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Syntheses and X-ray Structures of Novel Main Group Bis(dialkylamino)phosphinimides[†]

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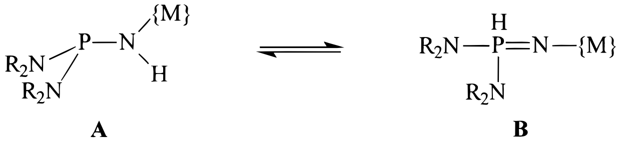
Reactions of aminobis(dicyclohexylamino)phosphane with several aluminum trialkyls R_3Al (R = Me, Et, *t*-Bu) yield the simple Lewis acid−base adducts $(Cy_2N)_2P(H)N(H)AlR_3$ (R = Me, **1**; Et, **2**; *t*-Bu, **3**). Dimeric phosphiniminoalanes $[(Cy_2N)_2P(H)NAlR_2]_2$ (R = Me, **4**; Et, **5**) were obtained by reactions of aminobis(dicyclohexylamino)phosphane with the corresponding dialkyl aluminum hydride R_2AlH. X-ray structure analyses were obtained from **1**, **3**, **4**, and **5**.

1. Introduction

Since the pioneering work of Kealy and Pauson in the early 1950s,[1] cyclopentadienyl-substituted transition metal complexes have been investigated intensively. In particular, group 4 compounds Cp_xML_y became popular due to their potential as alkene polymerization catalysts.[2] During the past decade several research groups expanded this work to metal complexes bearing ligands such as carborane $C_2B_9H_{11}$[3] or the nitrogen-donor R_3PN^-, which are described as isolobal to cyclopentadienyl.[4]

In addition, the substitution of the transition metal center by a main group metal fragment gained increasing interest. Very recently, Stephan et al.[5] synthesized a number of group 13 phosphinimines and phosphinimides, and Cavell et al.[6] reported (iminophosphorano)methanide and methanediide complexes.[7]

Scheme 1



{M} = group 4 metal fragment
R = e.g. *i*-Pr, Cy

Within our own studies on phosphazene chemistry, we investigated in detail the synthesis and reactivity of aminobis(dialkylamino)phosphanes. In this context, we focused our interest on complexation reactions of these triaminophosphanes with early transition metal (group 4) compounds; for example, the substitution of one hydrogen of the NH_2 group by a Cp_2MCl fragment (M = Ti, Zr) led to $(R_2N)_2PN(H)Ti(Cl)Cp_2$ and $(R_2N)_2P(H)NZr(Cl)Cp_2$, respectively.[8] Furthermore, we studied the influence of different ligands at the metal center on the resulting equilibrium between the kinetically favored (NH)-phosphanylamido **A** and the thermodynamically stable tautomeric (PH)-iminophosphorane form **B**. The equilibrium position corresponds to the Lewis acidity of the metal center: due to the increasing electrophilicity of the metal fragment, the generation of the PH-form is preferred. Computational studies unambiguously confirm the experimental results.[9]

Expanding these studies to main group metals, we have now investigated reactions of aminobis(diorganylamino)phosphanes with trialkylalanes and dialkyl aluminum hydrides. Herein we present the syntheses and structures of several bis(dicyclohexylamino)iminophosphorane trialkylalane Lewis acid base adducts $(Cy_2N)_2P(H)N(H)AlR_3$ (R = Me, **1**; Et, **2**; *t*-Bu, **3**). In addition, the first dimeric bis(dicyclohexylamino)iminophosphorane dialkylalane heterocycles $[(Cy_2N)_2P(H)NAlR_2]_2$ (R = Me, **4**; Et, **5**) have been prepared and structurally characterized.

[†] Dedicated to Professor Manfred Meisel on the occasion of his 60th birthday.

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(7) In addition, Jordan et al. published similar neutral and anionic Al and Ga compounds and demonstrated their potential application as olefin polymerisation catalysts. See for example: Dagorne, S.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1999**, *18*, 4619.

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2. Experimental Section

2.1. General Considerations. All manipulations were performed in a glovebox under N_2 atmosphere or with standard Schlenk techniques. Neat Me_3Al and Et_3Al were purchased from Aldrich and used as received. t-Bu_3Al,[10] Me_2AlH,[11] Et_2AlH,[12] and $(Cy_2N)_2PNH_2$[8a] were prepared by literature methods. A Bruker AMX 300 spectrometer was used for NMR spectroscopy. ^1H and $^{13}C\{^1H\}$ spectra were referenced to internal C_6D_5H (δ^1H 7.154, $\delta^{13}C$ 128.0), ^{31}P spectra to external H_3PO_4. Mass spectra were recorded on a VG Masslab 12-250 spectrometer in the electron impact mode (EI) at 16 eV. 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 Bis(dicyclohexylamino)iminophosphorane−Trialkylalane Adducts $(Cy_2N)_2P(H)N(H)AlR_3$ (R = Me, 1; Et, 2; *t*-Bu, 3). A solution of trialkylaluminum (2 mmol) in pentane was added dropwise at −78 °C to a solution of aminobis(dicyclohexylamino)phosphane (2 mmol, 0.81 g) in pentane. Immediately, a white solid was formed. The suspension was slowly warmed to room temperature, and the solid was separated by filtration. Crystalline materials were obtained from a solution in pentane/hexane (**1**, **3**) and pentane/hexane/toluene (**2**), respectively.

$(Cy_2N)_2P(H)N(H)AlMe_3$ (M = 479.69 g/mol) (1): yield 0.91 g (1.90 mmol, 95%); mp 136 °C (dec). Anal. Calcd (found) for $C_{27}H_{55}AlN_3P$: H, 11.56 (11.48); C, 67.61 (67.42). ^1H NMR (300 MHz, C_6D_5H, 25 °C): 7.05 (dd, $^1J_{HP} = 571.4$ Hz; $^3J_{HH} = 11.6$ Hz, 1H, P*H*), 2.91 (m, 4H, PNC*H*), 1.85−1.30 (m, 40H, C*H₂*), −0.18 (s, 9 H, AlC*H₃*). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): 55.8 (d, $^2J_{CP} = 5.3$ Hz, PN*C*); 34.9 (d, $^3J_{CP} = 2.3$ Hz, PNC*C*), 33.3 (d, $^3J_{CP} = 2.3$ Hz, PNC*C*), 27.1 (s, PNCC*C*), 27.0 (s, PNCC*C*), 25.7 s, PNCCC*C*), −5.4 (s, Al*C*H₃). ^{31}P NMR (80 MHz, C_6D_5H, 25 °C): 15.9 (ddquin; $^1J_{PH} = 571.4$ Hz; $^2J_{PH} = 15.3$ Hz; $^3J_{PH} = 16.5$ Hz). MS (EI, 16 eV): *m/z* (%) 479 (1) [M^+], 464 (1) [$M^+ - CH_3$], 407 (1) [$M^+ - AlMe_3$], 397 (1) [$M^+ - Cy$], 299 (1) [$M^+ - NCy_2$], 227 (20) [$M^+ - NCy_2 - AlMe_3$], 180 (18) [NCy_2^+], 138 (100) [$NC_9H_{16}^+$].

$(Cy_2N)_2P(H)N(H)AlEt_3$ (M = 521.69 g/mol) (2): yield 0.96 g (1.84 mmol, 92%); mp 151 °C (dec). Anal. Calcd (found) for $C_{30}H_{61}AlN_3P$: H, 11.79 (11.68); C, 69.07 (69.01). ^1H NMR (300 MHz, C_6D_5H, 25 °C): 7.09 (dd, $^1J_{HP} = 572.0$ Hz; $^3J_{HH} = 11.2$ Hz, 1H, P*H*), 2.93 (m, 4H, PNC*H*), 1.8−0.9 (m, 40H, C*H₂*), 1.68 (t, $^3J_{HH} = 8.1$ Hz, 9H, AlCC*H₃*), 0.41 (q, $^3J_{HH} = 8.1$ Hz, 6H, AlC*H₂*). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): 55.8 (d, $^2J_{CP} = 5.0$ Hz, PN*C*), 34.9 (d, $^3J_{CP} = 2.7$ Hz, PNC*C*), 33.3 (d, $^3J_{CP} = 2.3$ Hz, PNC*C*), 27.1 (s, PNCC*C*), 27.0 (s, PNCC*C*), 25.7 (s, PNCCC*C*), 11.8 (s, AlC*C*H₃), 2.8 (s, Al*C*H₂). ^{31}P NMR (80 MHz, C_6D_5H, 25 °C): 17.1 (ddquin; $^1J_{PH} = 572.0$ Hz; $^2J_{PH} = 14.0$ Hz; $^3J_{PH} = 16.5$ Hz). MS (EI, 16 eV): *m/z* (%) 492 (1) [$M^+ - Et$], 407 (1) [$M^+ - AlEt_3$], 227 (9) [$M^+ - AlEt_3 - NCy_2$], 180 (11) [NCy_2], 138 (100) [$NC_9H_{16}^+$].

$(Cy_2N)_2P(H)N(H)Al(t\text{-}Bu)_3$ (M = 605.92 g/mol) (3): yield 1.07 g (1.76 mmol, 88%); mp 158 °C (dec). Anal. Calcd (found) for $C_{36}H_{73}AlN_3P$: H, 12.14 (12.02); C, 71.36 (71.28). ^1H NMR (300 MHz, C_6D_5H, 25 °C): 7.00 (dd, $^1J_{HP} = 583.0$ Hz; $^3J_{HH} = 11.6$ Hz, 1H, P*H*), 3.45 (m, 4H, PNC*H*), 1.8−1.0 (m, 40H, C*H₂*), 1.47 (s, 27H, AlCC*H₃*). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): 56.0 (d, $^2J_{CP} = 6.8$ Hz, PN*C*), 35.4 (d, $^3J_{CP} = 3.4$ Hz, PNC*C*), 35.3 (d, $^3J_{CP} = 3.4$ Hz, PNC*C*), 27.2 (s, PNCC*C*), 27.0 (s, PNCC*C*), 25.7 (s, PNCCC*C*), 33.8 (s, AlC*C*H₃), 26.5 (s, Al*C*). ^{31}P NMR (80 MHz, C_6D_5H, 25 °C): 31.1 (ddquin; $^1J_{PH} = 583.0$ Hz; $^2J_{PH} = 14.0$ Hz; $^3J_{PH} = 15.3$ Hz). MS (EI, 16 eV): *m/z* (%) 548 (1) [$M^+ - t\text{-}Bu$], 425 (5) [$M^+ - NCy_2$], 227 (20) [$M^+ - Al(t\text{-}Bu)_3 - NCy_2$], 180 (10) [$NCy_2$], 138 (100) [$NC_9H_{16}^+$].

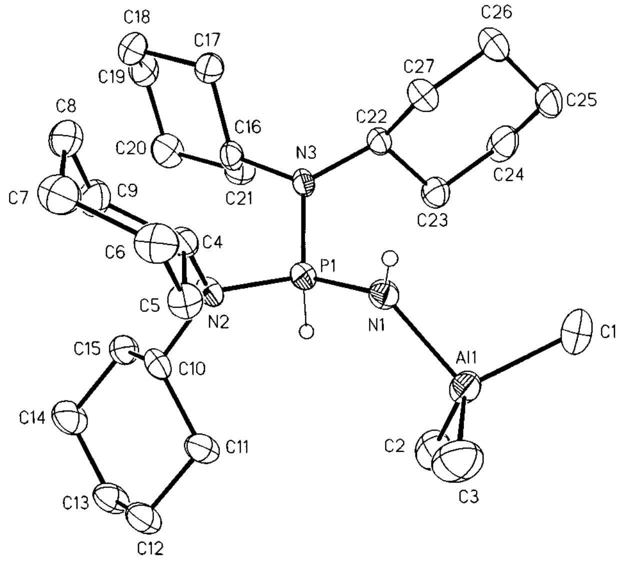

Figure 1. ORTEP plot (50% probability level; H(C) omitted for clarity) showing the solid-state structure and atom-numbering scheme for **1**.

2.3. General Synthesis of Bis(dicyclohexylamino)iminophosphorane−Dialkylalane Heterocycles $[(Cy_2N)_2P(H)NAlR_2]_2$ (R = Me, 4; Et, 5). A solution of dialkylaluminum hydride (2 mmol) in pentane was added dropwise at −78 °C to a solution of aminobis(dicyclohexylamino)phosphane (2 mmol, 0.81 g) in pentane. Warming up within 1 h to room temperature was accompanied by gas evolution and formation of a white solid. After stirring for 1 h, the suspension was heated under reflux for 15 min. Cooling to room temperature gave a white solid, which was separated by filtration. Crystalline materials were obtained after recrystallization from pentane/hexane/toluene (**4**) and hexane/diethyl ether (**5**), respectively.

$[(Cy_2N)_2P(H)NAlMe_2]_2$ (M = 927.30 g/mol) (4): yield 0.79 g (0.85 mmol, 85%); mp > 290 °C. Anal. Calcd (found) for $C_{52}H_{102}Al_2N_6P_2$: H, 11.09 (11.02); C, 67.35 (67.23). ^1H NMR (300 MHz, C_6D_5H, 25 °C): 7.28 (d, $^1J_{PH} = 549$ Hz, 2H, P*H*), 3.45 (quin, $^3J_{HP} = 13.09$ Hz, 8H, PNC*H*), 1.9−1.2 (m, 80H, C*H₂*), −0.22 (s, 12H, AlC*H₃*). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): 54.5 (dd, $^2J_{PC} = 3.05$ Hz, PN*C*), 35.4, 35.2 (s, PNC*C*), 27.6, 27.5 (s, PNCC*C*), 26.4 (s, PNCCC*C*), −4.0 (s, Al*C*H₃). ^{31}P NMR (80 MHz, C_6D_5H, 25 °C): 5.4 (dquin, $^1J_{PH} = 549$ Hz, $^3J_{PH} = 15.26$ Hz). MS (EI, 16 eV): *m/z* (%) 912 (1) [$M^+ - CH_3$], 732 (1) [$M^+ - CH_3 - NCy_2$], 448 (1) [($M^+/2) - CH_3$], 227 (2) [($M^+/2) - Al(CH_3)_2NCy_2$], 180 (33) [NCy_2^+], 138 (100) [$NC_9H_{16}^+$].

$[(Cy_2N)_2P(H)NAlEt_2]_2$ (M = 982.52 g/mol) (5): yield 0.74 g (0.75 mmol, 75%); mp 227 °C (dec). Anal. Calcd (found) for $C_{56}H_{110}Al_2N_6P_2$: H, 11.29 (11.21); C, 68.46 (68.41). ^1H NMR (300 MHz, C_6D_5H, 25 °C): 7.38 (d, $^1J_{PH} = 549$ Hz, 2H, P*H*), 3.42 (m, $^3J_{HP} = 12.32$ Hz, 8H, PNC*H*), 1.9−1.0 (m, 80H, C*H₂*), 1.10 (t, $^3J_{HH} = 8.09$ Hz, 12H, AlCC*H₃*), −0.04 (q, $^3J_{HH} = 8.09$ Hz, 8H, AlC*H₂*). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): 54.7 (dd, $^2J_{PC} = 3.43$ Hz, PN*C*), 35.5, 35.3 (s, PNC*C*), 27.8, 27.5 (s, PNCC*C*), 26.4 (s, PNCCC*C*); 11.7 (s, AlC*C*H₃). ^{31}P NMR (80 MHz, C_6D_5H, 25 °C): 6.5 (ddquin, $^1J_{PH} = 549$ Hz, $^3J_{PH} = 15.26$ Hz). MS (EI, 16 eV): *m/z* (%) 983 (1) [M^+], 954 (80) [$M^+ - C_2H_5$], 803 (23) [$M^+ - NCy_2$], 774 (5) [$M^+ - C_2H_5 - NCy_2$], 592 (45) [$M^+ - 2NCy_2 - C_2H_5$], 180 (100 [NCy_2^+], 138 (54) [$NC_9H_{16}^+$].

X-ray Structure Solution and Refinement. Crystallographic data of **1**, **3**, **4**, and **5** are summarized in Table 1, selected bond lengths and angles in Table 2. Figures 1−4 show the ORTEP diagrams of the solid-state structures of **1**, **3**, **4**, and **5**. Data were collected on a Nonius Kappa-CCD diffractometer. Structures were solved by direct methods (SHELXS-

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Table 1. Crystallographic Data and Measurements for $(Cy_2N)_2P(H)N(H)AlMe_3$ (1), $(Cy_2N)_2P(H)N(H)Al(t\text{-}Bu)_3$ (3), $[(Cy_2N)_2P(H)NAlMe_2]_2$ (4), and $[(Cy_2N)_2P(H)NAlEt_2]_2$ (5)

	1	3	4	5
mol formula	$C_{27}H_{55}AlN_3P$	$C_{36}H_{73}AlN_3P$	$C_{52}H_{102}Al_2N_6P_2$	$C_{56}H_{110}Al_2N_6P_2{\cdot}OEt_2$
fw	479.69	605.92	927.30	1057.52
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	10.5525(7)	11.7878(2)	9.0387(2)	9.6873(6)
b, Å	10.8527(9)	35.4013(10)	11.3829(4)	12.8200(9)
c, Å	15.0268(11)	18.3712(4)	14.5238(5)	14.2885(12)
α, deg	95.024(3)		97.738(2)	98.725(4)
β, deg	105.047(4)	91.813(2)	106.838(2)	105.978(4)
γ, deg	111.370(4)		101.366(2)	106.748(4)
V, Å^3	1515.6(2)	7662.5(3)	1372.61(7)	1581.3(2)
Z	2	8	1	1
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
(wavelength, Å)	(0.71073)	(0.71073)	(0.71073)	(0.71073)
μ, mm^{-1}	0.138	0.121	0.150	0.139
temp, K	123(2)	123(2)	123(2)	123(2)
D_{calcd}, g cm^{-3}	1.051	1.050	1.122	1.111
cryst dimens, mm	0.40 × 0.20 × 0.10	0.60 × 0.50 × 0.40	0.20 × 0.15 × 0.05	0.45 × 0.20 × 0.20
$2\theta_{max}$, deg	50.0	50.0	50.0	50.0
no. of rflns recorded	10 221	37 915	20 460	22 067
no. of nonequiv rflns recorded	5224	13032	4825	5539
R_{merg}	0.040	0.047	0.033	0.043
no. of params/restraints	295/2	751/4	313/81	321/22
R1[a]; wR2[b]	0.041, 0.103	0.050, 0.139	0.037, 0.096	0.047, 0.135
goodness of fit[c]	0.953	1.056	1.077	1.071
final max, min $\Delta\rho$, e Å^{-3}	0.287, −0.260	0.963, −0.413	0.282, −0.286	0.489, −0.531

[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 $= \{\sum[w(|F_o^2| - |F_c^2|)^2]/(N_{observns} - N_{params})\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1, 3, 4, and 5

		1			
P1−N1	1.586(2)	Al1−C2	1.977(2)	N1−P1−N3	111.5(1)
P1−N2	1.642(2)	Al1−C3	1.985(2)	N2−P1−N3	106.4(1)
P1−N3	1.649(2)			N1−Al1−C2	107.2(1)
Al1−N1	1.941(2)	P1−N1−Al1	131.8(1)	N1−Al1−C1	105.4(1)
Al1−C1	1.993(2)	N1−P1−N2	118.2(1)	N1−Al1−C3	107.1(1)
		3			
P1−N1	1.587(2)	Al1−C5	2.026(3)	N1−P1−N3	118.7(1)
P1−N2	1.654(2)	Al1−C9	2.048(3)	N2−P1−N3	106.5(1)
P1−N3	1.644(2)			N1−Al1−C1	108.5(1)
Al1−N1	1.949(2)	P1−N1−Al1	139.4(1)	N1−Al1−C5	106.7(1)
Al1−C1	2.030(3)	N1−P1−N2	113.6(1)	N1−Al1−C9	100.4(1)
		3′			
P1′−N1′	1.590(2)	Al1′−C5′	2.045(2)	N1′−P1′−N3′	111.0(1)
P1′−N2′	1.647(2)	Al1′−C9′	2.044(3)	N2′−P1′−N3′	113.9(1)
P1′−N3′	1.639(2)			N1′−Al1′−C1′	110.7(1)
Al1′−N1′	1.947(2)	P1′−N1′−Al1′	144.0(1)	N1′−Al1′−C5′	100.9(1)
Al1′−C1′	2.034(2)	N1′−P1′−N2′	112.2(1)	N1′−Al1′−C9′	102.7(1)
		4			
P1−N1	1.559(1)	Al1−C2	1.981(2)	N1−P1−N2	118.6(1)
P1−N2	1.661(1)			N1−P1−N3	114.1(1)
P1−N3	1.664(1)	P1−N1−Al1	123.7(1)	N2−P1−N3	107.3(1)
Al1−N1	1.925(2)	P1−N1−Al1a	143.5(1)	N1−Al1−C1	112.3(1)
Al1−N1a	1.893(1)	Al1−N1−Al1a	92.7(1)	N1−Al1−C2	112.7(1)
Al1−C1	1.978(2)	N1−Al1−N1a	87.3(1)	C1−Al1−C2	110.1(1)
		5			
P1−N1	1.556(2)	Al1−C3	1.993(2)	N1−P1−N2	114.6(1)
P1−N2	1.662(2)			N1−P1−N3	120.0(1)
P1−N3	1.658(2)	P1− N1−Al1	143.9(1)	N2−P1−N3	105.6(1)
Al1−N1	1.892(2)	P1− N1−Al1a	123.6(1)	N1−Al1−C1	117.9(1)
Al1−N1a	1.931(2)	Al1−N1−Al1a	92.0(1)	N1−Al1−C3	115.6(1)
Al1−C1	1.981(2)	N1−Al1−N1a	88.0(1)	C1−Al1−C3	111.3(1)

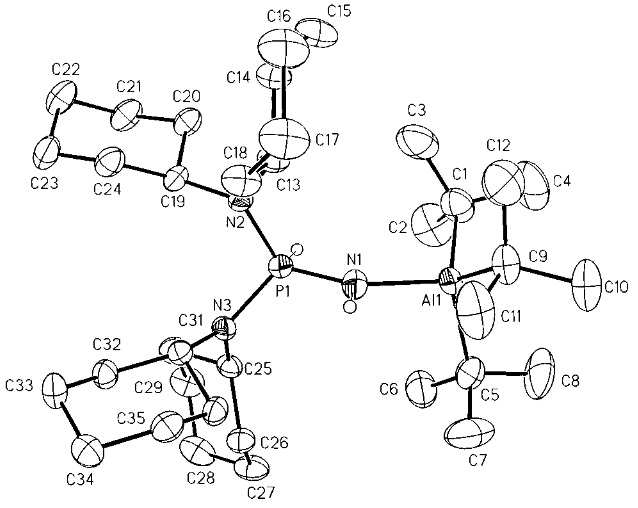

Figure 2. ORTEP plot (50% probability level; one independent molecule; H(C) omitted for clarity) showing the solid-state structure and atom-numbering scheme for **3**.

97)[13] and refined by full-matrix least-squares on F^2 (SHELXL-97).[14] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms, localized by difference electron density determination, using a riding model (coordinates of H(N) and H(P) free). In **4** one cyclohexyl group and in **5** the solvent is disordered.

3. Results and Discussion

Lewis acid base reactions between aminobis(dicyclohexylamino)phosphane $(Cy_2N)_2PNH_2$ with several aluminum trialkyls R_3Al result in almost quantitative yield of simple adducts $(Cy_2N)_2P(H)N(H)AlR_3$ (R = Me, **1**; Et, **2**; *t*-Bu, **3**). As expected by the HSAB principle, the Al center is coordinated by the "hard" N-base rather than by the "soft" P-base. Due to the strong Lewis acidity of the Al compounds, only the (PH)-iminophosphorane form was formed. We have previously obtained an analogous result.[8a]

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[13] Sheldrick, G. M. *SHELXS-97*, Program for Structure Solution: *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[14] Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; Universität Göttingen, 1997.

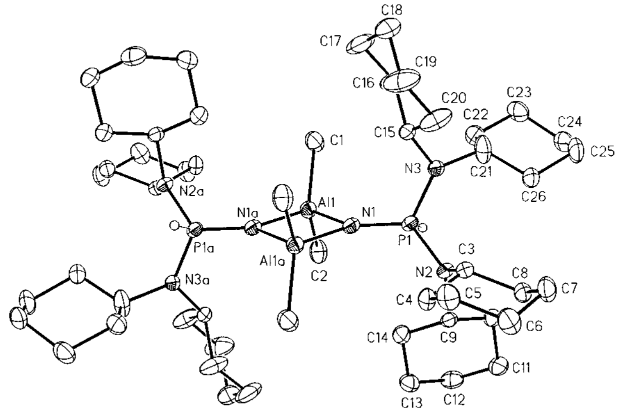


Figure 3. ORTEP plot (50% probability level; H(C) and disordered parts omitted for clarity) showing the solid-state structure and atom-numbering scheme for **4**.

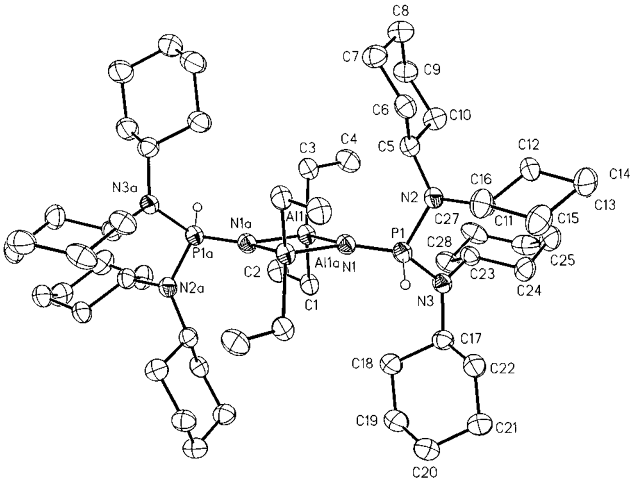
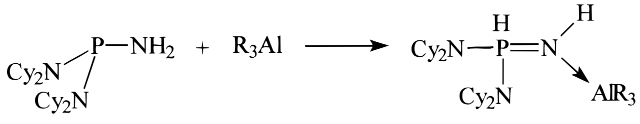


Figure 4. ORTEP plot (50% probability level; H(C) omitted for clarity) showing the solid-state structure and atom-numbering scheme for **5**.

Scheme 2

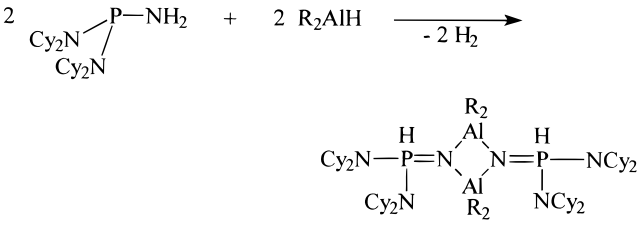


(R = Me **1**, Et **2**, *t*-Bu **3**)

Compared to the starting compounds R_3Al, ^1H NMR spectra of **1**−**3** show signals due to the organic ligands on Al shifted to lower field. In addition, a doublet (δ 7.05 ppm **1**, 7.09 ppm **2**, 7.00 ppm **3**) with a typical $^1J_{HP}$ coupling constant of 570−580 Hz is observable,[15] indicating the formation of the (PH)-iminophosphorane form. ^{31}P NMR spectra show resonances at δ 15.9 ppm (**1**), 17.1 ppm (**2**), and 31.1 ppm (**3**). These shifts correspond well to the Lewis acidity of the aluminum trialkyl. Me_3Al is the strongest base within the Altrialkyl group, leading to an upfield shift of the ^{31}P NMR resonance.

The highest peaks in the mass spectra of **1**−**3** correspond to the molecular ion (**1**) and to fragments of the molecular ion minus Et (**2**) and *t*-Bu (**3**), respectively. This demonstrates the relative bond strength of the adducts in the gas phase.

Scheme 3



(R = Me **4**, Et **5**)

Single crystals of **1** and **3** suitable for a X-ray structure determination were obtained from solutions in pentane/hexane. The structures of **1** and **3** undoubtedly prove the presence of P-hydrophosphorane−AlR_3 adducts in the solid state as expected from the multinuclear NMR and high-resolution MS studies.

1 crystallizes in the triclinic space group $P\bar{1}$ (No. 2) and **3** in the monoclinic space group $P2_1/c$ (No. 14) with two independent molecules in the asymmetric unit.

The P1−N1 bond distances (1.586(2) Å, **1**; 1.587(2), 1.590(2) Å, **3**) lie in the upper range for PN double bonds, while the P1−N2 and P1−N3 (1.642(2), 1.649(2) Å, **1**; 1.654(2), 1.644(2) Å; 1.647(2), 1.639(2) Å, **3**) bond lengths show values typical for P−N single bonds.[16] As expected, the PN distances are shortened, compared to the starting triaminophosphane.

Despite the increased steric bulk of *t*-Bu_3Al compared to Me_3Al, which should result in an elongation of the Al−N distances, the values observed for **1** and **3** are almost equal (1.941(2) Å, **1**; 1.949(2) and 1.947(2) Å, **3**). However, the P−N−Al angle increases from 131.8(1)° (**1**) to 139.4(1)° and 144.0(1)° (**3**), respectively. This should lead to a shortened Al−N distance. Obviously, these opposing effects compensate each other and clearly demonstrate the low steric hindrance at the N1 atom.

The Al atom resides in distorted tetrahedral environments. The average C−Al distances (1.99 Å, **1**; 2.04 Å, **3**) and C−Al−C bond angles (112°, **1**; 113°, **3**) are within the expected range.

Dehydrogenation reactions between aminobis(dicyclohexylamino)phosphane $(Cy_2N)_2PNH_2$ with dialkyl aluminum hydrides R_2AlH give the dimeric phosphiniminoalanes $[(Cy_2N)_2P(H)NAlR_2]_2$ (R = Me, **4**; Et, **5**). ^1H NMR spectra of **4** and **5** show signals due to the organic ligands on Al shifted to lower field, compared to R_2AlH. The formation of the (PH)-iminophosphorane form is clearly evidenced by a doublet (δ 7.28 ppm, **4**; 7.38 ppm, **5**) with a typical $^1J_{HP}$ coupling constant of 549 Hz. Compared to the simple Lewis acid−base adducts, resonances in ^{31}P NMR spectra are shifted to higher field (δ 5.4 ppm (**4**), 6.5 ppm (**5**)).

Due to the chirality of the phosphorus atoms, the ^{13}C NMR spectra show doublets of doublets for the PNC carbon atoms.

Mass spectra of **4** and **5** demonstrate their thermal stability. Peaks with the highest mass observed correspond to the molecular ion (**5**) and to a fragment of the molecular ion minus Me (**4**).

Single crystals of **4** and **5** suitable for a X-ray structure analysis were obtained from solutions in pentane/

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[15] Schmidtpeter, A.; Rossknecht, H.; Schumann, K. *Z. Anorg. Allg. Chem.* **1972**, *171*, 894.

[16] Wells, A. F. In *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 1984.

hexane/toluene (**4**) and hexane/Et_2O (**5**). The structures of **4** and **5** undoubtedly prove the presence of dimeric PH-iminoalanes in the solid state.

4 and **5** crystallize in the triclinic space group $P\bar{1}$ (No. 2) with one molecule in the unit cell, showing crystallographic C_i-symmetry. As observed for **1** and **3**, the P1−N1 bond distances (1.559(1) Å, **4**; 1.556(2) Å, **5**) show typical values for PN double bonds.[16] Compared to the adducts, they are shortened. The P1−N2 and P1−N3 (1.661(1), 1.664(1) Å, **4**; 1.662(2), 1.658(2) Å, **5**) bond lengths show no unusual values. As expected, the nitrogen atoms N1, N2, and N3 exhibit a nearly planar geometry.

The Al atom resides in distorted tetrahedral environments. The average C−Al distances are 1.98 Å (**4**) and 1.99 Å (**5**), and C−Al−C bond angles are 110° (**4**) and 111° (**5**). The Al−N distances (1.925(2), 1.893(1) Å, **4**; 1.892(2), 1.931(2) Å, **5**) are slightly shortened compared to **1** and **3**. Within the planar Al_2N_2 core, the endocyclic Al−N−Al angles are 92.7(1)° (**4**) and 92.0(1)° (**5**) and the N−Al−N angles are 87.3(1)° (**4**) and 88.0(1)° (**5**). The general structural features of **4** and **5** are very similar to those described for comparable heterocycles recently prepared by Stephan et al.[5]

4. Conclusions

Simple Lewis acid−base adducts $(Cy_2N)_2P(H)N(H)$-AlR_3 were obtained by reactions of $(Cy_2N)_2PNH_2$ with aluminum trialkyls. In contrast, dialkyl aluminum hydrides reacted with elimination of H_2 to form dimeric phosphiniminoalanes $[(Cy_2N)_2P(H)NAlR_2]_2$. Due to the strong acidic character of the Al center, only iminophosphoranes (PH-form) were formed. This corresponds to earlier results observed for group 4 metal complexes. The existence of the tautomeric phosphanylamido (NH) form was not detected.

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Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates for **1**, **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000059E