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# Synthesis and characterization of Group 13 hydrides and metal–metal bonded dimers stabilized by the macrocyclic bis(amidophosphine) ligand $[P_2N_2]$ ($[P_2N_2] = [PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh]$)

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## Abstract

Addition of $LiAlH_4$ to the monomeric chlorides *syn*-$MCl[P_2N_2]$ (M = Al (**1**), Ga (**2**), In (**3**)) results in the formation of the aluminum hydride *syn*-$AlH[P_2N_2]$ (**4**). The solution $^1H$- and $^{31}P\{^1H\}$-NMR spectra are consistent with a $C_{2v}$ symmetric species in solution. The X-ray crystal structure shows the hydride to be monomeric, and free from interaction with either salt (LiCl) or external base ($Et_2O$). The coordination of both phosphines of the macrocycle to the metal center is found in the solid state. Solution molecular weight measurements are consistent with a monomeric structure. The gallium hydride *syn*-$GaH[P_2N_2]$ (**5**) is synthesized by the addition of $LiGaH_4$ to *syn*-$MCl[P_2N_2]$ (M = Ga (**2**), In (**3**)). This species is unstable and could only be characterized in solution. Reduction of *syn*-$MCl[P_2N_2]$ (M = Ga (**2**), In (**3**)) with $KC_8$ yields the reduced, dimeric species {*syn*-$M[P_2N_2]\}_2$ (M = Ga (**6**), In (**7**)). The solution $^1H$- and $^{31}P\{^1H\}$-NMR spectra are consistent with $C_{2v}$ symmetric species in solution. The X-ray crystal structures of the gallium and indium complexes confirm the presence of unsupported metal–metal bonds in both cases. The features of the solution $^1H$- and $^{31}P\{^1H\}$-NMR spectra suggest that both dimers are fluxional in solution.

*Keywords:* Aluminum; Gallium; Indium; Hydride; Macrocycle; Metal–metal bonds

## 1. Introduction

The generation of monomeric, salt- and base-free aluminum, gallium, and indium hydrides has been the subject of continued research [1–11], as well as being intimately linked to the study of lower oxidation states of these elements [1–14] and metal–metal bonded dimers [5–14]. Recent work has shown that it is possible to use bulky aryl groups to synthesize unassociated halide derivatives of aluminum, gallium and indium, and hydride species of aluminum and gallium [2–4]. Similarly, dimeric species containing bonds between two reduced Group 13 metal centers often employ bulky aryl groups [14], although substituted alkyl groups [6,13], amides [12,15] and carboranes [16] have also been reported. We recently reported the Group 13 bis(amidophosphine) complexes $MCl[P_2N_2]$ ($[P_2N_2] = [PhP(CH_2SiMe_2N\text{–}SiMe_2CH_2)_2PPh]$, M = Al, Ga), in which the central metal was found to exist in a monomeric environment [17]. Herein we report our findings regarding the synthesis of aluminum and gallium hydride species, as well as reduced forms of gallium and indium, stabilized by the macrocyclic ligand system $[P_2N_2]$.

## 2. Results and discussion

### 2.1. Synthesis of hydride complexes of aluminum and gallium

The reaction of *syn*-$AlCl[P_2N_2]$ (**1**) [17] with $LiAlH_4$ in ether generates *syn*-$AlH[P_2N_2]$ (**4**) in moderate yield

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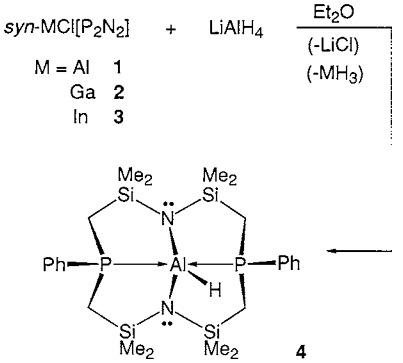
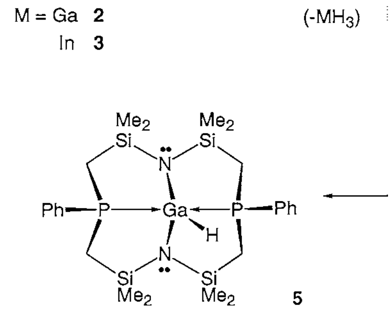
(Eq. (1)); the $^1$H-NMR spectrum of the product indicates a $C_{2v}$ symmetric complex in solution. Due to the quadrupolar aluminum center, the hydride resonance in the $^1$H-NMR spectrum was not observed. The $^{31}$P{$^1$H}-NMR spectrum of **4** consists of a singlet at −46.5 ppm; this is in contrast to the broad peak found for *syn*-AlCl[$P_2N_2$] (**1**) and that expected for a phosphorus atom bound to a quadrupolar nucleus [18,19]. Treatment of the gallium (**2**) and indium (**3**) analogues with $LiAlH_4$ also results in *syn*-AlH[$P_2N_2$] (**4**), although in lower yields (Eq. (1)). This type of transmetallation has been seen previously for Group 13 metals complexed by the [2,6-bis(dimethylaminomethyl)phenyl] ligand system [2–4] as well as yttrium bis(benzamidinato) complexes [20].



(1)

The aluminum hydride complex **4** is isolated as a colorless, air- and moisture-sensitive solid. Mass spectral and microanalytical data along with solution molecular-weight studies suggest that **4** is monomeric and free from interaction with LiCl or external base.

The addition of *syn*-MCl[$P_2N_2$] (M = Ga (**2**), In (**3**)) to an ethereal solution of $LiGaH_4$ yields *syn*-GaH[$P_2N_2$] (**5**) in low yield (Eq. (2)). The $^1$H-NMR spectrum of the product exhibits the same general features as aluminum hydride **4**. The lower quadrupolar moment of gallium allows for the Ga*H* signal to be observed (δ 5.25), although the peak is still broad enough to mask any coupling to phosphorus-31. This is in the region reported for other molecules with a terminal GaH moiety [3,4]. The $^{31}$P{$^1$H}-NMR spectrum of *syn*-GaH[$P_2N_2$] (**5**) consists of a singlet at −34.7 ppm.



(2)

Prolonged standing of solutions of **5** results in the formation of *syn*-$H_2$[$P_2N_2$] (detected by $^1$H-NMR spectroscopy) concurrent with the deposition of gallium metal. The instability of *syn*-GaH[$P_2N_2$] (**5**) did not allow for characterization by IR spectroscopy, mass spectrometry, elemental analysis or X-ray diffraction, and is reflected in the low yield of **5**. The greater thermal stability of *syn*-AlH[$P_2N_2$] (**4**) versus *syn*-GaH[$P_2N_2$] (**5**) may be due to aluminum's preference for higher coordination numbers. For example, progressively increasing the number of tertiary donors results in higher thermal stability of alane, whereas polydentate donors destabilize gallane relative to monodentate donors [21].

The analogous synthesis of an indium hydride is more problematic. Although some cationic compounds containing In–H bonds have been structurally characterized [22–26], neutral indium hydrides have only recently been isolated [27–29]. Attempts at in situ reactions with $LiInH_4$, as well as those with reagents such as LiH, KH, or $KEt_3BH$ either result in no reaction or decomposition to *syn*-$H_2$[$P_2N_2$], indium metal, and other unknown products.

### 2.1.1. *Solid-state structure of syn-AlH[P₂N₂] (**4**)*

The molecular structure and numbering scheme of **4** are illustrated in Fig. 1. Complete details of the structural analyses of **4**, **6** and **7** are compiled in Table 1. As the hydride ligand was located, but not refined, information regarding the aluminum hydride bond length or angles involving this proton are not available. The metal center exhibits trigonal bipyramidal geometry, with the bond angles involving Al, P(1) and P(2) being nearly identical in hydride **4** and chloride **1** [17].

The aluminum–phosphorus bond lengths (2.517(3) and 2.522(3) Å) are longer than those in *syn*-AlCl[$P_2N_2$]

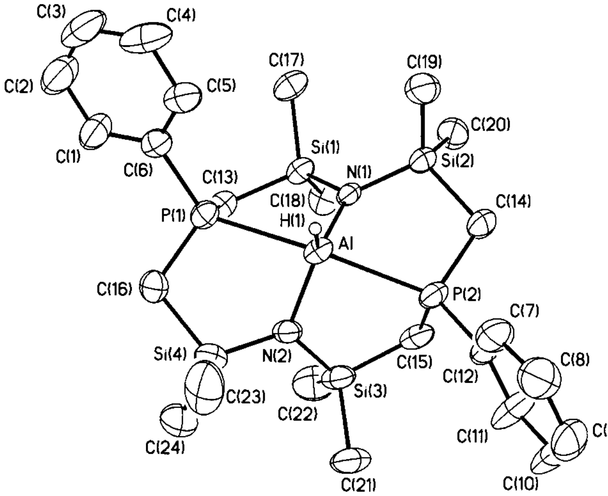


Fig. 1. Molecular structure of *syn*-AlH[$P_2N_2$] (**4**); 33% probability thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity.

Table 1
Crystallographic data

| Compound | *syn*-AlH$[P_2N_2]$ (**4**) | \{*syn*-Ga$[P_2N_2]$\}$_2$ (**6**) | \{*syn*-In$[P_2N_2]$\}$_2$ (**7**) |
|---|---|---|---|
| Formula | $C_{24}H_{43}AlN_2P_2Si_4$ | $C_{48}H_{84}Ga_2N_4P_4Si_8$ | $C_{48}H_{84}In_2N_4P_4Si_8$ |
| Formula weight (g mol$^{-1}$) | 560.88 | 1205.24 | 1295.44 |
| Color (habit) | Colorless plate | Colorless needle | Colorless needle |
| Size (mm) | 0.20 × 0.10 × 0.10 | 0.50 × 0.15 × 0.10 | 0.35 × 0.25 × 0.22 |
| Crystal system | Monoclinic | Tetragonal | Tetragonal |
| Space group | $C2/c$ | $P\bar{4}2_1c$ | $P\bar{4}2_1c$ |
| $a$ (Å) | 37.865(2) | 16.9622(4) | 17.149(2) |
| $b$ (Å) | 9.1760(4) | – | – |
| $c$ (Å) | 22.687(1) | 21.2288(2) | 21.649(2) |
| $\beta$ (°) | 123.954(1) | – | – |
| $V$ (Å$^3$) | 6538.6(5) | 6107.9(2) | 6366.5(13) |
| $Z$ | 8 | 4 | 4 |
| $T$ (°C) | 25 | −93 | 21 |
| Radiation | Mo–$K_\alpha$ | Mo–$K_\alpha$ | Mo–$K_\alpha$ |
| $\lambda$ (Å) | 0.71073 | 0.71069 | 0.71069 |
| $\mu$ (cm$^{-1}$) | 3.22 | 11.79 | 9.93 |
| Transmission factors | – | 0.80–1.00 | 0.97–1.00 |
| $R$ | 0.0815 [a] | 0.052 [a] | 0.038 [b] |
| $R_w$ | 0.1307 [a] | 0.087 [a] | 0.032 [b] |
| $R_{int}$ | 0.0786 | 0.05408 | 0.10709 |
| $2\theta$ range | 2.60–42.00 | 3.40–60.06 | 3.76–59.98 |
| Reflections | 3452 | 4353 | 5247 |
| Parameters | 301 | 298 | 298 |
| Absorption correction | None | Semi-empirical | $\psi$ scan |
| Data collection | Siemens SMART | D*TREK | MSC/AFC Diffractometer Control |
| Diffractometer | Siemens SMART CCD | Rigaku ADSC CCD | Rigaku AFC6S |

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ $(I \geq 3\sigma(I))$, $R_w$ $(F^2) = (\Sigma\, w(|F_o^2| - |F_c^2|)^2/\Sigma\, w|F_o|^4)^{1/2}$.

[b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w(F) = (\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2)^{1/2}$.

(**1**) (2.481(1) and 2.465(1) Å) [17]. No variation is seen in the aluminum–amide bond lengths of 1.903(5) and 1.910(5) Å, which are similar to those in the starting aluminum chloride **1** (1.886(3) and 1.903(3) Å) [17], as well as that determined for $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ (1.89(1) Å) [30]. The hydride complex **4** represents a structurally characterized aluminum mono-hydride species which does not interact with either salt or external base. A list of selected bond lengths and angles for **4** are presented in Table 2.

### 2.1.2. Solution structure of syn-AlH[$P_2N_2$] (4)

Although the crystal structure of **4** clearly indicates the presence of two bound phosphine donors, the observation of a sharp singlet in the $^{31}P\{^1H\}$-NMR spectrum of **4** is somewhat counterintuitive. As already mentioned, in the starting chloride *syn*-AlCl$[P_2N_2]$ (**1**), the $^{31}P\{^1H\}$-NMR spectrum consists of a very broad singlet at −43.6 ppm (s, $\Delta_{1/2} = 340$ Hz) due to coupling of the bound phosphine donors with the quadrupolar $^{27}Al$ nucleus. The observation of a sharp singlet would suggest that the phosphine donors in **4** are unbound in solution; however, the chemical shift of the singlet at −46.5 ppm is inconsistent with this since we have previously shown that phosphines which do not coordinate to a metal center in the $[P_2N_2]$ ligand system most often appear at ∼ −38 ppm in the $^{31}P\{^1H\}$-NMR spectrum [17].

A fluxional process also seems unlikely given the fact that the macrocycle while flexible always has the donors poised for coordination. Indeed, cooling a toluene-$d_8$ solution of **4** to −90°C does not result in any appreciable difference in the $^{31}P\{^1H\}$-NMR spectrum. The possibility that the monomer **4** is in equilibrium with a dimer via bridging hydrides that somehow weakens the Al–P interaction can be excluded since solution molecular weight measurements (isopiestic method, Signer apparatus, 520 ± 50 g mol$^{-1}$) indicate a monomeric solution structure. Compound **4** exhibits a $\nu$(Al–H) stretch at 1594 cm$^{-1}$ in the IR spectrum; this medium

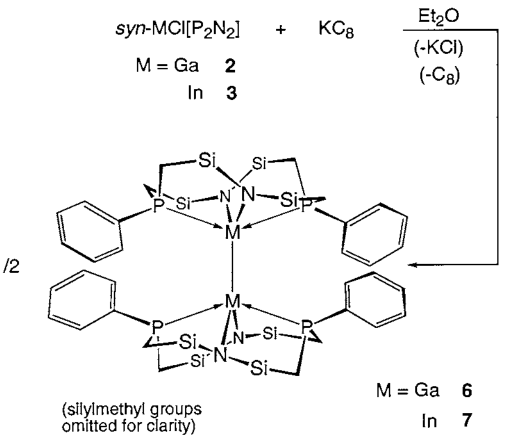
Table 2
Selected bond lengths (Å) and angles (°) for *syn*-AlH$[P_2N_2]$ (**4**)

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| N(1)–Al(1) | 1.903(5) | N(2)–Al(1) | 1.910(5) |
| P(1)–Al(1) | 2.522(3) | P(2)–Al(1) | 2.517(3) |
| *Bond angles* | | | |
| N(1)–Al(1)–N(2) | 114.9(2) | N(1)–Al(1)–P(1) | 89.2(2) |
| N(1)–Al(1)–P(2) | 83.3(2) | N(2)–Al(1)–P(1) | 82.6(2) |
| N(2)–Al(1)–P(2) | 89.3(2) | P(1)–Al(1)–P(2) | 165.53(11) |
| Al(1)–P(1)–C(6) | 130.0(3) | Al(1)–P(2)–C(12) | 131.2(3) |

intensity peak shifts to 1129 cm$^{-1}$ upon deuteration. This is at the lower end of the determined range for a terminal aluminum hydride. The low solubility of **4** in ether or toluene did not allow for a definitive solution IR peak assignment to be made. In spite of this unusually low value, we conclude that **4** is monomeric both in the solid and solution states. We suggest that the sharp singlet in the $^{31}P\{^{1}H\}$-NMR spectrum of **4** is the result of hybridization along the axial positions of the trigonal bipyramid, such that coupling of the $^{27}Al$ nucleus to $^{31}P$ is significantly reduced as compared to the chloride **1**.

### 2.2. Synthesis of metal–metal bonded dimers of gallium and indium

The addition of either *syn*-GaCl[$P_2N_2$] (**2**) or *syn*-InCl[$P_2N_2$] (**3**) to a slurry of $KC_8$ (1.1 equivalent) in diethyl ether is accompanied by the gradual dissipation of the brown color of the reducing agent to yield a black slurry of graphite (Eq. (3)). Extraction into toluene yields a white solid which crystallizes as colorless needles. The $^{1}H$-NMR spectra of the products indicate a single symmetric species in solution. The $^{31}P\{^{1}H\}$-NMR spectra exhibit a single slightly broadened peak downfield of the starting chloride ($\delta$ −25.5 ppm, $\Delta_{1/2}$ = 10 Hz for {*syn*-Ga[$P_2N_2$]}$_2$ (**6**); $\delta$ −37.7 ppm, $\Delta_{1/2}$ = 24 Hz for {*syn*-In[$P_2N_2$]}$_2$ (**7**)).



(3)

The gallium(II) and indium(II) species can be prepared in moderate yields; however the attempted reduction of *syn*-AlCl[$P_2N_2$] (**1**) with $KC_8$ did not yield a characterizable product, although metal–metal dimers of Al(II) have been reported [5,8,31]. The unfavorable steric interaction of the phenyl rings of two *syn*-Al[$P_2N_2$] units may prevent the close approach of two monomers and a metal–metal bond from being formed. The reduced species {*syn*-Ga[$P_2N_2$]}$_2$ (**6**) and {*syn*-In[$P_2N_2$]}$_2$ (**7**) were studied by X-ray crystallography.

#### 2.2.1. Structure of {syn-Ga[$P_2N_2$]}$_2$ (6) and {syn-In[$P_2N_2$]}$_2$ (7)

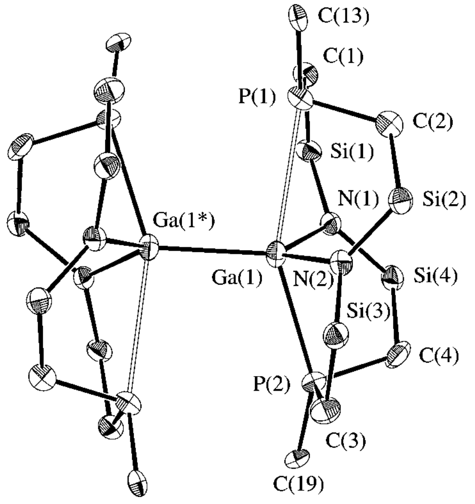


Fig. 2. Molecular structure of {*syn*-Ga[$P_2N_2$]}$_2$ (**6**); 50% probability thermal ellipsoids are shown. Hydrogen atoms and phenyl rings are omitted for clarity.

Fig. 2 presents the molecular structure and numbering scheme of **6**. The compound contains an unsupported metal–metal bond between two Ga(II) centers. The gallium–gallium bond length of 2.5206(8) Å is similar to that reported for the tetra(amido) species $(tmp)_2Ga–Ga(tmp)_2$ (tmp = 2,2,6,6-tetramethylpiperidino) (Ga–Ga = 2.525(1) Å) [12]. The metal–metal bond lengths in gallium(II) dimers fall into two approximate categories: those supported by bulky alkyls such as substituted aryls or organosilyls (~2.5–2.6 Å) [6,12–14] and those ligated by halides (~2.4 Å) [10,11], although some anomalously short contacts are also known [15,16]. Compound **6** exhibits a slightly staggered geometry; the dihedral angle between the two $GaN_2$ planes is 27.92°. By comparison, the $GaC_2$ planes in $(Trip)_2Ga–Ga(Trip)_2$ (Trip = 2,4,6-triisopropylphenyl) are skewed by 43.8° [14], and the $GaSi_2$ planes in $[(Me_3Si)_3Si]_2Ga–Ga[Si(SiMe_3)_3]_2$ by 80° [13]. The gallium–nitrogen bond lengths (1.958(3) and 1.968(3) Å) are slightly longer than in other amido–gallium systems (~1.84–1.90 Å) [12,15] and may reflect the steric constraints of the macrocyclic [$P_2N_2$] ligand system. Compound **6** also contains two short (2.6591(11) Å) and two long (3.1459(11) Å) gallium–phosphorus bonds. The gallium center is best described as a distorted tetrahedron, with angles involving the metal ranging from 126.63(9) to 81.59(9)°. Bond lengths

Table 3
Selected bond lengths (Å) for {*syn*–Ga[$P_2N_2$]}$_2$ (**6**) and {*syn*–In[$P_2N_2$]}$_2$ (**7**)

| {*syn*–Ga[$P_2N_2$]}$_2$ (**6**) | | {*syn*–In[$P_2N_2$]}$_2$ (**7**) | |
|---|---|---|---|
| Ga(1)*–Ga(1) | 2.5206(8) | In(1)*–In(1) | 2.7618(12) |
| P(1)–Ga(1) | 3.1459(11) | P(1)–In(1) | 2.870(4) |
| P(2)–Ga(1) | 2.6591(11) | P(2)–In(1) | 2.879(4) |
| N(1)–Ga(1) | 1.958(3) | N(1)–In(1) | 2.170(8) |
| N(2)–Ga(1) | 1.968(3) | N(2)–In(1) | 2.160(8) |

Table 4
Selected bond angles (°) for $\{syn\text{-Ga}[P_2N_2]\}_2$ (**6**) (left) and $\{syn\text{-In}[P_2N_2]\}_2$ (**7**) (right)

| $\{syn\text{-Ga}[P_2N_2]\}_2$ (**6**) | | $\{syn\text{-In}[P_2N_2]\}_2$ (**7**) | |
|---|---|---|---|
| P(1)–Ga(1)–P(2) | 155.22(3) | P(1)–In(1)–P(2) | 149.87(10) |
| N(1)–Ga(1)–N(2) | 105.46(12) | N(1)–In(1)–N(2) | 107.32(9) |
| Ga(1)*–Ga(1)–P(1) | 95.00(3) | In(1)*–In(1)–P(1) | 102.79(10) |
| Ga(1)*–Ga(1)–P(2) | 109.75(3) | In(1)*–In(1)–P(2) | 125.6(2) |
| Ga(1)*–Ga(1)–N(1) | 125.47(9) | In(1)*–In(1)–N(1) | 131.1(2) |
| Ga(1)*–Ga(1)–N(2) | 126.63(9) | In(1)*–In(1)–N(2) | 103.3(3) |
| Ga(1)–P(1)–C(13) | 156.51(13) | In(1)–P(1)–C(13) | 143.9(5) |
| Ga(1)–P(2)–C(19) | 144.86(13) | In(1)–P(2)–C(19) | 142.8(4) |

and angles for **6** and **7** are presented in Tables 3 and 4, respectively.

The molecular structure and numbering scheme of **7** are illustrated in Fig. 3. As for **6**, $\{syn\text{-In}[P_2N_2]\}_2$ (**7**) is dimeric with a metal–metal bond between two In(II) nuclei. The indium centers in **7** exhibit distorted trigonal bipyramidal geometries (Table 4). The P(1)–In(1)–P(2) and N(1)–In(1)–N(2) bond angles (149.87(10) and 103.3(3)° respectively) are smaller than expected (180 and 120°) and indicate larger deviations from ideal than in *syn*-AlCl[$P_2N_2$] (**1**) or *syn*-GaCl[$P_2N_2$] (**2**) [17]. The indium centers are each equally coordinated by two phosphine donors (2.870(4) and 2.879(4) Å) in contrast to the situation found for the gallium analogue. A limited number of indium(II) dimers have been structurally characterized; among these are those supported by bulky alkyl [7] or aryl groups [32], cyclic bis(amides) [9] or halogens [33]. The metal–metal bond in **7** (2.7618(12) Å) is similar to that in the cyclic bis(amido) species $\{(Bu^tNMe_2SiSiMe_2NBu^t)In\}_2$ (2.768(1) Å) [9]. The dihedral angle between the two $InN_2$ planes in **7** is 24.65°, which is slightly less than that observed in the gallium analogue **6**.

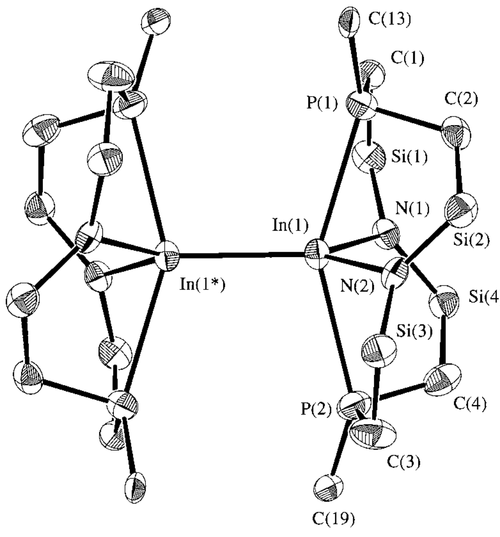


Fig. 3. Molecular structure of $\{syn\text{-In}[P_2N_2]\}_2$ (**7**); 33% probability thermal ellipsoids are shown. Hydrogen atoms and phenyl rings are omitted for clarity.

### 2.2.2. Solution structure of $\{syn\text{-Ga}[P_2N_2]\}_2$ (6) and $\{syn\text{-In}[P_2N_2]\}_2$ (7)

The observation of $^1H$- and $^{31}P\{^1H\}$-NMR spectra for **6** and **7** indicate that these monomers couple via metal–metal bonds and are dimeric in solution. Different phosphorus environments were not observed in the $^{31}P\{^1H\}$-NMR spectrum of **6**; cooling to −90°C resulted in no evidence for decoalescence and some fluxional process. We conclude that the solid-state structure for the gallium dimer is different than that observed in solution, and that in solution, both **6** and **7** exhibit structures similar to that observed in the solid state for the indium dimer **7**; in other words, the unsymmetrical Ga–P bond lengths are only found in the solid state.

## 3. Experimental

### 3.1. General methods

Unless otherwise stated, all manipulations were performed under an atmosphere of dry, oxygen-free dinitrogen or argon by means of standard Schlenk or glovebox techniques. The glovebox used was a Vacuum Atmospheres HE-553-2 model equipped with a MO-40-2H purification system and a −40°C freezer. $^1H$- and $^{31}P\{^1H\}$-NMR spectroscopy were performed on an AMX 500 instrument operating at 500.1 and 121.4 MHz, respectively. $^1H$-NMR spectra were referenced to internal $C_6D_5H$ (7.15 ppm) or $C_6D_5CD_2H$ (2.09 ppm). $^{31}P\{^1H\}$-NMR spectra were referenced to external $P(OMe)_3$ (141.0 ppm with respect to 85% $H_3PO_4$ at 0.0 ppm). Mass spectral studies were carried out on a Kratos MS 50 using an EI source. Infrared spectroscopy was performed on a BOMEM MB-100 spectrometer. Microanalyses (C, H, N) were performed by Mr P. Borda of this department.

*syn*-$Li_2$(dioxane)[$P_2N_2$] [34], *syn*-AlCl[$P_2N_2$] [17], and *syn*-GaCl[$P_2N_2$] [17] were prepared by published procedures. $InCl_3$ was purchased from Alfa Chemicals and sublimed prior to use. $LiAlH_4$ was purchased from Aldrich and used as received. $LiGaH_4$ was prepared by a literature method [35]. $KC_8$ was prepared by the addition of potassium metal to solid graphite at 160°C under a purge of argon.

Toluene was refluxed over $CaH_2$ prior to a final distillation from sodium benzophenone ketyl under an argon atmosphere. Diethyl ether was refluxed over sodium benzophenone ketyl under an argon atmosphere. Deuterated solvents were dried by distillation from sodium benzophenone ketyl; oxygen was removed by three freeze–pump–thaw cycles.

### 3.2. Synthesis of syn-InCl[$P_2N_2$] (**3**)

To a slurry of $InCl_3$ (180 mg; 0.79 mmol) in toluene (10 ml) was added a toluene solution (10 ml) of *syn*-$Li_2$(dioxane)[$P_2N_2$], (500 mg; 0.79 mmol). The reaction mixture was stirred for 12 h. The reaction mixture was then passed through a frit lined with Celite to remove LiCl. The solvent was removed in vacuo to yield **3** (430 mg; 80% yield) as a waxy white solid. Anal. Calc. for $C_{24}H_{42}InClN_2P_2Si_4$: C, 42.19; H, 6.20; N, 4.10. Found: C, 42.55; H, 6.20; N, 3.99. $^1$H-NMR ($C_6D_6$): $\delta$ 7.95 (t, 4H, *o*-Ph, $^3J_{H-H} = 8.5$ Hz, $^3J_{H-P} = 8.5$ Hz), 7.07 (m, 6H, *m*,*p*-Ph), 0.90 (ABX m, 8H, ring C$H_2$, $^2J_{H-H} = 15.5$ Hz, $^2J_{H-P} = 14.0$ Hz), 0.28 and 0.20 (s, 12H, Si$Me_2$). $^{31}$P{$^1$H}-NMR ($C_6D_6$): $\delta$ −40.5 (s, 400 Hz peak width at half height). *m*/*z* 684 [$M^+$].

### 3.3. Synthesis of syn-AlH[$P_2N_2$] (**4**)

Method 1: To a −78°C solution of $LiAlH_4$ (12 mg; 0.32 mmol) in ether (10 ml) was added an ethereal solution (10 ml) of *syn*-AlCl[$P_2N_2$] (**1**) (160 mg; 0.26 mmol). The reaction vessel was left to warm with stirring. The reaction mixture was then passed through a frit lined with Celite to remove LiCl. The solvent was removed in vacuo and the residue extracted into a minimum amount of toluene (approximately 3 ml). Slow evaporation of the solvent gave large colorless plates of **4** (54 mg; 37% yield).

Method 2: To a −78°C solution of $LiAlH_4$ (12 mg; 0.32 mmol) in ether (10 ml) was added an ethereal solution (10 ml) of *syn*-GaCl[$P_2N_2$] (**2**) (170 mg; 0.27 mmol). The reaction mixture was left to warm with stirring. The reaction mixture was then passed through a frit lined with Celite to remove LiCl. The solvent was removed in vacuo and the residue extracted into toluene. Evaporation of the solvent afforded **4** as a white powder (45 mg; 30% yield).

Method 3: To a −78°C solution of $LiAlH_4$ (12 mg; 0.32 mmol) in ether (10 ml) was added an ethereal solution (10 ml) of *syn*-InCl[$P_2N_2$] (**3**) (200 mg; 0.30 mmol). Upon warming, the mixture became black and deposited indium metal. The reaction mixture was then passed through a frit lined with Celite to remove LiCl and In(0). The solvent was removed in vacuo and the residue extracted into toluene. Evaporation of the solvent yielded **4** (26 mg; 16% yield) as a white powder. Anal. Calc. for $C_{24}H_{43}AlN_2P_2Si_4$: C, 51.39; H, 7.65; N, 4.86. Found: C, 51.26; H, 7.65; N, 4.86. $^1$H-NMR ($C_6D_6$): $\delta$ 7.77 (t, 4H, *o*-Ph, $^3J_{H-H} = 6.9$ Hz, $^3J_{H-P} = 6.9$ Hz), 7.08 (m, 6H, *m*,*p*-Ph), 1.01 (ABX m, 8H, ring C$H_2$, $^2J_{H-H} = 13.8$ Hz, $^2J_{H-P} = 6.9$ Hz), 0.34 and 0.21 (s, 12H, Si$Me_2$). $^{31}$P{$^1$H}-NMR ($C_6D_6$): $\delta$ −46.5 (s, 340 Hz peak width at half height). IR (KBr, $cm^{-1}$): 1594m (Al–H), 1129sh (Al–D). *m*/*z* 559 [$M^+$–H]. Mol. wt. (Signer, isopiestic method, toluene) 520 ± 50; calc. 560.88.

### 3.4. Synthesis of syn-GaH[$P_2N_2$] (**5**)

Method 1: To a freshly prepared solution of $LiGaH_4$ maintained at −78°C (21 mg; 0.25 mmol) in ether (10 ml) was added an ethereal solution (10 ml) of *syn*-GaCl[$P_2N_2$] (**2**) (150 mg; 0.24 mmol). The reaction mixture was left to warm with stirring, during which time some metal deposition was evident. The reaction mixture was then passed through a frit lined with Celite to remove LiCl and Ga(0). The solvent was removed in vacuo and the residue extracted into toluene. Evaporation of the solvent afforded a white powder (34 mg; 24% yield).

Method 2: To a freshly prepared solution of $LiGaH_4$ maintained at −78°C (21 mg; 0.26 mmol) in ether (10 ml) was added an ethereal solution (10 ml) of *syn*-InCl[$P_2N_2$] (**3**) (160 mg; 0.23 mmol). Upon warming, the mixture became black and deposited gallium and indium metal. The reaction mixture was then passed through a frit lined with Celite to remove LiCl, Ga(0) and In(0). The solvent was removed in vacuo and the residue extracted into toluene. Evaporation of the solvent gave a white powder (15 mg; 11% yield). The unstable nature of **5** did not allow for a suitable IR, elemental analysis or mass spectrum to be obtained. Prolonged standing (~days) of solutions of **5** resulted in the slow decomposition to *syn*-$H_2$[$P_2N_2$] and gallium metal. $^1$H-NMR ($C_6D_6$): $\delta$ 7.47 (t, 4H, *o*-Ph, $^3J_{H-H} = 6.6$ Hz, $^3J_{H-P} = 6.6$ Hz), 7.11 (m, 6H, *m*,*p*-Ph), 5.25 (br s, 1H, Ga*H*), 1.75 and 0.93 (ABX m, 8H, ring C$H_2$, $^2J_{H-H} = 13.2$ Hz, $^2J_{H-P} = 7.6$ Hz), 0.48 and 0.25 (s, 12H, Si$Me_2$). $^{31}$P{$^1$H}-NMR ($C_6D_6$): $\delta$ −34.7 (s).

### 3.5. Synthesis of {syn-Ga[$P_2N_2$]}$_2$ (**6**)

To a slurry of $KC_8$ (25 mg; 0.19 mmol) in ether (10 ml) was added an ethereal solution (10 ml) of *syn*-GaCl[$P_2N_2$] (**2**) (100 mg; 0.17 mmol). The reaction mixture was stirred for 24 h. The reaction mixture was then passed through a frit lined with Celite to remove KCl and $C_{(gr)}$. The solvent was removed in vacuo to yield a white solid. The residue was taken up in a minimum amount of toluene (approximately 2 ml). Slow evaporation of the solvent afforded **6** (33 mg; 33% yield) as small colorless needles. Anal. Calc. for $C_{48}H_{84}Ga_2N_4P_4Si_8$: C, 47.84; H, 7.02; N, 4.65. Found: C, 47.54; H, 6.94; N, 4.49. $^1$H-NMR ($C_6D_6$): $\delta$ 7.48 (br t, 4H, *o*-Ph), 7.20 and 7.08 (m, 6H, *m*,*p*-Ph), 0.93 (ABX m, 8H, ring C$H_2$, $^2J_{H-H} = 12.9$ Hz, $^2J_{H-P} = 5.9$ Hz), 0.52 and 0.33 (s, 12H, Si$Me_2$). $^{31}$P{$^1$H}-NMR

($C_6D_6$): $\delta$ −25.5 (10 Hz peak width at half height). *m*/*z* 603 [$M^+$(monomer)].

### 3.6. Synthesis of {*syn*-In[$P_2N_2$]}$_2$ (7)

To a slurry of $KC_8$ (22 mg; 0.16 mmol) in ether (10 ml) was added an ethereal solution (10 ml) of *syn*-InCl[$P_2N_2$] (**3**) (98 mg; 0.14 mmol). The reaction mixture was stirred for 24 h. The reaction mixture was then passed through a frit lined with Celite to remove KCl and $C_{(gr)}$. The solvent was removed in vacuo to yield a white solid. The residue was taken up in a minimum amount of toluene (approximately 2 ml). Slow evaporation of the solvent afforded large colorless needles of **7** (54 mg; 58% yield). Anal. Calc. for $C_{48}H_{84}In_2N_4P_4Si_8$ C, 44.50; H, 6.54; N, 4.32. Found: C, 44.14; H, 6.23; N, 4.19. $^1H$-NMR ($C_6D_6$): $\delta$ 7.48 (br t, 4H, *o*-Ph), 7.02 (br m, 6H, *m*,*p*-Ph), 1.13 (br ABX m, 8H, ring $CH_2$), 0.42 and 0.39 (s, 12H, Si$Me_2$). $^{31}P\{^1H\}$-NMR ($C_6D_6$): $\delta$ −37.4 (24 Hz peak width at half height). *m*/*z* 647 [$M^+$ (monomer)].

### 3.7. X-ray crystallographic analyses of *syn*-AlH[$P_2N_2$] (4), {*syn*-Ga[$P_2N_2$]}$_2$ (6) and {*syn*-In[$P_2N_2$]}$_2$ (7)

Crystallographic data appear in Table 1. Cell constants for **4** were calculated from reflection data obtained from 60 data frames collected at different parts of the Ewald sphere. The final unit-cell parameters were obtained by least-squares on the setting angles for 42 220 reflections with $2\theta = 4.0–60.1°$ for **6** and 25 reflections with $2\theta = 20.9–31.4°$ for **7**. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, showed only small random fluctuations. The data were processed [36] and corrected for Lorentz and polarization effects, and absorption (empirical, based on analysis of symmetry-equivalent data for **6**, azimuthal scans for **7**).

The structure of **4** was solved by direct methods. The structure of **7** was solved by the Patterson method and that of **6** by isomorphous replacement. Complexes **6** and **7** both have crystallographic $C_2$ symmetry. The nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in calculated positions with C–H = 0.98 Å and $B_H = 1.2B_{\text{bonded atom}}$. Secondary extinction corrections were not necessary. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [37].

Selected bond lengths and bond angles appear in Tables 2–4. Complete tables of bond lengths and bond angles, final atomic coordinates, hydrogen atom parameters and anisotropic thermal parameters are included as supporting information.

## 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, no. 128893 for compound **4**, no. 129641 for compound **6** and no. 129642 for compound **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk].

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