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Syntheses and Molecular Structures of Bis(*tert*-butylamido)cyclodiphosph(III)azane Cage Complexes of Thallium(I) and Indium(II)

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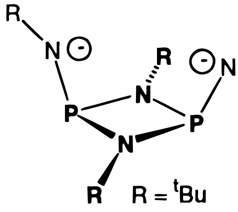
The interaction of $[(^t\mathrm{BuNP})_2(^t\mathrm{BuNLi}\cdot\mathrm{THF})_2]$ with TlCl or InCl in toluene/tetrahydrofuran mixtures has produced the cyclodiphosph(III)azane complexes $[(^t\mathrm{BuNP})_2(^t\mathrm{BuNTl})_2]$, **1**, and $[(^t\mathrm{BuNP})_2(^t\mathrm{BuN})_2\mathrm{In}]_2$, **2**, respectively. While **1** is the expected dinuclear thallium(I) heterocube, **2** is a dimer of mononuclear indium(II) cages that are connected by an unsupported indium−indium bond. The extremely air-sensitive **1** crystallizes in the monoclinic space group $P2_1/c$, with unit cell dimensions $a = 14.5050(6)$ Å, $b = 16.5265(7)$ Å, $c = 9.9864(1)$ Å, $\beta = 96.3006(9)°$, and $Z = 4$. Orange-yellow **2** crystallizes with four molecules in the orthorhombic space group *Pbca*, having unit cell dimensions $a = 12.9249(2)$ Å, $b = 18.3492(1)$ Å, and $c = 18.7763(3)$ Å.

Polynuclear compounds of low-valent group 13 derivatives have been attracting attention[1] because they feature intriguing intra- and intermolecular metal−metal interactions that often defy description in terms of simple bonding models.[2] We are investigating the coordination chemistry of the chelating bis(*tert*-butylamido)cyclodiphosphazane $[(^t\mathrm{BuNP})_2(^t\mathrm{BuN})_2]^{2-}$, **A**,[3]



A

and have recently shown that this ligand can incorporate two lithium atoms to give dinuclear heterocubic molecules.[4] On the basis of these results and Veith's prior work on isostructural bis(*tert*-butylamido)cyclodisilazane complexes,[5] we considered it likely that this cyclodiphosphazane[6] would also form dinuclear, heterocubic molecules with monovalent group 13 metals. Herein we report on the syntheses and X-ray structural characterizations of the first such cyclodiphosphazane complexes of group 13 metals.

Experimental Section

General Considerations. All operations were done in standard Schlenk-type 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. ^{1}H and ^{13}C NMR spectra are referenced relative to C_6D_5H at 7.15 ppm and to C_6D_6 at 128.0 ppm, respectively. Melting points were obtained on a Mel-Temp apparatus; they are uncorrected. E & R Microanalytical Laboratory, Corona, NY, performed the elemental analyses.

The monochlorides of thallium and indium were purchased from Aldrich and were used as received. The cyclodiphosphazane *cis*-$[(^t\mathrm{BuNP})_2(^t\mathrm{BuNH})_2]$ and its dilithium salt were prepared by published procedures.[4]

Synthesis of $[(^t\mathrm{BuNP})_2(^t\mathrm{BuNTl})_2]$, 1. A 100-mL three-neck flask was charged with 0.816 g, 3.40 mmol, of TlCl, 10 mL of THF, and a magnetic stirring bar. Exactly 0.843 g, 1.67 mol, of $[(^t\mathrm{BuNP})_2(^t\mathrm{BuNLi}\cdot\mathrm{THF})_2]$ dissolved in 20 mL of THF was then added dropwise to the stirred TlCl suspension at −78 °C. The initially light-yellow reaction mixture became increasingly darker, and after being stirred at 23 °C for 2 days, it was a greenish-yellow suspension. Removal of the solvent in vacuo produced a dry, yellow-green solid, which was extracted with 20 mL of toluene. Upon filtration, this extract afforded an extremely

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[1] (a) Uhl, W.; Layh, M.; Hiller, W. *J. Organomet. Chem.* **1989**, *368*, 139. (b) Schumann, H.; Janiak, C.; Pickardt, J.; Boerner, U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 789. (c) Rheingold, A. L.; Liable-Sands, L. M.; Trofimenko, S. *J. Chem. Soc., Chem. Commun.* **1997**, 1691. (d) Schumann, H.; Janiak, C.; Khan, M. A.; Zuckerman, J. J. *J. Organomet. Chem.* **1988**, *354*, 7. (e) Hellmann, K. W.; Gade, L. H.; Steiner, A.; Stalke, D.; Moeller, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 160. (f) Veith, M.; Spaniol, A.; Poehlmann, J.; Gross, F.; Huch, V. *Chem. Ber.* **1993**, *126*, 1413. (g) Li, X. W.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 7578. (h) Henkel, S.; Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 3, 681. (i) Uhl, W.; Graupner, R.; Hiller, W.; Neumayer, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 62. (j) Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Bond, M. R.; Carrano, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 2070. (k) Klinkhammer, K. W.; Henkel, S. *J. Organomet. Chem.* **1994**, *480*, 167. (l) Uhl, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1386.

[2] For a detailed discussion of metal−metal interactions in low-valent group 13 compounds, see: Janiak, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 5924.

[3] Bis(amino)cyclodiphosph(III)azanes are a well-known class of inorganic heterocycles whose function as chelating bis(amide) ligands, however, had not previously been explored. For leading references on these molecules, see: (a) Tarassoli, A.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1982**, *21*, 2684. (b) Hill, T. G.; Haltiwanger, R. C.; Thompson, M. L.; Katz, S. A.; Norman, A. D. *Inorg. Chem.* **1994**, *33*, 1770. (c) Bulloch, G.; Keat, R. J. *Chem. Soc., Dalton Trans.* **1974**, 2010.

[4] Schranz, I.; Stahl, L.; Staples, R. J. *Inorg. Chem.* **1998**, *37*, 1493.

[5] (a) Veith, M.; Goffing, F.; Huch, V. *Chem. Ber.* **1988**, *121*, 943. (b) Veith, M.; Goffing, F.; Becker, S.; Huch, V. *J. Organomet. Chem* **1991**, *406*, 105.

[6] Cyclodiphosph(III)azanes are also called diazadiphosphetidines−a naming system preferred by CAS.

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air-sensitive lemon-yellow solution, which was concentrated to 10 mL and stored at −7 °C. After 10 days, 0.568 g, 0.752 mmol, of yellow plates was isolated. Concentration of the supernate to 5 mL gave an additional 0.377 g, 0.500 mmol, of **1** for an overall yield of 0.945 g, 1.25 mmol, 73.6%. Mp: 138−140 °C. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 1.453 (br s, 18 H, N^{t}Bu), 1.315 (br s, 18 H, N^{t}Bu). ^{13}C NMR (75 MHz, benzene-d_6, 25 °C): δ 53.6 (br), 34.79 (br t, $J_{\mathrm{TlC}} = 50$ Hz), 25.50 (br d, $J_{\mathrm{TlC}} = 48$ Hz). ^{31}P NMR (121 MHz, benzene-d_6, 25 °C): δ 206.3 (br t, $J_{\mathrm{TlP}} = 29$ Hz). Anal. Calcd for $C_{16}H_{36}N_4P_2Tl_2$: C, 25.43; H, 4.81; N, 7.42. Found: C, 25.41; H, 4.61; N, 7.36.

Synthesis of [(^{t}BuNP)$_2$(^{t}BuN)$_2$In]$_2$, 2. To 0.527 g, 3.51 mmol, of InCl in 15 mL of THF was added 0.859 g, 1.70 mmol, of [(^{t}BuNP)$_2$(^{t}BuNLi·THF)$_2$] dissolved in 20 mL of toluene. The initially light-yellow reaction mixture became increasingly darker, finally forming a gray-green suspension. This suspension was filtered to give a clear, light yellow filtrate, which was concentrated to 5 mL. After the flask had been stored for several days at −15 °C, 0.679 g, 0.544 mmol, of yellow-orange crystals of **2** was isolated. Yield: 31%, based on InCl; 62%, based on InCl$_2$. Mp: 118 °C. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 1.502 (s, 18 H, N^{t}Bu), 1.451 (s, 18 H, N^{t}Bu). ^{13}C NMR (75 MHz, benzene-d_6, 25 °C): δ 54.04 (d, $J_{\mathrm{PC}} = 15.7$ Hz), 53.78 (t, 10.1 Hz), 36.03 (d, $J_{\mathrm{PC}} = 10.7$ Hz), 30.48 (br d, $J_{\mathrm{PC}} = 7.0$ Hz). ^{31}P NMR (121 MHz, benzene-d_6, 25 °C): δ 158.13 (s). Anal. Calcd for $C_{32}H_{72}N_8P_4In_2$: C, 41.66; H, 7.87; N, 12.15. Found: C, 41.86; H, 8.00; N, 11.91.

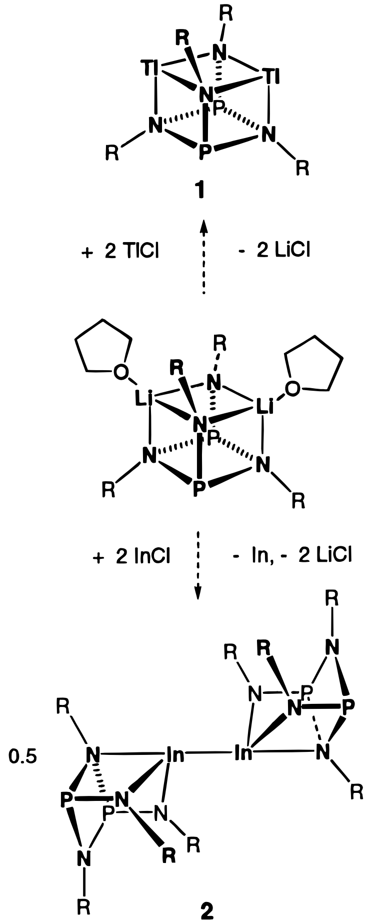
X-ray Diffraction Studies. (a) [(^{t}BuNP)$_2$(^{t}BuNTl)$_2$], 1. Exactly 11 152 total reflection data were collected at 213 K in the 3.8−55.8° 2θ range with a Siemens SMART CCD diffractometer. Of these data, having indices $-17 \le h \le 17$, $-21 \le k \le 18$, $-8 \le l \le 12$, 4904 were considered unique and observed ($I > 2\sigma(I)$) and used in the refinement. Cell parameters were retrieved with SMART[7] software and refined with SAINT[8] on all observed reflections. An empirical absorption correction was applied with SADABS.[9] The structure was solved in the unambiguous space group $P2_1/c$ (No. 14) with the direct methods option of the SHELXS-90 program[10] and refined by least-squares methods on F^2 with SHELXL-97,[11] incorporated in SHELXTL-PC V 5.03.[12] Hydrogen atom positions were calculated by geometrical methods and refined using a riding model. The crystal showed no decay during the data collection.

[(^{t}BuNP)$_2$(^{t}BuN)$_2$In]$_2$, 2. A total of 20 263 reflection data were collected at 213 K in the 2θ range 4.3−55.8°, having indices $-16 \le h \le 16$, $-23 \le k \le 18$, $-21 \le l \le 24$. Of these data, 4899 were considered unique 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 unambiguous space group *Pbca* (No. 61) and refined in a manner strictly analogous to that for **1**.

Results

The slow addition of a THF solution of [(^{t}BuNP)$_2$(^{t}BuNLi·THF)$_2$] to a suspension of TlCl in toluene/THF, Scheme 1, formed a greenish-orange reaction mixture from which bright yellow crystals of [(^{t}BuNP)$_2$(^{t}BuNTl)$_2$], **1**, were isolated upon cooling. In solution and even in the solid state, **1** is an extremely air-sensitive compound that blackens on the slightest exposure to oxygen.

Scheme 1



The analogous reaction of [(^{t}BuNP)$_2$(^{t}BuNLi·THF)$_2$] with InCl yielded orange-yellow [(^{t}BuNP)$_2$(^{t}BuN)$_2$In]$_2$, **2**. Although much less air-sensitive than the thallium derivative, this complex slowly decomposed in solution with the formation of metallic indium.

We had anticipated, perhaps naively, that both compounds would have heterocubic structures, and the NMR data seemed to confirm this suspicion. Thus, for example, the spectra showed the expected two signals for the amido and imido *tert*-butyl groups but only one signal for equivalent P(III) centers. The ^{31}P NMR spectrum of the thallium derivative, in particular, lent further support to this compound's existence as a heterocubic molecule as it showed a broad triplet, indicative of coupling to two equivalent thallium atoms. Elemental analyses and the extreme difference in their chemical behaviors, however, suggested that the indium compound was not isostructural with the thallium derivative. Single-crystal X-ray studies confirmed the nonisostructural natures of **1** and **2** and also revealed the indium complex to be a dimer with an indium−indium bond.

The dithallium complex **1** crystallizes as a molecular solid whose sole intermolecular contacts are of the van der Waals type. Figure 1 shows an ORTEP drawing of this complex that emphasizes the coordination environment about the metal atoms. Crystal data and bond parameters are listed in Tables 1 and 2, respectively. The cage complex has C_{2v} symmetry and is isoelectronic and isostructural with a previously reported bis(*tert*-butylamido)cyclodisilazane dithallium analog.[5a] The size mismatch of its constituent atoms has distorted the molecular cage and resulted in exceedingly small bond angles around the thallium atoms, forcing the largest atoms to bear most of the angle strain. Nonbonding interactions between the metal atoms and the *tert*-butyl groups of the cyclodiphosphazane unit, in turn, have pushed the organic substituents well below the plane of

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(7) *SMART V 4.043 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(8) *SAINT V 4.035 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(9) SADABS program for absorption corrections using the Siemens CCD Detector System, based on: Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

(10) Sheldrick, G. M. *SHELXS-90, Program for the Solution of Crystal Structures;* University of Göttingen: Göttingen, Germany, 1990.

(11) Sheldrick, G. M. *SHELXL-97, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

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

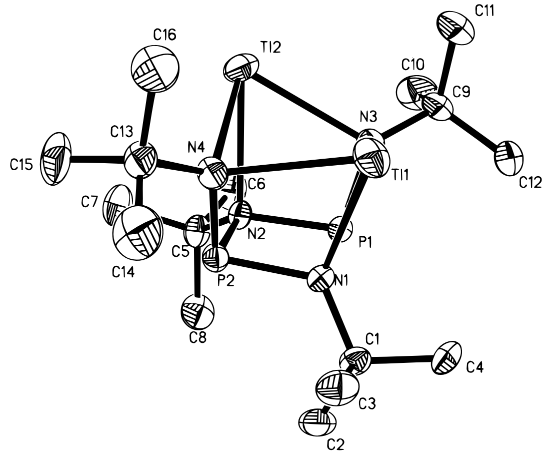

Figure 1. Perspective view and labeling scheme for **1**, emphasizing the highly pyramidalized thallium atoms.

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

mol formula	$C_{16}H_{36}N_4P_2Tl_2$	$C_{32}H_{72}N_8P_4In_2$
fw	755.17	922.50
space group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)
a, Å	14.5050(6)	12.9249(2)
b, Å	16.5265(7)	18.3492(1)
c, Å	9.9864(1)	18.7763(3)
β, deg	96.3006(9)	90
V, Å^3	2379.5(2)	4453.0(1)
Z	4	4
ρ(calc), g cm^{-3}	2.108	1.376
λ, Å	0.710 73	0.710 73
temp, K	213	213
μ, cm^{-1}	136.88	12.10
$R(F)^a$	0.0240	0.0337
$R_w(F^2)^b$	0.0539	0.0654

[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 $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Lengths and Angles for **1**

	Bond Lengths (Å)		
Tl(1)−N(3)	2.587(3)	Tl(1)−N(4)	2.587(3)
Tl(2)−N(3)	2.559(3)	Tl(2)−N(4)	2.565(3)
Tl(1)−N(1)	2.613(3)	Tl(2)−N(2)	2.622(3)
P(1)−N(1)	1.770(3)	P(1)−N(2)	1.769(3)
P(2)−N(1)	1.775(3)	P(2)−N(2)	1.778(3)
P(1)−N(3)	1.659(3)	P(2)−N(4)	1.658(3)
Tl(1)−Tl(2)	3.5462(3)		
	Bond Angles (deg)		
N(3)−Tl(1)−N(4)	79.44(10)	N(3)−Tl(2)−N(4)	80.02(10)
Tl(1)−N(3)−Tl(2)	87.54(10)	Tl(1)−N(4)−Tl(2)	87.00(10)
N(3)−Tl(1)−N(1)	60.92(10)	N(4)−Tl(1)−N(1)	60.86(10)
N(2)−Tl(2)−N(4)	60.94(10)	N(3)−Tl(2)−N(2)	60.93(10)
Tl(1)−N(3)−P(1)	101.9(2)	P(1)−N(3)−Tl(2)	102.2(2)
Tl(1)−N(4)−P(2)	101.5(2)	Tl(2)−N(4)−P(2)	102.3(2)
N(1)−P(1)−N(3)	99.9(2)	N(2)−P(1)−N(3)	100.0(2)
N(1)−P(2)−N(4)	100.2(2)	N(2)−P(2)−N(4)	99.8(2)
P(2)−N(1)−Tl(1)	97.31(13)	P(1)−N(2)−Tl(2)	96.76(13)
P(2)−N(2)−Tl(2)	96.84(13)	P(1)−N(1)−Tl(1)	97.09(13)
N(1)−P(1)−N(2)	82.7(2)	N(1)−P(2)−N(2)	82.4(2)
P(1)−N(1)−P(2)	97.4(2)	P(1)−N(2)−P(2)	97.3(2)

the $(P-N)_2$ ring. While slightly longer than twice the covalent radius of thallium,[13] the metal atom separation, 3.5462(3) Å, is considerably shorter than the sum of van der Waals radii of these atoms, 4.00 Å.[14] There are two distinct groups of elongated metal−amide bonds, namely those of the $(Tl-N)_2$ ring, 2.559(3)−2.587(3) Å, and those linking this ring to the cyclodiphosphazane moiety, 2.622(3) and 2.613(3) Å. Despite the apparent steric strain within the cage, the $(P-N)_2$ ring has remained almost perfectly planar, and its bond lengths and angles appear normal when compared to those of related cyclodiphosphazane complexes.

Table 3. Bond Lengths and Angles for **2**

	Bond Lengths (Å)		
In(1)−N(3)	2.131(2)	In(1)−N(4)	2.140(3)
In(2)−N(1)	2.315(2)	In(2)−P(1)	2.9873(8)
In(1)−P(2)	2.9917(3)	In(1)−In(1)’	2.7720(4)
P(1)−N(1)	1.801(3)	P(1)−N(2)	1.723(3)
P(2)−N(1)	1.798(3)	P(2)−N(2)	1.724(3)
P(1)−N(3)	1.670(3)	P(2)−N(4)	1.672(3)
	Bond Angles (deg)		
In(1A)−In(1)−N(3)	126.82(7)	In(1A)−In(1)−N(4)	126.20(7)
N(3)−In(1)−N(4)	103.56(10)	N(3)−In(1)−N(1)	63.37(9)
N(4)−In(1)−N(1)	69.17(9)	P(1)−N(3)−In(1)	102.94(12)
P(2)−N(4)−In(1)	102.72(12)	P(1)−N(3)−In(1)	102.94(120)
P(1)−N(1)−In(1)	92.20(10)	N(1)−P(2)−N(4)	93.72(12)
N(2)−P(2)−N(4)	108.99(13)	N(1)−P(1)−N(3)	93.70(12)
N(1)−P(1)−N(2)	80.50(12)	N(2)−P(1)−N(3)	101.59(9)
N(1)−P(2)−N(2)	80.59(12)	P(1)−N(1)−P(2)	96.30(12)
P(1)−N(2)−P(2)	102.11(13)		

Bright orange **2** forms molecular crystals that are composed of isolated dimers. These $[(^tBuNP)_2(^tBuN)_2In]_2$ units are centrosymmetric and, like those of the dithallium complex, isoelectronic and isostructural with those of the cyclodisilazane analogue $[(^tBuNSiMe)_2(^tBuN)_2In]_2$.[5b] Unlike this cyclodisilazane analogue, however, **2** is not afflicted with a site disorder in the solid state, and its structure determination thus yielded more reliable bond parameters. The heterocubic moieties are decidedly unsymmetrical and are connected by a short indium−indium bond, 2.7720(4) Å, that is bisected by the inversion center of the space group. This off-center location of the indium atoms has bent the proximal *tert*-butyl substituents of the cyclodiphosphazane unit out of the plane of this ring to the point where they are almost perpendicular to the indium−indium bond. The indium atoms are to a first approximation four-coordinate but, because of the rather long N−In donor bond, are better described as having a 3 + 1 coordination environment. With its four nearest nitrogen atoms, the central diindium unit forms an almost completely planar moiety from which the indium atoms deviate by only 0.0656 Å. The geometry of their coordination environment indicates that the indium atoms are nearly sp^2-hybridized and that the amido and ring imido nitrogen atoms donate their lone-pair electrons into the empty p orbital on the metal. This description is consistent with the short indium−nitrogen bonds of the planar unit, 2.131(2) and 2.140(3) Å, and the comparatively long In−N (1) bond, 2.314 Å. (See Table 3 and Figure 2.)

Discussion

The monochlorides of indium and thallium show different chemical behaviors toward $[(^tBuNP)_2(^tBuNLi\cdot THF)_2]$ in THF/toluene solutions under identical conditions. Whereas thallium chloride reacts in a straightforward metathetical exchange, indium monochloride undergoes a redox disproportionation to afford an indium(II) dimer. In light of the redox properties of these group 13 congeners and the greater propensity of thallium to exhibit the +1 oxidation state, the isolation of nonanalogous products from these reactions is not unusual. Most authenticated indium(II) compounds were, in fact, formed by similar redox disproportionations, although at least one compound was synthesized from the indium(II) starting material In_2Br_4-

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(13) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: New York, 1984.

(14) Cotton, F. A.; Wilkinson, G.; Gaus, P. L. *Basic Inorganic Chemistry*, 3rd ed.; Wiley: New York, 1995.

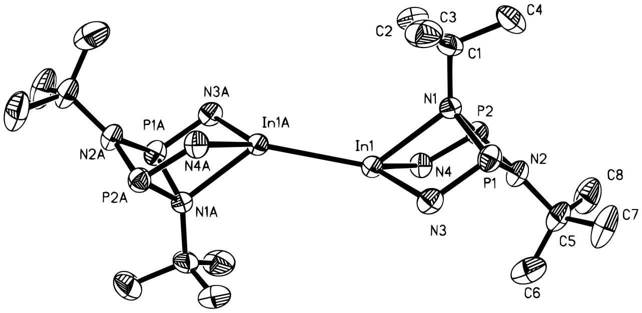

Figure 2. Perspective view and labeling scheme of **2**, showing the almost perfectly planar N(3)N(4)In−In(A)N(3A)N(4A) unit of the molecule. The *tert*-butyl substituents of these nitrogen atoms have been omitted for clarity.

(tmeda)$_2$.[1a] Interestingly, however, the cyclodisilazane analogue of **2** was prepared by the sodium reduction of the indium(III) complex [(Me$_3$SiN^{t}Bu)$_2$(N^{t}Bu)$_2$]InCl.[5b]

Molecular indium(II) compounds were first characterized in 1976.[16] Even to date only about a dozen such compounds, mainly with halide, amido, and hydrocarbyl ligands, have been reported. Despite the structural differences of their ligands, these complexes exhibit indium−indium bonds of almost identical lengths, ranging from 2.744(2) to 2.828(1) Å. It is noteworthy that the organometallic species have both the longest, 2.828(1) Å, {[(Me$_3$Si)$_2$CH]$_2$In}$_2$,[1a] and the shortest, 2.744(2) Å, {[2,4,6-(CF$_3$)$_3$C$_6$H$_2$]$_2$In}$_2$,[1j] metal−metal bond. The first X-ray structurally authenticated indium(II) dimer In$_2$Br$_3$I(tmeda)$_2$, a mixed-ligand complex, also displays a rather short indium−indium bond of 2.775(2) Å.[15] Prior to the isolation of the title compound, only two indium(II) dimers with amide ligands had been X-ray structurally characterized, namely [Me$_3$C(CH$_2$NSiMe$_3$)$_3$In]$_2$, In−In = 2.8076(9) Å,[1e] and [(Me$_3$SiN^{t}Bu)$_2$(N^{t}Bu)$_2$In]$_2$,[5b] In−In = 2.768(1) Å. The indium−indium bonds of the isoelectronic [(Me$_3$SiN^{t}Bu)$_2$(N^{t}Bu)$_2$In]$_2$[5b] and [(^{t}BuNP)$_2$(^{t}BuN)$_2$In]$_2$ are identical in length, 2.768(1) and 2.7720(4) Å, but given the isostructural and isoelectronic nature of these complexes, this observation is hardly surprising. On the basis of their diamagnetism and the derived indium−indium bond lengths—twice the covalent radius of indium—all of these compounds can be unambiguously formulated as having indium−indium single bonds.

The increasing number of reports on molecular indium(II) complexes seems to have validated the prediction that, given suitable ligands, indium(II) compounds should be quite accessible.[17] These synthetic successes, however, should not detract from the fact that the thermodynamically preferred oxidation state for indium is III, as demonstrated by the redox instability of all indium(II) species in solution. Molecular complexes of indium in this oxidation state have been isolable only when kinetically stabilized by sterically demanding monodentate ligands or specialized chelating ligands, like **A**. The susceptibility to decomposition appears to be greatest in compounds in which the metal exhibits coordination numbers lower than 4, as exemplified by the light sensitivity of {[(Me$_3$Si)$_2$CH]$_2$In}$_2$[1a] even in the solid state.

The dithallium complex, while less surprising in its composition, has arguably a more unusual structure than **2**. Here two highly pyramidalized metal centers are brought in close contact by the bridging **A**, making it a rare heterocubic group 13 amide complex in which both thallium atoms occupy one face of the cube. Theoretical calculations[2] support the notion that the metal−metal contacts in complexes such as **1** are nonbonding. The most convincing proof of the absence of a bond in **1**, however, is the molecular structure itself, which implies that the lone-pair electrons of the thallium atoms are pointing away from the diametrically opposite metal atom.

In a recent article, we noted the isostructural natures of bis(*tert*-butylamido)cyclodisilazanes and bis(*tert*-butylamido)cyclodiphosphazanes and demonstrated that these two ligands form isostructural lithium and magnesium complexes.[4] With the isolation of the title complexes, we have now extended this analogy to the post transition metals and have shown that bis(*tert*-butylamido)cyclodiphosphazane, just like its cyclodisilazane analogue, can hold metals in proximity, either with or without a formal metal−metal bond.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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