound directly to the phosphorus atom gives rise to a doublet of doublets ($\delta = 7.05$, $^1J_{PH} = 563.3$, $^3J_{HH} = 11.9$ Hz), which clearly indicates a species with the $(>N)_2P(H)NH$- moiety. Very similar $^{31}$P- and $^1$H-NMR spectra were observed for compound **5** ($^{31}$P-NMR: $\delta = 13.8$; $^1$H NMR: $\delta = 7.22$, $^1J_{PH} = 578.6$, $^3J_{HH} = 10.8$ Hz).

The formation of the salt **5** in solution becomes apparent from the $^{27}$Al-NMR spectrum which shows the characteristic signal of $AlCl_4^-$ ($\delta = 101.2$). The Al nuclei in the cation gives rise to a broadened resonance at $\delta = 100.2$. Single crystals of products **4** and **5** were obtained by recrystallisation from dichloromethane and dichloromethane/pentane. Their molecular structures were verified by X-ray structure analyses to be bis(diisopropylamino)phosphane imine-*N*-trimethylalane (**4**) and bis[bis(diisopropylamino)-phosphane iminato]dichloroaluminium(III) tetrachloroaluminate(III) (**5**) (Figures 4 and 5).

Figure 4. Molecular structure of the alane adduct **4**. C–H hydrogen atoms are omitted for clarity



Whereas the structure of compound **4** proves the formation of a *P*-hydrophosphane imine–$AlMe_3$ adduct, two equivalents of both **2a** and $AlCl_3$ react to give the salt **5**.

Figure 5. Molecular structure of **5**. C−H hydrogen atoms are omitted for clarity

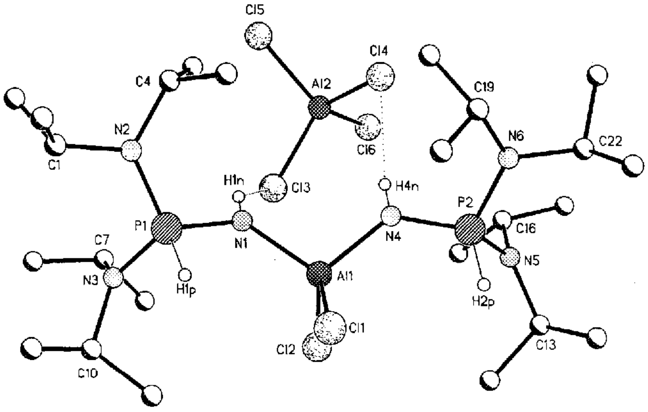


Table 2. Selected bond lengths [pm] and bond angles [°] of compounds **4** and **5**

| Bond | 4 | 5 | Bond angle | 4 | 5 |
|---|---|---|---|---|---|
| P1-N1 | 154.9(5) | 161.7(6) | P1-N1-Al1 | 136.4(3) | 130.4(4) |
| P2-N4 | – | 161.0(6) | P2-N4-Al1 | – | 128.1(4) |
| P1-N2 | 162.3(4) | 162.6(6) | N1-P1-N2 | 113.7(3) | 109.9(3) |
| P1-N3 | 161.4(4) | 1.626(6) | N1-P1-N3 | 121.8(3) | 118.0(4) |
| P2-N5 | – | 162.4(6) | N2-P1-N3 | 109.2(2) | 107.2(3) |
| P2-N6 | – | 165.1(6) | N4-P2-N5 | – | 117.8(3) |
| Al1-N1 | 192.8(6) | 184.7(7) | N4-P2-N6 | – | 109.5(3) |
| Al1-N4 | – | 184.9(6) | N5-P2-N6 | – | 108.8(3) |
|  |  |  | N1-Al1-N4 | – | 106.8(3) |

The cation in **5** consists of two phosphane imine groups, which are linked by their imine nitrogen atoms by a bridging $AlCl_2$ group. The anion $[AlCl_4]^-$ shows only a slight deviation from the ideal tetrahedral geometry, whereby two chlorine atoms participate in the formation of weak Cl−H−N hydrogen bonds (N1−C13: 351, N4−C14: 360 pm). The imine hydrogen atoms and the P−H hydrogen atoms adopt an almost antiperiplanar conformation in both compounds.

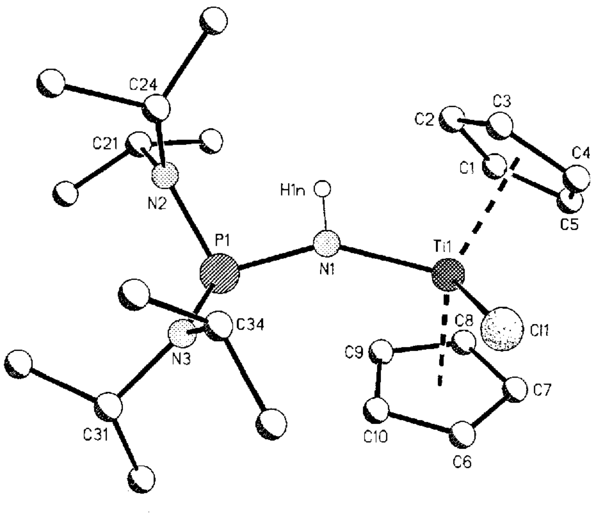
Whilst the Al−N bond length (Table 2) in **4** [192.8(6) pm] is of similar magnitude as reported for compounds containing an imine nitrogen−aluminium moiety [$(Me_2CNAlMe_2)_2$: 195.5, 193.0 pm[21]; $N(PPh_2NSiMe_3)_2AlMe_2$: 194.0 pm[22]], the Al−N bond lengths in **5** are significantly shortened [184.7(7), 184.9(6) pm]. The situation is reversed in the case of the P−N(H) bond lengths for both compounds [**4**: 154.9(5); **5**: 161.7(6), 161.0(6) pm]. The bond lengths between the phosphorus and the two nitrogen atoms of the diorganylamino groups differ only slightly for both compounds [**4**, **5**: 163 pm (average)]. These results reflect a different extent of polarisation in the P−N−Al fragment in both compounds. The further bond lengths and angles show no particularity.

Replacement of the hydrogen at the $NH_2$ group in **2a** by a transition metal fragment was easily achieved by metallation with *n*-butyllithium (at −30 °C in THF) and subsequent reaction with a transition metal halide. For **2a** and titanocene dichloride this afforded the titanocene complex **6a** (Scheme 2), which was isolated by crystallisation from diethyl ether as dark red crystals. On gentle heating to 40 °C, **6a** slowly rearranges in solution to the thermodynamically more stable *P*-hydrophosphane iminato isomer **6b**.

The rearrangement of **6a** to its phosphorane tautomer **6b** was unambiguously proven by a significant shielding of the phosphorus atom (**6a**: $\delta = 98.6$; **6b**: $\delta = -3.9$) as well as the characteristic PH coupling constant ($^1J_{PH} = 521.4$ Hz).

The results of an X-ray structure analysis of the titanocene complex **6a** are illustrated in Figure 6, and selected structural parameters are given in Table 1. The P−N bond lengths and angles in **6a** differ only slightly from those in **2b** except for the planarity at the titanium-bound nitrogen (Σ N1: 359°). The Ti−N bond length of 193.7(3) pm is significantly shorter than those found in the related compound $(\eta^5\text{-Cp})_2\text{Ti}(\eta^1\text{-NC}_4\text{H}_4)_2$[23] (208.5 pm). The planarity at N1, the short Ti−N bond, the nearly eclipsed conformation of the lone pair at N1 and the chlorine atom indicate $p_\pi$-$d_\pi$ interaction between titanium and nitrogen. The preference of this conformation was predicted by Lauher and Hoffmann[24] for $Cp_2M(NR_2)L'$ complexes (L′ = non π-donor ligand) and is explained in terms of a π-back donation from the N lone pair to an empty $a_1$ orbital of the bent titanocene unit.

Figure 6. Molecular structure of **6a**. C−H hydrogen atoms are omitted for clarity



A proton transfer from N to P was not observed in the case of the *N*-borylated phosphane **7**, which was obtained by treatment of lithiated **2a** with *B*-Cl-9-BBN at −78 °C in THF (Scheme 2). The higher thermodynamic stability of aminophosphane **7** compared to its P−H isomer was already demonstrated by Bertrand et al., who observed the formation of analogous *N*-borylated aminophosphanes by hydrogen transfer from the corresponding *P*-hydrophosphane iminato isomer, obtained by reaction of bis(diorganylamino)phosphanyl azides with trialkylboranes[25]. The structure of **7** was derived from its NMR spectroscopic data, which are in accordance with those found for compounds of the type $(iPr_2N)_2P{-}NH{-}BR_2$.

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## Experimental

All manipulations were carried out with the exclusion of air and moisture under argon. Solvents were dried by using standard procedures. The bis(diorganylamino)chlorophosphanes **1a**[2b], **1b**[26], **1c**[27], and *B*-Cl−9-BBN[28] were prepared by literature methods. Tetracarbonylnickel, $\mathrm{Ni(CO)_4}$, dichlorobis(cyclopentadienyl)titanium(IV), $\mathrm{Cp_2TiCl_2}$, trimethylalane, $\mathrm{AlMe_3}$ (2 M in toluene), and aluminium trichloride were used as supplied. – NMR: Bruker AMX 300; $^{31}$P: 121.5 MHz, external standard 85% $\mathrm{H_3PO_4}$; $^{1}$H: 300.1 MHz, external standard TMS; $^{13}$C: 75.5 MHz, external standard TMS; $^{11}$B: 96.3 MHz, external standard $\mathrm{BF_3 \cdot O(C_2H_5)}$; $^{27}$Al: 300.1 MHz, $\mathrm{Al(H_2O)_6^{3+}}$ external standard; positive signs denote shifts to lower frequencies. – MS: Kratos Instruments Concept 1H, Kratos Instruments, MS 50, VG Instruments VG 12-250 (EI, 70 eV). – Melting points were determined in sealed glass capillaries and are uncorrected.

*Aminobis(diisopropylamino)phosphane* (**2a**), *Aminobis(dicyclohexylamino)phosphane* (**2b**), *und Aminobis(diphenylamino)phosphane* (**2c**): To a suspension of 15 ml of $\mathrm{LiNH_2}$ (1.1 g) in 75 ml of liquid ammonia a solution of 50 mmol of **1** (**a**: 13.3 g; **b**: 21.3 g; **c**: 20.1 g) in 25 ml of THF is slowly added at −40°C. After stirring of the combined solutions at −35°C for some time (**a**: 45 min; **b**: 6 h; **c**: 45 min) the ammonia is evaporated and the organic solvent removed under reduced pressure. To the remaining residue 30 ml of pentane (**c**: pentane/toluene, 1:1) is added, the precipitated LiCl is filtered off and the solvent removed under reduced pressure. Pure **2b** and **2c** are obtained as colourless solids by recrystallisation from diethyl ether at −78°C, whereas the liquid **2a** is purified by distillation at $10^{-3}$ Torr at 45−50°C.

**2a**: Yield: 16.8 g (68%), b.p. 40−43°C/$10^{-3}$ Torr. – $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta$ = 77.0 (s). – $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta$ = 44.2 (d, $^{2}J_{\mathrm{CP}}$ = 12.2 Hz, PNC), 25.1 (d, $^{3}J_{\mathrm{CP}}$ = 8.6 Hz, $\mathrm{CH_3}$). – $^{1}$H NMR ($\mathrm{C_6D_6}$): $\delta$ = 3.6 (m, 4H, CH), 1.1 (d, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, 24H, $\mathrm{CH_3}$), $\mathrm{NH_2}$ not detected.

**2b**: Yield: 14.6 (72%), m.p. 43−45°C (dec.). – $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta$ = 80.4 (s). – $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta$ = 54.5 (d, $^{2}J_{\mathrm{CP}}$ = 9.9 Hz, PNC), 36.6 (d, $^{3}J_{\mathrm{CP}}$ = 8.4 Hz, $\mathrm{NC}C$), 35.3 (d, $^{3}J_{\mathrm{CP}}$ = 6.8 Hz, $\mathrm{NC}C$), 27.9 (s, $\mathrm{NCC}C$), 27.7 (s, $\mathrm{NCC}C$), 26.6 (s, $\mathrm{NCCC}C$). – MS (180°C/70 eV), *m*/*z* (%): 407 (6) [$\mathrm{M^+}$], 324 (1) [$\mathrm{M^+ - C_6H_{11}}$], 227 (52) [$\mathrm{M^+ - N(C_6H_{11})_2}$], 181 (55) [$\mathrm{HN(C_6H_{11})_2^+}$], 138 (100) [$\mathrm{NC_9H_{16}^+}$], and other fragments. – $\mathrm{C_{24}H_{46}N_3P}$: calcd. 407.3429; found 407.3441 (MS).

**2c**: Yield: 13.6 g (67%), m.p. 72−76°C (dec.). – $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta$ = 71.5 (s). – $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta$ = 146.3 (d, $^{2}J_{\mathrm{CP}}$ = 8.7 Hz, PNC), 129.8 (s, C-*p*-ph), 125.3 (d, $^{3}J_{\mathrm{CP}}$ = 8.4 Hz, C-*o*-ph), 123.8 (d, $^{4}J_{\mathrm{CP}}$ = 0.9 Hz, C-*m*-ph). – $^{1}$H NMR ($\mathrm{C_6D_6}$): $\delta$ = 7.25−6.95 (m, 20H, Ph), 1.70 (d, $^{2}J_{\mathrm{HP}}$ = 17.1 Hz, 2H, $\mathrm{NH_2}$).

*[Aminobis(diisopropylamino)phosphane]tricarbonylnickel(0)* (**3**): To a solution of 2.47 g (10 mmol) of **2a** in 15 ml of toluene 17 mg (10 mmol) of tetracarbonylnickel(0) is quickly added, and the mixture is stirred for 20 min. The resulting solution is stored for several days at −80°C. The separated colourless crystals of **3** are collected by filtration. Yield: 2.3 g (59%), m.p. 20°C. – $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta$ = 125.6 (s). – $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta$ = 197.7 (s, CO), 191.9 (s, CO), 46.7 (d, $^{2}J_{\mathrm{CP}}$ = 14.1 Hz, PNC), 23.5 (d, $^{3}J_{\mathrm{CP}}$ = 2.1 Hz, $\mathrm{C}C\mathrm{H_3}$). – $^{1}$H NMR ($\mathrm{C_6D_6}$): $\delta$ = 3.84 (m, 4H, CH), 1.97 [s (b), 2H, $\mathrm{NH_2}$], 1.23 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 24H, $\mathrm{CH_3}$). – MS (180°C/70 eV), *m*/*z* (%): 389 (5) [$\mathrm{M^+}$], 361 (30) [$\mathrm{M^+ - CO}$], 247 (9) [$\mathrm{M^+ - Ni(CO)_3}$], 147 (100) [$\mathrm{M^+ - Ni(CO)_3 - N(C_3H_7)_2}$], and other fragments.

*Bis(diisopropylamino)phosphane Imine-N−Trimethylalane* (**4**): To a solution of 1.8 g (7.3 mmol) of **2a** in 40 ml of pentane 3.7 ml (7.3 mmol, 2 M in hexane) of $\mathrm{AlMe_3}$ is added dropwise at −78°C. While stirring the reaction mixture is allowed to warm up to room temp. The resulting white precipitate of **4** is filtered off, dried in vacuo and recrystallised from a small amount of dichloromethane. Yield 1.74 g (75%), m.p. 123−125°C (dec.). – $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta$ = 13.7 (s). – $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta$ = 46.2 (d, $^{2}J_{\mathrm{CP}}$ = 5.34 Hz, PNC), 23.8 (d, $^{3}J_{\mathrm{CP}}$ = 2.7 Hz, $\mathrm{C}C\mathrm{H_3}$), 22.2 (d, $^{3}J_{\mathrm{CP}}$ = 2.7 Hz, $\mathrm{C}C\mathrm{H_3}$), −5.5 [s (b), $\mathrm{AlCH_3}$]. – $^{1}$H NMR ($\mathrm{C_6D_6}$): $\delta$ = 7.05 (dd, $^{1}J_{\mathrm{HP}}$ = 563.3, $^{3}J_{\mathrm{HH(imine)}}$ = 11.9 Hz, 1H, PH), 3.18 (d sept, $^{3}J_{\mathrm{HP}}$ = 17.1, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 4H, CH), 1.09 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 12H, $\mathrm{CCH_3}$), 0.96 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 12H, $\mathrm{CCH_3}$), −0.1 [s (b), 9H, $\mathrm{AlCH_3}$].

*Bis[bis(diisopropylamino)phosphane iminato]dichloroaluminium(III) Tetrachloroaluminate(III)* (**5**): To a solution of 0.56 g (2.3 mmol) of **2a** in 30 ml of dichloromethane 0.3 g (2.3 mmol) of $\mathrm{AlCl_3}$ of $\mathrm{AlCl_3}$ is added at −78°C. While stirring the reaction mixture is allowed to warm up to room temp. After evaporation of the solvent, **5** is obtained as a white powder and recrystallised from dichloromethane/pentane/toluene (1:1:1). Yield: 0.31 g, m.p. 162−165°C (dec.). – $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta$ = 13.8 (s). – $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta$ = 47.3 [s, (b), PNC], 24.3 (s, $\mathrm{C}C\mathrm{H_3}$), 23.3 (s, $\mathrm{C}C\mathrm{H_3}$). – $^{1}$H NMR ($\mathrm{C_6D_6}$): $\delta$ = 7.22 (dd, $^{1}J_{\mathrm{HP}}$ = 578.6, $^{3}J_{\mathrm{HH(imine)}}$ = 10.9 Hz, 2H, PH), 3.45 (d sept, $^{3}J_{\mathrm{HP}}$ = 17.1, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 8H, CH), 1.19 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 24H, $\mathrm{CCH_3}$), 1.13 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 24H, $\mathrm{CCH_3}$). – $^{27}$Al NMR: $\delta$ = 101.2 ($\mathrm{AlCl_4^-}$), 100.2 ($\mathrm{AlCl_2}$).

*[Bis(diisopropylamino)phosphanylamido]chlorobis(cyclopentadienyl)titanium(IV)* (**6a**) *and [Bis(diisopropylamino)phosphane imido]chlorobis(cyclopentadienyl)titanium(IV)* (**6b**): To a solution of 0.46 g (1.9 mmol) of **2a** in 20 ml of THF 1.8 ml (1.9 mmol, 1.6 M in *n*-hexane) of *n*-butyllithium is added at −40°C. The reaction mixture is allowed to warm up to −15°C, then a solution of 0.47 g (1.9 mmol) of $\mathrm{Cp_2TiCl_2}$ in 30 ml of THF is added rapidly. The resulting dark red solution is stirred for 1 h, then the organic solvent is removed in vacuo. To the residue 30 ml of pentane/toluene (1:1) is added. The precipitated LiCl is filtered off and the solvent removed in vacuo. **6a** is recrystallised from diethyl ether at −30°C. If the reaction solution is gently heated at 30°C for 4 h, **6a** rearranges to compound **6b**. The rearrangement is accompanied by partial decomposition of **6a**.

**6a**: Yield: 0.46 g (53%), m.p. 139°C (dec.). – $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta$ = 98.9 (s). – $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta$ = 114.5 (s, C-cp), 45.6 (d, $^{2}J_{\mathrm{CP}}$ = 11.4 Hz, PNC), 25.2 (d, $^{3}J_{\mathrm{CP}}$ = 8.8 Hz, $\mathrm{PNC}C$), 24.7 ($^{3}J_{\mathrm{CP}}$ = 5.7 Hz, $\mathrm{PNC}C$). – $^{1}$H NMR ($\mathrm{CDCl_3}$): $\delta$ = 6.24 (s, 10H, H-cp), 3.3 (m, 4H, NCH), 1.27 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 12H, $\mathrm{CCH_3}$), 1.17 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 12H, $\mathrm{CCH_3}$), NH not detected. – MS (180°C/70 eV), *m*/*z* (%): 459 (1) [$\mathrm{M^+}$], 394 (4) [$\mathrm{M^+}$ − cp], 359 (17) [$\mathrm{M^+ - N(C_3H_7)_2}$], 323 (11) [$\mathrm{M^+ - N(C_3H_7)_2 - Cl}$], 246 (42) [$\mathrm{M^+ - ClTi(Cp)_2}$], 213 (40) [$\mathrm{ClTi(Cp)_2}$], and other fragments. – $\mathrm{C_{22}H_{39}ClN_3PTi}$: calcd. 457.2049; found 457.2078 (MS).

**6b**: $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta$ = −3.9 (s). – $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta$ = 113.7 (s, C-cp), 45.1 (d, $^{2}J_{\mathrm{CP}}$ = 5.7 Hz, PNC), 24.0 (s, $\mathrm{PNC}C$), 23.8 (s, $\mathrm{PNC}C$). – $^{1}$H NMR ($\mathrm{CDCl_3}$): $\delta$ = 7.38 (d, $^{1}J_{\mathrm{HP}}$ = 525.8 Hz, 1H, PH), 6.07 (s, 10H, H-cp), 3.5 (dsept, $^{3}J_{\mathrm{HP}}$ = 16.5, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 4H, NCH), 1.29 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 12H, $\mathrm{CCH_3}$), 1.20 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 12H, $\mathrm{CCH_3}$).

*[(9-Borabicyclo[3.3.1]nonan-9-yl)amino]bis(diisopropylamino)phosphane* (**7**): To a solution of 0.49 g (2.0 mmol) of **2a** in 20 ml of THF 1.3 ml (2.0 mmol, 1.6 M in *n*-hexane) of *n*-butylltihium is added at −30°C. The solution is then cooled to −78°C, and a

Table 3. Crystallographic data and parameters of crystal structure determinations for **2b**, **c**, **3**, **4**, **5**, and **6a**

| | **2b** | **2c** | **3** | **4** | **5** | **6a** |
|---|---|---|---|---|---|---|
| formula | $C_{24}H_{46}N_3P$ | $C_{24}H_{22}N_3P$ | $C_{15}H_{30}N_3O_3PNi$ | $C_{15}H_{39}AlN_3P$ | $C_{24}H_{60}Al_2Cl_6N_6P_2$ | $C_{22}H_{39}ClN_3PTi$ |
| $M_r$ | 407.6 | 383.4 | 390.1 | 319.4 | 761.4 | 459.9 |
| crystal system | triclinic | triclinic | triclinic | orthorhombic | monoclinic | monoclinic |
| space group | P1 (no. 2) | P1 (no.2) | P1 (no.2) | $P2_12_12_1$ (no. 19) | Cc (no. 9) | C2/c (no. 15) |
| a [Å] | 9.846(1) | 9.623(2) | 9.208(2) | 9.687(1) | 9.624(2) | 29.708(4) |
| b [Å] | 10.858(2) | 10.678(2) | 14.358(2) | 12.270(2) | 27.826(2) | 10.530(1) |
| c [Å] | 12.796(2) | 11.264(1) | 16.671(2) | 17.754(2) | 15.018(3) | 16.168(1) |
| α [°] | 70.72(1) | 77.65(1) | 111.21(1) | 90° | 90° | 90° |
| β [°] | 74.07(1) | 89.00(1) | 92.12(1) | 90° | 91.19(1) | 103.79(1) |
| γ [°] | 80.61(1) | 63.80(1) | 91.55(1) | 90° | 90° | 90° |
| V [Å$^3$] | 1237.7(3) | 1010.6(3) | 2051(1) | 2110.2(4) | 4021(1) | 4912.0(9) |
| Z | 2 | 2 | 4 | 4 | 4 | 8 |
| ρ (gcm$^3$) | 1.09 | 1.26 | 1.27 | 1.01 | 1.26 | 1.24 |
| μ (mm$^{-1}$] | 1.06 | 1.30 | 2.23 | 1.52 | 5.26 | 4.65 |
| F(000) | 452 | 404 | 832 | 712 | 1616 | 1968 |
| diffracometer | Enraf-Nonius CAD4 | Enraf-Nonius CAD4 | Enraf-Nonius CAD4 | Enraf-Nonius CAD4 | Enraf-Nonius CAD4 | Enraf-Nonius CAD4 |
| radiation | CuKα | CuKα | CuKα | CuKα | CuKα | CuKα |
| λ [Å] | 1.54178 | 1.54178 | 1.54178 | 1.54178 | 1.54178 | 1.54178 |
| crystal size [mm] | 0.58 x 0.45 x 0.40 | 0.30 x 0.15 x 0.10 | 0.40 x 0.40 x 0.50 | 0.65 x 0.55 x 0.30 | 0.60 x 0.50 x 0.30 | 0.40 x 0.25 x 0.18 |
| T [K] | 200(2) | 200(2) | 193(2) | 208(2) | 200(2) | 208(2) |
| $2\theta_{max.}$ [°] | 120 | 120 | 120 | 120 | 130 | 120 |
| | $-10 \le h \le 11$ | $-9 \le h \le 10$ | $-10 \le h \le 10$ | $-10 \le h \le 3$ | $-11 \le h \le 11$ | $0 \le h \le 33$ |
| | $0 \le k \le 12$ | $0 \le k \le 11$ | $-16 \le k \le 14$ | $-13 \le k \le 5$ | $-32 \le k \le 14$ | $-11 \le k \le 0$ |
| | $-13 \le l \le 14$ | $-12 \le l \le 12$ | $0 \le l \le 18$ | $-18 \le l \le 19$ | $-17 \le l \le 1$ | $-18 \le l \le 17$ |
| no. of measured data | 3956 | 3234 | 6313 | 3938 | 4530 | 3719 |
| no. of unique data | 3670 | 2995 | 6072$^{a)}$ | 2912 | 3622 | 3640 |
| full matrix least-squares refinement on | $F^2$ | $F^2$ | F | $F^2$ | $F^2$ | $F^2$ |
| no. of parameters/restraints | 260/2 | 259/2 | 430 | 195/2 | 390/8 | 265/1 |
| R [for $I > 2\sigma(I)$] | 0.068 | 0.057 | 0.047 | 0.089 | 0.081 | 0.059 |
| wR2 | 0.185 | 0.166 | 0.055$^{b)}$ | 0.234 | 0.210 | 0.170 |

[a] 5760 reflections with $F > 4\sigma(F)$ used for all calculations. – [b] $R_w$.

solution of 0.31 g (2.0 mmol) of *B*-Cl–9-BBN in 10 ml of pentane is added dropwise. During stirring, the reaction mixture is allowed to warm up to room temp. The organic solvent is then removed under reduced pressure, pentane is added to the resulting residue, and the precipitated LiCl is filtered off. **7** is purified by crystallisation from a small amount of pentane at −80 °C. Yield: 0.58 g (80%), m.p. 87 °C (dec.). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 73.8 (s). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 45.4 (d, $^2J_{CP}$ = 12.6 Hz, PNC), 33.7 (d, $^4J_{CP}$ = 33 Hz, BC*C*), 29.2 (m, b, BC), 24.2 (s, BCC*C*), 25.2 (d, $^3J_{CP}$ = 7.6 Hz, PNC*C*), 23.7 (d, $^3J_{CP}$ = 5.7 Hz, PNC*C*). – $^1H$ NMR ($CDCl_3$): δ = 4.76 [s (b), NH], 3.48 (d sept, $^3J_{HP}$ = 10.8, $^3J_{HH}$ = 5.6 Hz, 4 H, NCH), 1.9–1.3 (m, 14 H, 9-BBN), 1.15 (d, $^3J_{HH}$ = 5.6 Hz, 12 H, $NCCH_3$), 1.13 (d, $^3J_{HH}$ = 5.6 Hz, 12 H, $NCCH_3$). – $^{11}B$ NMR ($CDCl_3$): δ = 59.4 [s (b), *w*/2 = 420 Hz]. – MS (180 °C/70 eV), *m/z* (%): 367 (12) [$M^+$], 267 (100) [$M^+$ – $iPr_2N$], 231 (22) [$M^+$ – $C_8H_{15}BN$], and other fragments. – $C_{20}H_{43}BN_3P$: calcd. 366.3288; found 366.3305 (MS).

*X-Ray Structure Determination of* **2b**,**c**, **3**, **4**, **5**, *and* **6a**: The structures were solved by direct methods (SHELXTL-Plus[29]. The non-hydrogen atoms were refined anisotropically, H atoms were refined by using a riding model [full-matrix least-squares refinement on $F^2$ (SHELXL-93[30]), and *F* (SHELXTL-Plus[29] for **3**), respectively]. An absorption correction was applied on the basis of Ψ scans (**2c**, min./max. transmission = 0.734/0.976; **5** = 0.147/0.953, **6a** = 0.475/0.972) and DIFABS[31] (**2b**, **3**, **4**). In the case of **5** the absolute structure was determined by *x* refinement[32] [Flack's *x* parameter −0.02(3)], in the case of **4** the absolute structure could not be determined reliably. With **2b** and **5** an extinction correction was applied. Details on data collection and structure refinement are given in Table 3. – Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-59318.

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☆ Dedicated to Prof. Dr. Drs. h.c. *H. G. von Schnering* on the occasion of his 65th birthday.

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