Ring Opening of Dilithio Bis(amido)cyclodiphosphazanes As a Route to 1,3-Diaza-2λ^2-phosphaallyl Gallium Complexes

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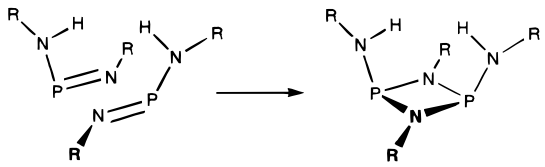
Gallium trichloride reacted with [(^{t}BuNP)$_2$(^{t}BuNLi·THF)$_2$] or [(^{t}BuNP)$_2$(PhNLi·THF)$_2$] to form {[(^{t}BuNP)$_2$(^{t}BuN)$_2$]-GaCl}, **1**, and {[(^{t}BuNP)$_2$(PhN)$_2$]GaCl·THF}, **3**, respectively. Treatment of either gallium complex with [(^{t}BuNP)$_2$-(^{t}BuNLi·THF)$_2$] produced {[(^{t}BuNP)$_2$(RN)$_2$]Ga(^{t}BuNPN^{t}Bu)}, R = ^{t}Bu (**2**), R = Ph (**4**), respectively. The complexes **1** and **2** were X-ray structurally characterized, and **2** was shown to contain a 1,3-diaza-2λ^2-phosphaallyl ligand. Compound **1** has C_s symmetry and crystallizes with two molecules in a monoclinic unit cell, space group $P2_1/m$ (No. 11), having dimensions (213 K) a = 9.5478(6) Å, b = 11.9540(7) Å, c = 97.808(1) Å, β = 97.808(1)°. The crystal data (213 K) for **2** are orthorhombic, space group *Pnma* (No. 62), a = 19.0514(2) Å, b = 17.5082(1) Å, c = 9.6695(1) Å, and Z = 4.

Introduction

Bis(amino)cyclodiphosphazanes[1,2] are diamino-substituted inorganic heterocycles that are formally derived from the [2 + 2] cycloaddition of two amino(imino)phosphine molecules,[3] as shown in Scheme 1. Although these phosphorus−nitrogen ring compounds are not as common as phosphazenes, they do have a well-developed chemistry.[4] We are investigating bis-(1°-amino)cyclodiphosphazanes as chelating bis(amido) ligands, an aspect of their chemistry that had previously received very little attention.[5] These robust molecules and their complexes have high thermal stability and were thought to resist ring-opening reactions.[3c]

Recently we reported the syntheses and molecular structures of thallium(I) and indium(II) cage complexes of [(^{t}BuNP)$_2$-(^{t}BuN)$_2$]$^{2-}$.[6] In our investigation of the ligand properties of this dianion we have now turned our attention to the lighter, and more Lewis acidic, group 13 metals.

Scheme 1



Here we describe the syntheses of a new bis(anilido)-cyclodiphosphazane ligand, its dilithio salt, and four new gallium(III) complexes. Two of these gallium compounds bear conventional bis(amido)cyclodiphosphazane ligands, while the other two are mixed-ligand complexes, containing both bis-(amido)cyclodiphosphazane and 1,3-diaza-2-phosphaallyl moieties. The heteroallyllic ligand must have been derived from the cycloreversion (ring opening) of a dilithio bis(amido)-cyclodiphosphazane. Although this reaction has been reported once before,[7] it has never been observed for cyclodiphosphazanes bearing the comparatively small *tert*-butyl substituents, nor for bis(amido)cyclodiphosphazane cage complexes.

Experimental Section

General. All operations were performed in standard Schlenk glassware under a protective atmosphere of argon. Solvents were thoroughly dried and freed of molecular oxygen by distillation from sodium or potassium benzophenone ketyl immediately before use. NMR spectra were recorded on a Varian VXR-300 spectrometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra are referenced relative to C_6D_5H at 7.15 ppm, C_6D_6 at 128.0 ppm, and P(OEt)$_3$ at 137.0 ppm, respectively. Melting points were obtained on a Mel-Temp apparatus; they are uncorrected. E & R Microanalytical Laboratory, Parsippany, NJ, performed the elemental analyses.

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Gallium trichloride was purchased from Aldrich and was used as received. The cyclodiphosphazane *cis*-[(^{t}BuNP)$_2$(^{t}BuNH)$_2$] and its dilithium salt were prepared by published procedures.[6]

Synthesis of [(^{t}BuNP)$_2$(PhNH)$_2$], cpda. In a 250 mL two-necked flask were dissolved 1.34 g (4.86 mmol) of [ClP(μ-N^{t}Bu)$_2$PCl][8] and 1.35 mL (9.71 mmol) of triethylamine in 5 mL of toluene. To this mixture was added dropwise at room temperature 0.89 mL (9.71 mmol) of aniline, dissolved in 10 mL of toluene. The dropping funnel was then replaced with a reflux condenser, and the thick white reaction mixture was refluxed for 2 h. The solution was allowed to cool to room temperature and then filtered through a medium-porosity frit. After the clear filtrate had been stored at −12 °C for 2 days, 1.26 g (67.0%) of colorless rectangular crystals was isolated.

Mp: 133−136 °C. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ = 7.16 (d, 4H, *o*-Ph), 7.08 (t, 4H, *m*-Ph), 6.83 (t, 2H, *p*-Ph), 4.75 (s, br, 2H, NH), 1.26 (s, 18 H, N^{t}Bu). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 25 °C): δ = 143.5 (d, J_{PC} = 2.7 Hz), 129.4 (s), 121.4 (s), 118.9 (s, br), 51.7 (t, J_{PC} = 13.5 Hz), 31.1 (d, J_{PC} = 6.4 Hz). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, 25 °C): δ = 99.9 (s). Anal. Calcd for $C_{20}H_{30}N_4P_2$: C, 61.84; H, 7.78; N, 14.42. Found: C, 61.88; H, 7.91; N, 14.22.

Synthesis of [(^{t}BuNP)$_2$ (PhNLi·THF)$_2$], cpdaLi$_2$. A 250 mL two-necked flask was charged with 3.5 g (8.9 mmol) of cpda. The solid was dissolved in 40 mL of THF, and the flask was then fitted with a dropping funnel and an oil bubbler. To the dropping funnel was added 7.1 mL (17.8 mmol) of *n*-butyllithium in hexanes. The flask was cooled to 0 °C, and the butyllithium solution was added dropwise to the cyclodiphosphazane solution, resulting in a slow gas evolution. After the reaction mixture had warmed to room temperature, the dropping funnel was replaced with a reflux condenser, and the reaction mixture was refluxed for 16 h. The solution volume was reduced to 15 mL, and the flask was placed in a freezer (−12 °C). Several crops of crystals yielded a total of 3.0 g (91%) of product.

Mp: 280 °C dec. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ = 7.30 (d, 4H, *m*-Ph), 7.23 (t, 4H, *o*-Ph), 6.78 (t, 2H, *p*-Ph), 3.38 (m, 8H, THF), 1.43 (s, 18 H, N^{t}Bu), 1.15 (m, 8H, THF). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 25 °C): δ = 129.7 (s), 120.0 (s), 119.7 (s), 115.5 (s), 68.8 (s), 52.6 (t, J_{PC} = 15.5 Hz), 30.4 (d, J_{PC} = 6.4 Hz), 25.5 (s). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, 25 °C): δ = 162.9 (s). Anal. Calcd for $C_{28}H_{44}N_4Li_2O_2P_2$: C, 61.76; H, 8.14; N, 10.29. Found: C, 61.61; H, 8.34; N, 10.54.

Synthesis of {[(^{t}BuNP)$_2$(^{t}BuN)$_2$]GaCl}, 1. To $GaCl_3$ (0.242 g, 1.37 mmol), dissolved in 10 mL of toluene, was added dropwise at −78 °C [(^{t}BuNP)$_2$(^{t}BuNLi·THF)$_2$] (0.693 g, 1.37 mol), dissolved in 20 mL of toluene. The initially clear solution was allowed to warm to room temperature and then kept at 55 °C for 6 h. It was then filtered through a medium-porosity frit, concentrated to 5 mL, and stored at −18 °C. After 3 days 0.480 g (77.4%) of colorless **1** was isolated.

Mp: 128−130 °C. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ = 1.375 (s, 18H; N^{t}Bu), 1.345 (s, 18H, N^{t}Bu). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 25 °C): δ = 54.28 (d, J_{PC} = 12 Hz), 53.98 (t, J_{PC} = 8.7 Hz), 34.43 (d, J_{PC} = 12 Hz), 29.75 (t, J_{PC} = 6.7 Hz). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, 25 °C): δ = 161.89 (s). Anal. Calcd for $C_{16}H_{36}N_4ClP_2Ga$: C, 42.55; H, 8.04; N, 12.41. Found: C, 42.79; H, 8.28; N, 12.64.

Synthesis of {[(^{t}BuNP)$_2$(^{t}BuN)$_2$]Ga(^{t}BuNPN^{t}Bu)}, 2. A sample of **1**, 0.64 g, 1.4 mmol, was combined with 0.71 g, 1.4 mmol, of [(^{t}BuNP)$_2$(^{t}BuNLi·THF)$_2$] in a two-neck flask. These reagents were dissolved in 10 mL of toluene, and the colorless solution was heated with stirring at 80 °C for 20 h. The ensuing yellow-beige suspension was then filtered through a medium-porosity frit, and the clear light-yellow solution was concentrated to 5 mL. After the solution had been stored at −18 °C for 3 days, yellow plates of **2** formed, 0.59 g, 65%.

Mp: 260 °C dec. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ = 1.593 (s, 18H, N^{t}Bu), 1.506 (s, 18H, N^{t}Bu), 1.466 (s, 18H, N^{t}Bu). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 25 °C): δ = 57.63 (d, J_{PC} = 22.5 Hz), 55.75 (d, J_{PC} = 9.0 Hz), 53.50 (t, J_{PC} = 15.0 Hz), 34.88 (d, J_{PC} = 8.6 Hz), 34.38 (d, J_{PC} = 12.8 Hz), 30.59 (t, J_{PC} = 7.1 Hz). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, 25 °C): δ = 373.5 (s), 160.1 (s). Anal. Calcd for $C_{24}H_{54}N_6P_3Ga$: C, 48.91; H, 9.24; N, 14.26. Found: C, 48.72; H, 9.47; N, 14.11.

Synthesis of {[(^{t}BuNP)$_2$(PhN)$_2$]GaCl·THF}, 3. Gallium trichloride, 0.292 g, 1.66 mmol, was dissolved in 5 mL of toluene, and the colorless, clear solution was cooled to −78 °C. Then 0.903 g, 1.66 mmol, of [(^{t}BuNP)$_2$(PhNLi·THF)$_2$], dissolved in 20 mL of toluene, was transferred to a dropping funnel and added dropwise to the gallium chloride solution. The reaction mixture, which slowly turned yellow, was kept at 40 °C for 2 h and then stirred at room temperature. After 16 h all volatile components were removed in vacuo and the orange-yellow residue was extracted with 20 mL of hexanes. This dilute solution yielded after 6 days at −18 °C thin, pale-yellow needles (0.574 g, 63.2%) of **3**.

Mp: 126−128 °C. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ = 7.264 (d, 4H, *o*-Ph), 7.154 (t, 4H, *m*-Ph), 6.819 (s, 2H, *p*-Ph), 3.645 (m, 4H, THF), 1.440 (s, 18H, N^{t}Bu), 0.878 (m, 4H, THF); (300 MHz, toluene-d_8, − 40 °C) δ = 7.27 (d, 4H, *o*-Ph), 7.16 (t, 4H, *m*-Ph), 6.82 (s, 2H, *p*-Ph), 3.66 (m, 4H, THF), 1.421 (s, 9H, N^{t}Bu), 1.393 (s, 9H, N^{t}Bu), 0.89 (t, 4H, THF). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 25 °C): δ = 148.5 (d, J_{PC} = 22.5 Hz), 129.4(s), 119.9(s), 119.5 (d, J_{PC} = 13.7 Hz), 70.7 (s, THF), 52.9 (br), 30.2 (br), 24.6 (d, THF). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, 25 °C): δ = 152.3 (s). MS (FAB-MBNA): 490.3(2.8%) = M^+ − THF. Anal. Calcd for $C_{24}H_{36}N_4ClGaOP_2$: C, 51.11; H, 6.44; N, 9.94. Found: C, 52.45; H, 6.88; N, 10.08.

Variable-Temperature NMR Analysis for 3. The signals for the two N^{t}Bu groups at 1.421 and 1.393 coalesced at 273 K. The free energy of activation for this site exchange was calculated, using the relationship $\Delta G_c^{\ddagger} = (4.575 \times 10^{-3})T_c[9.972 + \log(T_c/\delta\nu)]$.[9]

Synthesis of {[(^{t}BuNP)$_2$(PhN)$_2$]Ga(^{t}BuNPN^{t}Bu)}, 4. A 100-mL two-neck flask was charged with 0.512 g, 0.908 mmol, of **3** and 0.460 g, 0.913 mmol, of [(^{t}BuNP)$_2$(^{t}BuNLi·THF)$_2$]. These reagents were dissolved in 12 mL of toluene, and the solution was stirred at 70 °C for 12 h. The ensuing yellow suspension was allowed to cool and filtered through a medium-porosity frit, and the clear, light-yellow solution was evaporated to dryness. The residue was taken up in 5 mL of hexanes and stored at −23 °C for 5 days to yield 0.321 g (58.4%) of a yellow solid.

Mp: 178 °C. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ = 7.42 (d, 4H, *o*-Ph), 7.21 (t, 4H, *m*-Ph), 6.86 (s, 2H, *p*-Ph), 1.449 (s, 18H, N^{t}Bu), 1.154 (s, 18H, N^{t}Bu). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 25 °C): δ = 150.1 (d, J_{PC} = 22.5 Hz), 129.1(s), 121.2 (d, J_{PC} = 13.7 Hz), 120.1(s), 55.33 (d, J_{PC} = 7.9 Hz), 52.78 (t, J_{PC} = 13.0 Hz), 33.66 (d, J_{PC} = 8.9 Hz), 30.41 (t, J_{PC} = 7.1 Hz). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, 25 °C): δ = 355.6 (s, 1P), 168.4 (s, 2P). Anal. Calcd for $C_{28}H_{46}N_6GaP_3$: C, 53.44; H, 7.37; N, 13.35. Found: C, 53.24; H, 7.53; N, 13.18.

X-ray Diffraction Studies. {**[(^{t}BuNP)$_2$(^{t}BuN)$_2$]GaCl**}, **1.** With a Bruker Smart CCD single-crystal diffractometer, 7546 intensity data were collected at 213 K in the 4.0−56.6° 2θ range. Of these data, having indices $-10 < h < 12$, $-15 < k < 9$, $-13 < l < 13$, 2895 were unique and observed ($I > 2\sigma(I)$) and used in the refinement. Cell parameters were retrieved with SMART[10] software and refined with SAINT[11] on all observed reflections. An empirical absorption correction was applied with SADABS.[12] The structure was solved in the centrosymmetric space group $P2_1/m$ (No. 11) with the direct methods option of the SHELXS-90 program[13] and refined by least-squares methods on F^2 with SHELXL-97,[14] incorporated in SHELXTL-PC

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Table 1. Crystal Data for **1** and **2**

mol formula	$C_{16}H_{34}N_4ClGaP_2$	$C_{24}H_{54}N_6GaP_3$
fw	449.58	587.35
space group	$P2_1/m$ (No. 11)	*Pnma* (No. 62)
a, Å	9.5478(6)	19.0514(2)
b, Å	11.9540(7)	17.5082(1)
c, Å	10.1501(6)	9.6695(1)
β, deg.	97.808(1)	90
V, Å^3	1147.7(1)	3225.32(5)
Z	2	4
ρ(calc), g cm^{-3}	1.301	1.210
λ, Å	0.710 73	0.710 73
temp, K	213	213
μ, cm^{-1}	14.61	10.24
$R(F)^a$	0.0364	0.0501
$R_w(F^2)^b$	0.0781	0.1309

^{a} $R = \sum|F_o - F_c|/\sum|F_o|$. ^{b} $R_w = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$ where $P = (F_o^2 + 2F_c^2)/3$. For **1**, $x = 0.0356$ and $y = 0.4440$. For **2**, $x = 0.0672$ and $y = 5.0200$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

1		**2**	
	Bond Lengths		
Ga(1)−Cl(1)	2.1600(9)	Ga(1)−N(4)	2.021(3)
Ga(1)−N(3)	1.886(3)	Ga(1)−N(2)	1.924(3)
Ga(1)−N(1)	2.089(3)	Ga(1)−N(3)	1.896(3)
P(1)−N(3)	1.692(2)	P(3)−N(4)	1.612(3)
P(1)−N(1)	1.808(2)	P(1)−N(2)	1.694(4)
P(1)−N(2)	1.727(2)	P(2)−N(3)	1.693(4)
		P(1)−N(1)	1.735(3)
		P(2)−N(1)	1.742(3)
	Bond Angles		
Cl(1)−Ga(1)−N(3)	121.12(6)	N(4A)−P(3)−N(4)	95.5(2)
N(3)−Ga(1)−N(3A)	116.01(11)	P(3)−N(4)−Ga(1)	96.10(13)
Cl(1)−Ga(1)−N(3)	126.45(8)	N(4)−Ga(1)−N(4A)	72.3(2)
N(1)−Ga(1)−N(3)	77.67(7)	N(4)−Ga(1)−N(3)	115.50(11)
Ga(1)−N(3)−P(1)	99.50(10)	N(4)−Ga(1)−N(2)	115.50(11)
Ga(1)−N(1)−P(1)	88.78(9)	N(2)−Ga(1)−N(3)	115.6(2)
N(1)−P(1)−N(3)	99.01(10)	Ga(1)−N(3)−P(2)	111.9(2)
P(1)−N(1)−P(1A)	96.46(12)	Ga(1)−N(2)−P(1)	111.1(2)
P(1)−N(2)−P(1A)	102.64(13)	N(3)−P(2)−N(1)	100.54(13)
N(1)−P(1)−N(2)	80.17(9)	N(2)−P(1)−N(1)	100.76(13)
		N(1)−P(1)−N(1A)	83.1(2)
		N(1)−P(2)−N(1A)	82.7(2)
		P(1)−N(1)−P(2)	96.85(14)

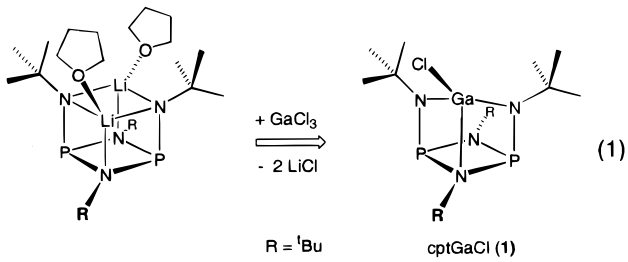
version 5.03.[15] Hydrogen atom positions were calculated by geometrical methods and refined using a riding model. The crystal showed no decay during the data collection. See Tables 1 and 2.

{**[(**^{t}**BuNP)$_2$(**^{t}**BuN)$_2$]Ga(**^{t}**BuNPN**^{t}**Bu)**}**, 2.** With a Bruker Smart CCD diffractometer 14466 intensity data were collected at 213 K from 4.3° to 55.4° in 2θ. The index ranges were $-24 < h < 17$, $-20 < k < 22$, $-12 < l < 11$. Of these data, 3589 were unique ($R_{int} = 0.0388$) and observed ($I > 2\sigma(I)$) and used in the refinement. An empirical absorption correction was applied with SADABS. The structure was solved in the space group *Pnma* (No. 62) and refined in a manner strictly analogous to that used for **1**.

Results and Discussion

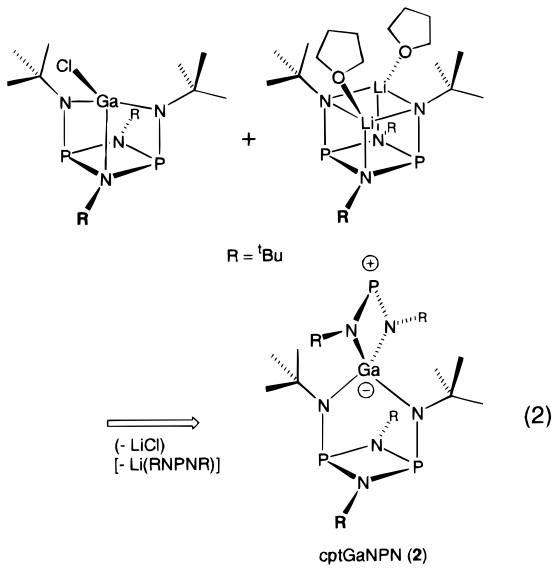
Salt elimination reactions are a convenient method for the synthesis of bis(amido) compounds of nonmetals and most reductively insensitive metals.[16] Treatment of gallium trichloride with [(^{t}BuNP)$_2$(^{t}BuNLi·THF)$_2$] = cptLi$_2$, eq 1, thus afforded colorless **1** in good yields.

Preliminary structural information on **1** was obtained by ^{1}H NMR techniques, which revealed one signal each for the *tert*-butylamido and *tert*-butylimido groups. There was one sharp singlet at 160.8 δ in the ^{31}P NMR spectrum, indicative of a symmetrically coordinated cyclodiphosphazane ligand. These data are consistent with a bis(*tert*-butylamido)cyclodiphosphazane gallium chloride complex, cptGaCl, although the appearance of both *tert*-butylimido groups as one signal implies that the molecule is fluxional in solution.



(1)

When reaction 1 was carried out with a slight excess of cptLi$_2$, however, it produced small amounts of a yellow compound. The identical yellow compound was the sole product in the reaction of pure cptGaCl with 1 equiv of [(^{t}BuNP)$_2$(^{t}BuNLi·THF)$_2$] (eq 2).



(2)

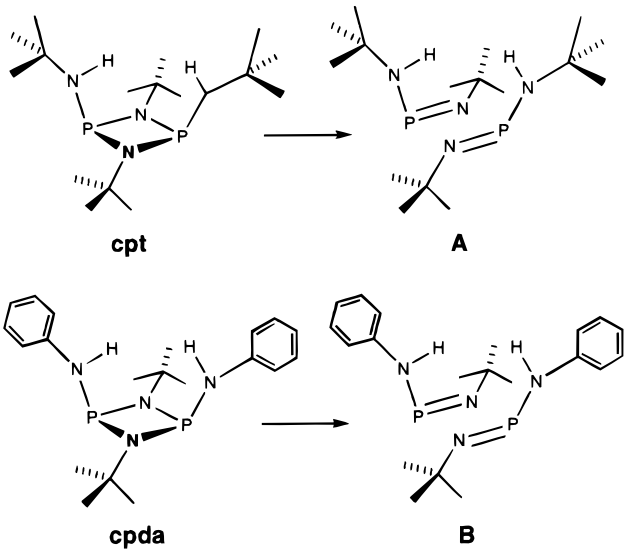
A ^{1}H NMR spectrum of this yellow solid, which consisted of three singlets of equal intensity, could not be interpreted in terms of a conventional bis(*tert*-butylamido)cyclodiphosphazane complex. The ^{31}P NMR spectrum was more informative, however, because it showed two singlets at 373.5 and 160.1 δ, respectively, in a 1:2 intensity ratio. Signals between 340 and 380 δ are highly diagnostic for 1,3-diaza-2-phosphaallyls,[7] and the NMR data thus suggested that the yellow complex **2** contained a diazaphosphaallyl species, in addition to a conventional bis(amido)cyclodiphosphazane ligand. Although the presence of a diazaphosphaallyl ligand seemed certain, it was uncertain whether it was formed from the breakup of coordinated bis(amido)cyclodiphosphazane or from excess dilithio bis(*tert*-butylamido)cyclodiphosphazane.

Ring-opened bis(amino)cyclodiphosphazanes with four identical organic substituents yield symmetric amino(imino)phosphines, **A** (Scheme 2), while those with different organic substituents on the amino and imino nitrogens produce asymmetric amino(imino)phosphines, **B**. Conclusive proof about the origin of the heteroallyllic ligands could thus come only from a reaction between a gallium complex and a dilithio bis(amido)-

(15) *SHELXTL 5.03 (PC-Version), Program Library for Structure Solution and Molecular Graphics*; Bruker Analytical Instruments Division: Madison, WI, 1995.

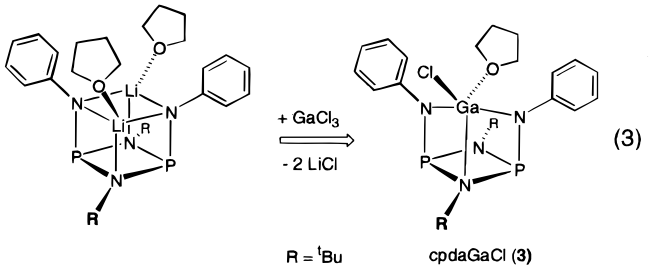
(16) See, for example: Lappert, M. F.; Sanger, A. R.; Srivastava, R. C.; Power, P. P. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, 1980.

Scheme 2



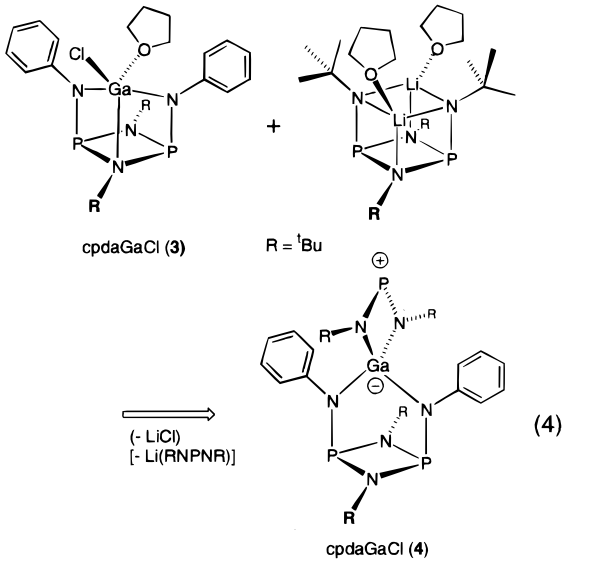
cyclodiphosphazane in which both compounds bore different organic substituents on the amido nitrogen atoms.

To synthesize a gallium cyclodiphosphazane complex without *tert*-butylamido substituents, we treated gallium chloride with $[(^tBuNP)_2(PhNLi\cdot THF)_2]$ = cpdaLi$_2$, eq 3. This reaction afforded the bis(anilido)cyclodiphosphazane complex $\{[(^tBuNP)_2(PhN)_2]GaCl\cdot THF\}$ = cpdaGaCl (**3**), which, due to its lesser steric bulk, was isolated as a THF solvate. This complex had similar NMR spectra as **1**, and like **1** it was fluxional at room temperature.



(3)

When **3** was allowed to react with cptLi$_2$, eq 4, pale yellow **4** was the only product. The ^{31}P NMR spectrum of this yellow

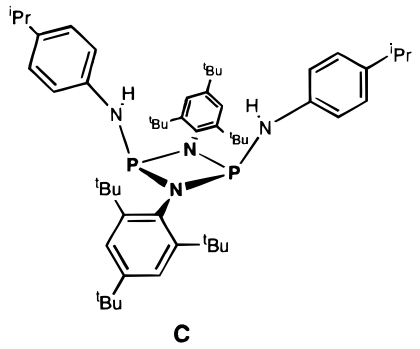


(4)

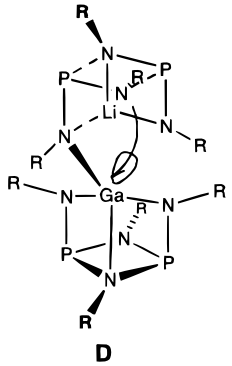
solid revealed a peak pattern almost identical with that of **2**, with two singlets in a 2:1 integrated ratio. The more intense signal was due to the bis(anilido)cyclodiphosphazane ligand, while the smaller signal was from a diazaphosphaallyl ligand. The ^{1}H NMR spectrum of **3** showed only two *tert*-butyl singlets of equal intensity, as would be expected for a complex in which both the bis(amido)cyclodiphosphazane and the heteroallyl ligand each had two equivalent *tert*-butyl groups.

Reaction 4 thus confirmed that the heteroallyl moiety originated from a bis(amido)cyclodiphosphazane with four identical substituents. Added cptLi$_2$, and not coordinated bis(anilido)cyclodiphosphazane, was the source of the diazaphosphaallyl ligand.

Ring Opening. The only previously reported ring opening of a cyclodiphosphazane involved 1,3-bis[(2,4,6-tris(*tert*-butyl)phenyl]-2,4-bis(4-isopropylphenyl)cyclodiphosphazane, **C**. This molecule furnished, after an 18 h toluene reflux in the presence of ZnMe$_2$, a spirocyclic zinc complex with two heteroallyl ligands.[7] Due to its very large substituents, however, this cyclodiphosphazane is, in essence, made to ring open. In fact, amino(imino)phosphines with very bulky substituents do not dimerize to form cyclodiphosphazanes, but remain monomeric instead.[17] The ring-opening reactions reported herein are unique for three reasons: (1) they involve dilithio salts of bis(amino)cyclodiphosphazanes, (2) the ring is substituted with comparatively small *tert*-butyl groups, and (3) they proceed under relatively mild conditions.



These cycloreversions are likely Lewis acid mediated, because we have not observed the formal monomer of cptLi$_2$ at the comparatively low temperatures of these reactions. Presumably the bis(amido)cylodiphosphazane displaces the chloride ligand and coordinates the bis(amido)cyclodiphosphazane gallium complex in an η^1 fashion. The (P−N)$_2$ ring then opens under the inductive effects exerted by both metals (**D**). Every



(17) Niecke, E.; Nieger, M.; Gärtner-Winkhaus, C.; Kramer, B. *Chem. Ber.* **1990**, *123*, 477.

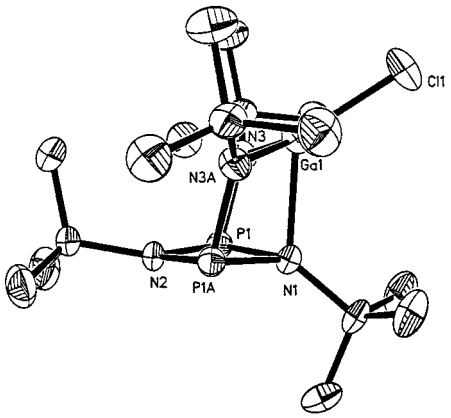


Figure 1. Perspective view of the solid-state structure of **1**.

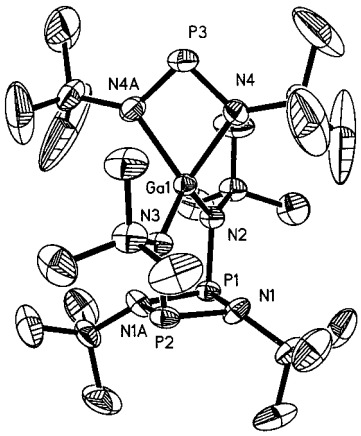


Figure 2. Perspective view of the solid-state structure of **2**.

diazaphosphaallyl ligand transferred in this manner generates 1 equiv of monolithio amido(imino)phosphine, but this species likely does not persist and quickly dimerizes to $cptLi_2$.

The plausibility of this mechanism is also supported by the observation that neither the heating of **1** or **3** in the absence of added dilithio salt nor the addition of bis(*tert*-butylamino)-cyclodiphosphazane to the gallium monochloro complexes yields diazaphosphaallyls. Excess chelating ligand in the form of dilithio bis(amido)cyclodiphosphazane is apparently required for the formation of the heteroallylic ligands.

The Crystal Structures of CPTGaCl and CPTGaNPN. Single-crystal X-ray diffraction studies showed that **1**, whose ORTEP diagram is shown in Figure 1, has indeed the expected structure. The compound crystallizes with no unusually short intermolecular contacts in the monoclinic space group $P2_1/m$. A crystallographic mirror plane, which contains gallium, chloride, and both cyclodiphosphazane ring nitrogen atoms, bisects the planar $(P-N)_2$ ring. Almost perpendicular to this ring are the two exocyclic P−N bonds, whose nitrogen atoms, together with the chloride ligand, form a trigonal planar primary coordination sphere around the metal. In addition to these covalent bonds, there is a donor bond from the lone pair electrons on the ring nitrogen atoms to the gallium atom. This fourth bond, which provides an intramolecular Lewis base stabilization, renders the gallium atom tetrahedral, albeit with angles that differ substantially from ideal tetrahedral values. Intramolecular donor bonds of this type are well documented for inorganic cage compounds; but they are weak and often lead to fluxionality in these symmetric molecules.[18]

The gallium−chloride bond has normal length, 2.1600(9) Å, but the symmetry-equivalent gallium−amide bonds, 1.886(2) Å, are slightly shorter than those in related compounds.[19] The N···Ga donor bond, 2.089(3) Å, is expectedly ca. 0.2 Å longer than the covalent Ga−N bonds and has the same length as the transannular Ga−N dative bond in the organogallium species $MeN[(CH_2)_3]Ga$.[20] It is, however, significantly shorter than the N−Ga donor bonds, 2.31(1) Å, in the five-coordinate gallium complex $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Ga(N_3)_2$.[21]

The dimensions of the cyclodiphosphazane ligand in **1** are similar to those in previously reported bis(amido)cyclodiphosphazane complexes.[5] The exocyclic P−N bonds are shortest, 1.692(2) Å, and the P−N bonds to the four-coordinate N2 are longest, 1.808(2) Å, with the endocyclic bonds to the three-coordinate N1 being of intermediate lengths, 1.727(2) Å.

The crystal structure of **2** consists of discrete, close-packed molecules. These zwitterionic spirocycles, whose ORTEP drawing is shown in Figure 2, have crystallographic C_s symmetry, but are almost C_{2v} symmetric. Nitrogen atoms 2 and 3, all phosphorus atoms, and the gallium atom lie in the crystallographic mirror plane. The metal is centered above the cyclodiphosphazane ring and is thus in a much more symmetrical environment than in **1**. Its coordination geometry is to a first approximation tetrahedral, but there are significant deviations from ideal tetrahedral dimensions, the most notable being the acute N2−Ga−N3 angle of 95.9°.

The upper half of this spirocyclic molecule is centered perpendicularly above the cyclodiphosphazane ring and consists of a completely planar 1,3-diaza-2λ^2-phospha-4λ^4-gallatacyclobutane moiety. A similar diazaphosphagallata ring, but with two exocyclic chloride ligands and synthesized by a different route, has been reported.[22] The endocyclic angles subtended at gallium and phosphorus in **2** are 72.3° and 95.9°, respectively, the larger element bearing most of the angle strain.

The P−N bonds, 1.612(3) Å, are intermediate between single (1.77 Å) and double (1.54 Å) bonds[23] and are similar in length to those in other derivatives of diazaphosphaallyl ligands.[7,24] The symmetry-equivalent gallium−amide bonds are unusually long, 2.021(3) Å, however, presumably reflecting the unfavorable angle between the gallium atom and the diazaphosphaallyl ligand. The short gallium−amide bonds with the cyclodiphosphazane ligand display a slight asymmetry (1.924(3), 1.896(3) Å) and are virtually identical in length to those in **1**, despite the higher coordination number of the metal atom in **2**. Both the endocyclic and exocyclic P−N bonds of the bis(*tert*-butylamido)cyclodiphosphazane ligand have normal lengths.

Crystals of neither **3** nor **4** were of sufficient quality for single-crystal X-ray analysis, but their NMR-spectroscopic data strongly suggested that they are structural analogues of **1** and

(18) (a) Scherer, O. J.; Wolmershäuser, G.; Conrad, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 404. (b) Veith, M.; Goffing, F.; Huch, V. *Chem. Ber.* **1988**, *121*, 943. (c) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237.

(19) (a) Harrison, W.; Storr, A.; Trotter, J. *J. Chem. Soc., Chem. Commun.* **1971**, 1101. (b) Amirkhalili, S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1206.

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(21) Cowley, A. H.; Gabbaï, F. P.; Olbrich, F.; Corbelin, S.; Lagow, R. J. *J. Organomet. Chem.* **1995**, *487*, C5.

(22) Oberdörfer, R.; Nieger, M.; Niecke, E. *Chem. Ber*. **1994**, *127*, 2397.

(23) Corbridge, D. E. C. *Phosphorus: An Outline of its Chemistry, Biochemistry and Technology*, 5th ed.; Elsevier: Amsterdam, 1995.

(24) (a) Pohl, S. *Z. Naturforsch.* **1977**, *32b*, 1342. (b) Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Williams, H. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1634. (c) Detsch, R.; Niecke, E.; Nieger, M.; Schoeller, W. W. *Chem. Ber.* **1992**, *125*, 1119.

2. The major structural difference is the coordinated THF molecule in **3**, which renders the gallium atom five-coordinate.

Molecular Fluxionality. The crystal structure of **1** shows that the *tert*-butyl groups of the imino nitrogen atoms are diastereotopic, supporting the earlier assumption that the molecule is fluxional in solution. A site exchange of the gallium atom between the two equivalent ring nitrogen atoms is the most plausible fluxional mode. From the maximum projected chemical shift difference of the diastereotopic ring *tert*-butyl groups and our inability to freeze out the ground state conformation, down to −90 °C, an upper limit of ca. 10 kcal/mol can be estimated for $\Delta G^{\ddagger}$.[9]

Compound **3** also displays one ^{1}H NMR signal for the ring *tert*-butyl substituents at room temperature, but two signals at −40 °C. Using a form of the Eyring equation, modified for dynamic NMR phenomena,[9] we calculated a free energy of activation of 14.4(4) kcal/mol. Because the gallium atom is coordinated by one THF molecule, the fluxionality in **3** is not merely a site exchange of this atom; it must be preceded (or at least accompanied) by THF dissociation. This is reflected in the higher free energy of activation for **3**. Processes like these are common for inorganic *seco*-heterocubes and have, for example, been reported for Ge(IV) complexes with isoelectronic bis(amido)cyclodisilazane ligands.[25] In these compounds the activation energies were similar to that in **3**, falling in the range 13−15 kcal/mol. The low activation energies for these E−N donor bonds, both in **1** and **3**, may be a consequence of the unfavorable bond geometries in these cage compounds.

Conclusion

Bis(amido)cyclodiphosphazane gallium chloride complexes react with dilithio bis(*tert*-butylamido)cyclodiphosphazane salts under comparatively mild conditions to furnish 1,3-diaza-2-phosphaallyl ligands. These results complement earlier reports on the ring opening of neutral bis(amino)cyclodiphosphazanes by Lewis acidic metals.[7] The ease of ring opening in the title compounds is surprising and suggests that the cycloreversion of cyclodiphosphazanes is more common than was once thought. While this reaction compromises the use of cyclodiphosphazane ligands in some applications, it may be a convenient source of diazaphosphaallyl ligands in others.

Acknowledgment. We thank the University of North Dakota and North Dakota EPSCoR for financial support.

Supporting Information Available: Two X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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