Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202300340

Chemistry Europe
European Chemical Societies Publishing

www.chemeurj.org

Special Collection

NHC-Stabilised Parent Tripentelyltrielanes

Robert Szlosek,[a] Michael A. K. Weinhart,[a] Gábor Balázs,[a] Michael Seidl,[a] Lisa Zimmermann,[a] and Manfred Scheer*[a]

Dedicated to Professor Werner Uhl

Abstract: A missing family of the extremely air sensitive tripentelyltrielanes was discovered. Their stabilisation was achieved by using the bulky NHC IDipp (NHC = N-heterocyclic carbene, IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene). The tripentelylgallanes and tripentelylalanes IDipp · $Ga(PH_2)_3$ (**1 a**), IDipp · $Ga(AsH_2)_3$ (**1 b**), IDipp · $Al(PH_2)_3$ (**2 a**) and IDipp · $Al(AsH_2)_3$ (**2 b**) were synthesised by salt metathesis of IDipp · ECl_3 (E=Al, Ga, In) with alkali metal pnictogenides such as $NaPH_2$/$LiPH_2$ · DME and $KAsH_2$, respectively. Moreover, the detection of the first NHC-stabilised tripentelylindiumane IDipp · $In(PH_2)_3$ (**3**) was possible by multinuclear NMR spectroscopy. Initial investigations of the coordination ability of these compounds resulted in the successful isolation of the coordination compound [IDipp · $Ga(PH_2)_2(\mu_3\text{-}PH_2\{HgC_6F_4\}_3)$] (**4**) by reaction of **1 a** with $(HgC_6F_4)_3$. The compounds were characterised by multinuclear NMR spectroscopy as well as single crystal X-ray diffraction studies. Supporting computational studies highlight the electronic features of the products.

Introduction

Hydrocarbon compounds are the most basic materials used as fuels and for the production of specialised chemicals. However, already hundreds of years ago, chemists discovered the inorganic equivalents made up by elements of the groups 13 and 15, forming the so-called group 13/15 compounds. Starting with the preparation of $H_3N \cdot BF_3$ by Gay-Lussac in 1809, many milestone discoveries such as borazine $B_3N_3H_6$ and $Me_3N \cdot BH_3$ followed.[1] Although isoelectronic towards their organic counterparts, these compounds differ drastically from them in terms of reactivity and physical properties due to their different bond polarity. In the last years, the focus has more and more shifted towards the heavier homologues, mainly phosphorus/arsenic on the group 15 side and aluminium/gallium on the group 13 side, partially owing to practical applications of 13/15 compounds such as GaAs in the semiconductor industry.[2,3] The demand for stable precursor compounds of this type has increased accordingly, for their use in, for example MOCVD processes (metal–organic chemical vapor deposition).[2,4]

Several stabilisation strategies for the parent 13/15 monomers $H_2E\text{-}PnH_2$ (E = Al/Ga, *Pn* = P, As) or disubstituted $HE\text{-}(PnH_2)_2$ compounds are known today, usually involving the use of donor molecules or a combination with a suitable Lewis acid.[5] Most examples include borane compounds, although simultaneous stabilisation of GaH_2PH_2 and AlH_2PH_2 by $\{W(CO)_5\}$ and NMe_3 was already reported several years ago.[6] When no additional Lewis acid is provided, the most common examples for the stabilisation of the parent monomers of the heavier homologues of group 13 are provided by β-diketiminates (Nacnac, Figure 1, **I**, **II** and **III**) or N-heterocyclic carbenes (NHC)

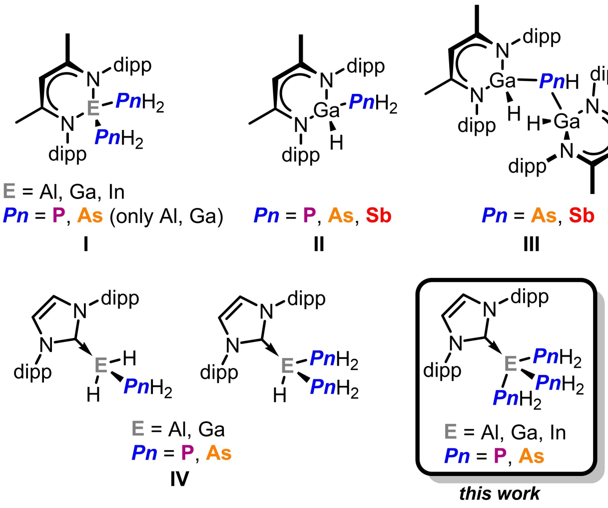


Figure 1. Examples for donor-stabilised parent pentelyltrielanes of Al, Ga and In (dipp = 2,6-diisopropylphenyl).

---

[a] R. Szlosek, Dr. M. A. K. Weinhart, Dr. G. Balázs, Dr. M. Seidl, L. Zimmermann, Prof. Dr. M. Scheer
Institut für Anorganische Chemie
Universität Regensburg
93053 Regensburg (Germany)
E-mail: manfred.scheer@ur.de
Homepage: http://www.uni-regensburg.de/chemie-pharmazie/anorganische-chemie-scheer

Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202300340

Part of a Special Collection on the p-block elements.

(Figure 1, **IV**). In particular, by employing the bulky NHC 1,3-bis-(2,6-diisopropylphenyl)-imidazolin-2-ylidene (IDipp),[7] our group synthesised the first examples of the stable mono- and disubstituted compounds IDipp · EH_2PnH_2 and IDipp · $EH(PnH_2)_2$ (E = Al, Ga; *Pn* = P, As).[8,9] Recently, especially β-diketiminates have been experiencing a tremendous gain in popularity in the field of group 13/15 element chemistry.[10] Pioneering works by S. Schulz *et al.* investigated the synthesis, characterisation and reactivity of Ga = *Pn* (*Pn* = P, As, Sb) multiple bonded species stabilised by Nacnac systems, resulting in a fascinating variety of structural motifs ranging from gallapnictenes to distibiranes.[11] Goicoechea *et al.* showed the successful synthesis of (Nacnac)-stabilised phosphanyl-phosphagallene and demonstrated its reactivity as a frustrated Lewis pair by conversions with H_2 and CO_2.[12] Furthermore, (Nacnac)$EHPnH_2$ (E = Ga, Al, In; *Pn* = P, As, Sb) and (Nacnac)$E(PnH_2)_2$ were reported by our own group as well as by the von Hänisch group.[13,14] Von Hänisch *et al.* were also able to synthesise neutral 13/(15/14)/13 chain compounds by oxidative addition of (Nacnac)$GaHPnH_2$ or silyl(di)phosphanes with (Nacnac)Ga.[14,15]

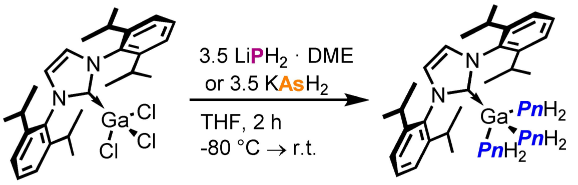
In view of tripentelyltrielanes $E(PnH_2)_3$, however, only tris(dialkylphosphanyl)boranes $B(PR_2)_3$ are known so far, as the strong bonds between phosphorus and boron in combination with bulky organic residues keep the molecules together as monomers despite lacking external stabilisation.[16] Still, the parent compound $B(PH_2)_3$ currently remains unknown. The same accounts for reports on tripentelyltrielanes of the heavier group 13 homologues, which is not surprising given the highly labile nature of the bonding between the heavier group 13 and group 15 elements.[17]

As the β-diketiminate ligand occupies two binding sites on the group 13 element, a tripentelyltrielane pattern is difficult to achieve by stabilisation from Nacnac substituents only. One possibility is provided by a strong 2-electron donor such as a NHC,[18] a cyclic (alkyl)(amino)carbene (CAAC)[19] or a tertiary amine.[20] But no such adducts have been reported to our knowledge to this date.

Herein we report the synthesis and characterisation of the first monomeric parent tripentelyltrielanes stabilised by the Lewis base IDipp. These include the elements Al, Ga and In on the group 13 and P and As on the group 15 side. Moreover, the first results of the reactivity of these compounds are presented and specific electronic features are discussed, highlighted by quantum chemical calculations.

Results and Discussion

As shown in previous work both experimentally and theoretically, hydrogen elimination from a mixture of PH_3 or AsH_3 and IDipp · PnH_3 (*Pn* = Al, Ga) does not lead all the way to the desired tripentelyltrielane, but instead ends at the first or second substitution step, respectively, as the intermediates become less and less prone to hydrogen elimination after each substitution step.[8,9] Therefore, salt metathesis provides a better synthetic pathway towards these 13/15-compounds. Thus, the reactions of IDipp · $GaCl_3$[21] with 3.5 equivalents of $LiPH_2$ · DME[22] and $KAsH_2$[23] [Equation (1)] were performed.



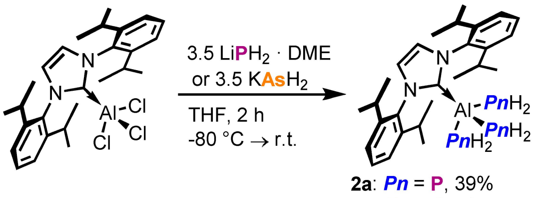
(1)

1a: *Pn* = P, 70%
1b: *Pn* = As, 47%

That way, the NHC-stabilised parent tripentelylgallanes IDipp · $Ga(PH_2)_3$ (**1a**) and IDipp · $Ga(AsH_2)_3$ (**1b**) were obtained analytically pure in good isolated yields of 70% and 47%, respectively. Alternatively, **1a** can also be synthesised by using $NaPH_2$[23] instead of $LiPH_2$ · DME, however with slightly lowered yields. Both products are colourless solids that display high sensitivity towards air and decompose slowly at room temperature. Thus, they can be stored for at least several months under an inert atmosphere at −30 °C. Simultaneously with presenting the salt metathesis in Equation (1), we investigated a possible one-pot reaction of formally generating $[M(PnH_2)_3]_n$ (M = Ga, Al; *Pn* = P, As) *in situ* and then adding the NHC to the reaction mixture in a simple one-pot reaction to break up the oligomers into NHC-stabilised monomers. Although possible, the route in Equation (1) proved to be far cleaner and higher yielding (cf. Supporting Information).

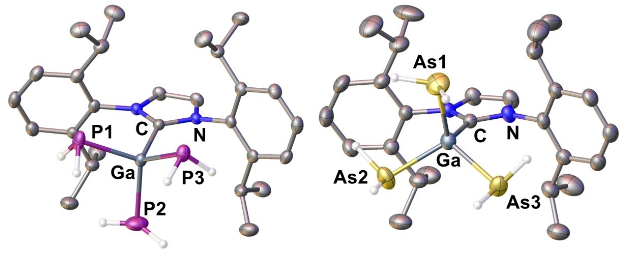
The $^{31}P\{^1H\}$ NMR spectrum of **1a** shows a singlet at −231.7 ppm that is split into a triplet in the ^{31}P NMR spectrum ($^1J_{HP} = 173$ Hz). This concurs with a doublet in the ^1H NMR spectrum at 0.99 ppm (6 H, $^1J_{HP} = 173$ Hz). The ^1H NMR spectrum of **1b** displays a distinct sharp singlet at 0.75 ppm for the AsH_2 moieties bound to Ga (6 H). Attempts to obtain LIFDI-MS data were unsuccessful due to the rapid decomposition of **1a** and **1b** upon ionisation, leading only to fragment peaks of [IDipp-H]$^+$ at $m/z = 398.29$. In case of **1b**, a fragment peak of [IDipp · $Ga(AsH_2)_2$]$^+$ was detected at $m/z = 611.09$. The purity of **1a** and **1b** was confirmed by elemental analysis. Single crystals of **1a/b** were obtained from a saturated *n*-hexane solution at −28 °C as small colourless needles and examined by single-crystal X-ray structure determination (Figure 2).

1a and **1b** crystallise in the monoclinic space group $P2_1/c$. The Ga–P and Ga–As bond distances of 2.3608(8)–2.3649(9) Å (Ga–P) and 2.4437(7)–2.4550(7) Å (Ga–As) are within the range of Ga–P and Ga–As single bonds (cf. IDipp · GaH_2PH_2: 2.3373(6) Å, IDipp · GaH_2AsH_2: 2.4503(12) Å).[8,9] The central $\{CGaP_3\}$ and $\{CGaAs_3\}$ units adopt tetrahedral geometries with P–Ga-P and Al–Ga-As bond angles of 109.86(13)°-110.87(14)° (P–Ga-P) and 109.40(3)°–111.83(3)° (As–Ga-As), respectively.



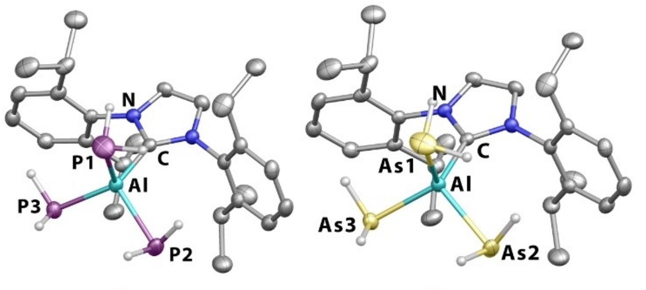
(2)

2a: *Pn* = P, 39%
2b: *Pn* = As, few crystals



1a **1b**

Figure 2. Molecular structure of **1a** and **1b** in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability level. Disordered parts and hydrogen atoms bound to carbon atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **1a**: C–Ga 2.064(9), Ga–P1 2.3514(7), Ga–P2 2.3554(8), Ga–P3 2.3609(7), C–Ga–P1 109.67(6), C–Ga–P2 105.68(7), C–Ga–P3 110.85(6), P1–Ga–P3 105.41(3), P1–Ga–P2 115.31(3), P2–Ga–P3 109.99(3). **1b**: C–Ga 2.068(3), Ga–As1 2.4526(8), Ga–As2 2.4634(9), Ga–As3 2.4583(8), C–Ga–As1 109.30(9), C–Ga–As2 108.75(10), C–Ga–As3 107.2(1), As1–Ga–As3 110.22(3), As1–Ga–As2 111.83(3), As2–Ga–As3 109.40(3).



2a **2b**

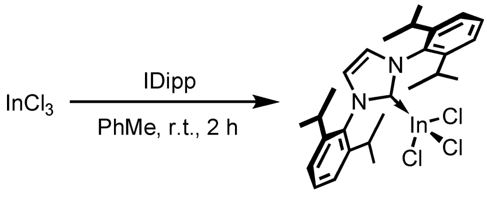
Figure 3. Molecular structure of **2a** and **2b** in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability level. Hydrogen atoms bound to carbon atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2a**: C–Al 2.0672(19), Al–P1 2.3672(8), Al–P2 2.3720(8), Al–P3 2.3616(8), C–Al–P1 107.94(6), C–Al–P2 111.23(5), C–Al–P3 109.50(6), P1–Al–P3 115.24(3), P1–Al–P2 108.43(3), P2–Al–P3 104.49(3). **2b**: C–Al 2.063(3), Al–As1 2.4631(9), Al–As2 2.4638(9), Al–As3 2.4583(9), C–Al–As1 108.48(8), C–Al–As2 111.10(8), C–Al–As3 110.21(8), As1–Al–As3 114.43(3), As1–Al–As2 108.39(4), As2–Al–As3 104.18(3).

After the successful synthesis of the gallium compounds, we turned our attention to aluminium, which displays even greater sensitivity towards decomposition in this type of compounds.[8,9] In addition to the apparent sensitivity, the weak bonding between the pnictogen atoms and aluminium complicate this chemistry further. Nevertheless, the salt elimination reactions of IDipp · $AlCl_3$ with $LiPH_2$ · DME and $KAsH_2$ were carried out [Equation (2)], yielding the novel branched compounds IDipp · $Al(PH_2)_3$ (**2a**) and IDipp · $Al(AsH_2)_3$ (**2b**). The tripentelylalanes are obtained as colourless solids (**2a**: 39%; **2b**: few crystals) that show extreme sensitivity towards air, and crystalline samples of **2a** and **2b** also decompose quickly in degassed mineral oil or perfluorinated oil. **2a** and **2b** are also rather unstable at room temperature in both solution and in the solid state and decompose fast and quantitatively under release of IDipp and PH_3 or AsH_3, respectively. The $^{31}P\{^1H\}$ NMR spectrum of a freshly prepared solution of **2a** at room temperature (C_6D_6) displays a sharp singlet at −252.0 ppm split into a triplet ($^1J_{HP}=175$ Hz) in the ^{31}P NMR spectrum. This coincides with a broadened doublet in the ^1H NMR spectrum at 0.66 ppm ($^1J_{HP}=175$ Hz, 6 H). The synthesis of **2b** is accompanied by several side products that were impossible to be separated or washed away due to a solubility that is very similar to that of the product. Separation of crystals under the microscope was not possible due to the fast thermal decomposition of **2b**. All variations of the reaction conditions (temperature, addition of reagents, stoichiometry) did not prevent the formation of these side products. Attempts to obtain MS data were unsuccessful due to the rapid decomposition of **2a** and **2b** upon ionisation, leading only to fragment peaks of $[\text{IDipp-H}]^+$ at $m/z=389.28$. However, despite the extraordinary sensitivity of **2a** and **2b**, by quick and careful manipulation, it was also possible to determine the structures of **2a** and **2b** by single-crystal X-ray structure analysis (Figure 3).

2a and **2b** crystallise as small, clear, colourless needles from saturated *n*-hexane solutions at −28 °C in the monoclinic space group $P2_1/c$. The Al–P and Al–As bond lengths of 2.3616(8)–2.3720(8) Å (P–Al) and 2.4583(9)–2.4638(9) Å (As–Al) are within the range of Al–P and Al–As single bonds, respectively (cf. IDipp · AlH_2PH_2: 2.3131(10) Å, IDipp · $AlH(AsH_2)_2$: 2.46 Å).[8,9] The P–Al–P and As–Al–As bond angles lie between 104.49(3)°–115.24(3)° (P–Al–P) and 104.18(3)°–114.43(3)° (As–Al–As) and reveal tetrahedral geometries at the $\{CAlP_3\}$ and $\{CAlAs_3\}$ units. Overall, the structural parameters of **2a/b** are almost identical to **1a/b**, as the *d*-block contraction of gallium causes a bonding feature that is very similar to that of its aluminium counterparts.

In all the above-mentioned reactions, an excess amount of $LiPH_2$·DME/$NaPH_2$ or $KAsH_2$ was necessary to ensure the completeness of the reaction, as otherwise a mixture of IDipp · $ECl_{3-x}(PnH_2)_x$ (E = Ga, Al; *Pn* = P, As) is formed, according to NMR data. However, we observed that this causes the partial NHC substitution by the pnictogenide reagent, as a lot of unbound IDipp is obtained, as identified by ^1H NMR spectroscopy. This prompted us to take a closer look at the reaction mixtures. And indeed, NMR spectroscopic investigations on the reaction between IDipp · $AlCl_3$ and $NaPH_2$ show the formation of $[Al(PH_2)_4]^-$ by a strongly broadened triplet of multiplets in the ^{31}P NMR spectrum at −247.5 ppm which explains the lowered yields of these reactions in general. Moreover, the controlled substitution of one or two chlorides from IDipp · $GaCl_3$ was also tested, which unfortunately resulted in inseparable mixtures of IDipp · $GaCl_{3-x}(PH_2)_x$ in all attempts.

Furthermore, the question came up whether a similar reaction pattern is also possible with the even heavier group 13 homologues. Hence, it was tested to perform the triple salt metathesis reaction on a suitable NHC · $InCl_3$ precursor. Since IDipp · $InCl_3$ (**A**) has not been described in literature, it was synthesised by direct synthesis from IDipp and $InCl_3$ [Equation (3)]. **A** is obtained as a white-greyish solid that can be stored under an inert atmosphere at room temperature for at least several months.

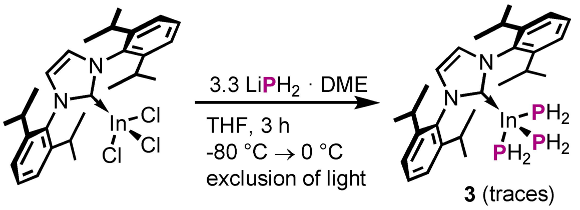


A (77%)

(3)

The ^{1}H NMR spectrum of **A** shows a characteristic set of signals for IDipp adducts with two separate doublets at 1.18 ppm and 1.38 ppm for the diastereotopic isopropyl CH_3 protons (cf. detailed data in the Supporting Information). Crystals suitable for single crystal X-ray structure determination were grown by slow evaporation of a solution of **A** in CH_2Cl_2. The molecular structure in the solid state (Figure 4) shows a tetrahedral geometry at the {$ClInCl_3$} unit with Cl–In–Cl bond angles between 105.37(8)° and 115.16(8)°. The In–Cl bonds lie between 2.3557(3)–2.3689(9) Å and are significantly shorter than the In–Br bonds in IDipp · $InBr_3$ (2.500 Å).

With a suitable precursor at hand, the analogous salt metathesis reactions with $LiPH_2$ · DME and $KAsH_2$ were investigated. To prevent decomposition by reduction towards an In(I) species, these reactions were performed under exclusion of light and careful temperature monitoring. Solid $LiPH_2$ · DME was added to a solution of **A** at −80 °C and the solution was allowed to reach 0 °C over the course of three hours [Equation (4)]. After work-up by extraction with toluene, small amounts of IDipp · $In(PH_2)_3$ (**3**) could be obtained and characterised by multinuclear NMR spectroscopy. Despite several washing steps with cold *n*-hexane (−60 °C), unbound IDipp could not be completely separated from the final product.



3 (traces)

(4)

3 was obtained by this reaction in very small amounts as colourless solids that decompose at room temperature and under ambient light. The reaction suffers from significant product loss due to decomposition by thermal pathways and especially IDipp substitution, as the IDipp-In bond is comparably weak and causes the release of large amounts of unbound IDipp. The $^{31}P\{^1H\}$ NMR spectrum of **3** in C_6D_6 shows a sharp singlet at −264.7 ppm (^{31}P NMR: triplet, $^1J_{HP} = 167$ Hz) for the {PH_2} moieties besides a small amount of PH_3 as the result of decomposition already at r.t. (Figure 5). The ^{1}H NMR spectrum shows a characteristic doublet at 0.65 ppm for the {PH_2} protons ($^1J_{HP} = 167$ Hz) with an integral ratio of overall 6 protons (Figure 6), thus confirming the existence of **3**.

When using $KAsH_2$ in the reaction (**4**), it could be visually confirmed that a reaction is taking place by precipitation of solid KCl, accompanied by a slight colour change of the solution. However, despite all our efforts, the presence of IDipp · $In(AsH_2)_3$ could not be confirmed by ^{1}H NMR spectroscopy, which always showed the presence of a product mixture. It was also not possible to grow crystals of any of the products for identification purposes, as the inseparable mixture decomposes quickly at −30 °C already under exclusion of light. However, according to DFT calculations (B3LYP–D4/def2-TZVP),[24–28,29] IDipp · $In(AsH_2)_3$ indeed represents a minimum on the potential energy surface that unfortunately still remains experimentally elusive.

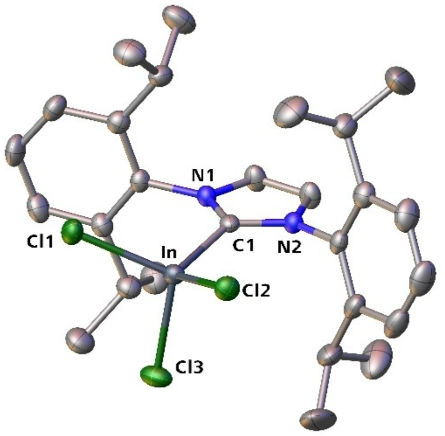


Figure 4. Molecular structure of **A** in the solid state. Anisotropic displacement ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–In 2.187(3), In–Cl1 2.3585(8), In–Cl2 2.3557(8), In–Cl3 2.3689(9), C1–In–Cl1 115.16(8), C1–In–Cl2 113.84(8), C1–In–Cl3 105.37(8).

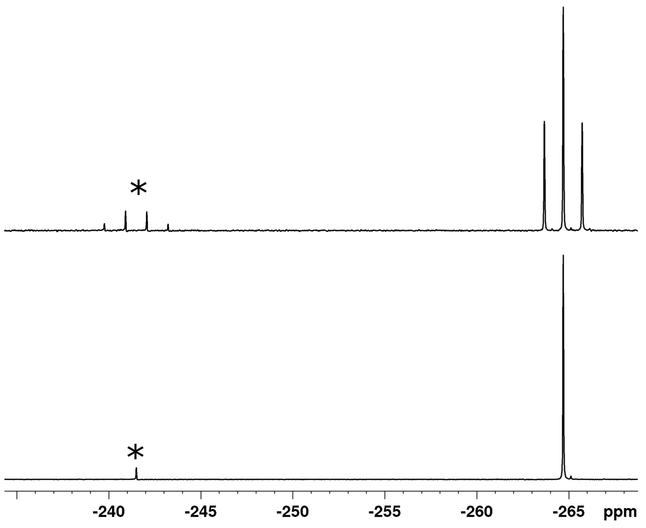


Figure 5. ^{31}P NMR (top) and $^{31}P\{^1H\}$ NMR (bottom) spectra of **3** (298 K, * = PH_3 resulting from sample decomposition).

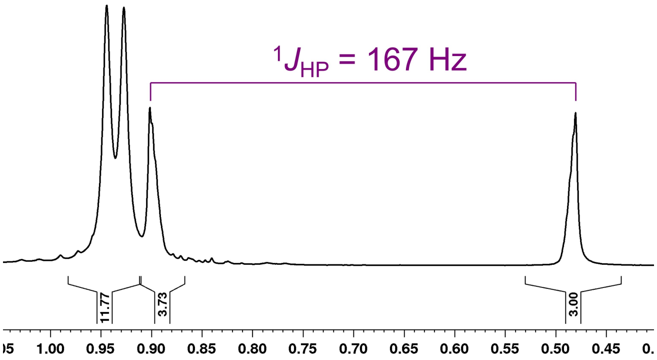


Figure 6. Section of the ^1H NMR spectrum of **3** revealing a doublet for the PH_2 protons (C_6D_6, 298 K).

The electronic structure and nature of bonding within the synthesised compounds was evaluated by NBO[30] analysis, employing density functional theory. NPA charge analysis (TPSSh/def2-TZVP)[28,31] revealed the polar nature of the interatomic bonds, which is largest for the triphosphanyl- and triarsanylalane (Figure 7a). The *Wiberg Bond Indices* for the pnictogen-triel bonds lie between 0.79–0.85 (**1 a**), 0.80–0.84 (**1 b**), 0.74–0.78 (**2 a**), and 0.76–0.81 (**2 b**). These combined DFT analyses indicate polarised albeit weak single bonds for these compounds.

As evident from NBO calculations, localised lone pairs can be assigned to all pnictogen atoms within these compounds (Figure 7b). Therefore, we assumed that the synthesised tripentelyltrielanes would display a versatile coordination chemistry as mono- or multidentate ligands towards main group elements and transition metals despite their high sensitivity. Due to displaying the best availability and stability, **1 a** was used as the reagent of choice for the following coordination attempts. Thus, reactions with many main group electrophiles and transition metal complexes such as $BH_3\cdots SMe_2$, $AlMe_3$, $Me(SO_3CF_3)$, AuCl(tht) (tht = tetrahydrothiophene), $[W(MeCN)_3(CO)_3]$, $[W(CO)_4(nbd)]$ (nbd = norbornadiene), $[Pt(PhCN)_2Cl_2]$, transition metal salts of weakly coordinating anions and many more were performed.

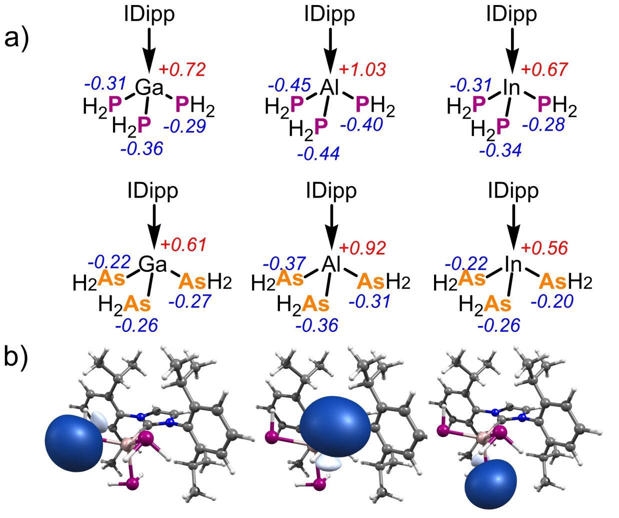
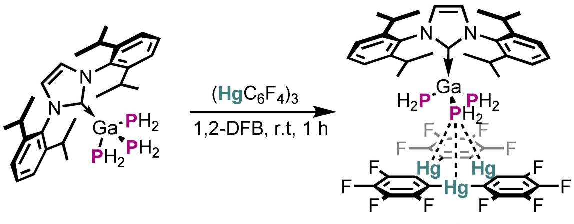


Figure 7. a) Calculated Natural Charges for NHC-stabilised tripentelyltrielanes of heavy group 13 elements (TPSSh/def2-TZVP // B3LYP–D4/def2-TZVP level of theory). b) Depiction of calculated lone pair orbitals of **1 a** (NBO).

Unfortunately, most of these reactions led to either intractable mixtures or the breakage of one or more Ga–P bonds rather than coordination. As the Ga–P bonds seemed particularly sensitive to classic coordination chemistry, we targeted to synthesise a more softly bound metal complex. Therefore, the trimeric *o*-perfluorophenylenemercury $(HgC_6F_4)_3$[32] was chosen as a Lewis-acidic compound known to be available for weak interactions. $(HgC_6F_4)_3$ has been a subject of many studies of coordination chemistry and has shown versatile coordination modes, covalent as well as non-covalent.[33,34]



4

(5)

When a solution of **1 a** in 1,2-difluorobenzene is added to a suspension $(HgC_6F_4)_3$ in 1,2-difluorobenzene, the immediate formation of a clear red solution is observed [Equation (5)]. The $^{31}P\{^1H\}$ spectrum of this reaction solution showed a slightly broadened singlet at −220.7 ppm, which is shifted downfield by roughly +12 ppm compared to the starting material and is indicative of a dynamic coordination of **1 a** to $(HgC_6F_4)_3$. After work-up, the colourless coordination compound $[IDipp \cdot Ga(PH_2)_2(\mu_3\text{-}PH_2\{HgC_6F_4\}_3)]$ (**4**) could be crystallised within a unidentifiable mixture of red-brown amorphous solids as clear colourless plates (Figure 8). **4** displays a high sensitivity towards air and decomposes at room temperature releasing PH_3. Low temperature NMR experiments to determine the dynamic binding situation failed as dissolving the compound in CD_2Cl_2 leads exclusively to unbound **1 a**, because the excess of CD_2Cl_2 causes the replacement of $IDipp \cdot Ga(PH_2)_3$, likely to be resulting in the complex $(HgC_6F_4)_3 \cdot CD_2Cl_2$.[34] Other solvents such as THF-d_8 are deemed unsuitable due to the poor solubility of **4** as well as the possible coordination of THF towards $(HgC_6F_4)_3$. DFT calculations (PWPB95-D4/def2-TZVPP//BP86-D4/def2-TZVP, CPCM = CH_2Cl_2)[26–28,35,36,37] suggest that the dissociation process of the adduct **4** into **1 a** and $(HgC_6F_4)_3$ is slightly exergonic by $-1.06\,\text{kcal}\,\text{mol}^{-1}$ at 298 K, further indicating the facile dissociation of **4**.

Single crystals suitable for X-ray structure determination were grown by layering a solution of **4** in 1,2-difluorobenzene with *n*-hexane at −30 °C. **4** crystallises in the monoclinic space group $P2_1/n$ as clear colourless plates (Figure 8). Its crystal structure shows one molecule of $IDipp \cdot Ga(PH_2)_3$ coordinated to the mercury ring system by one $\{PH_2\}$ arm. The P–Hg distances are very long and lie between

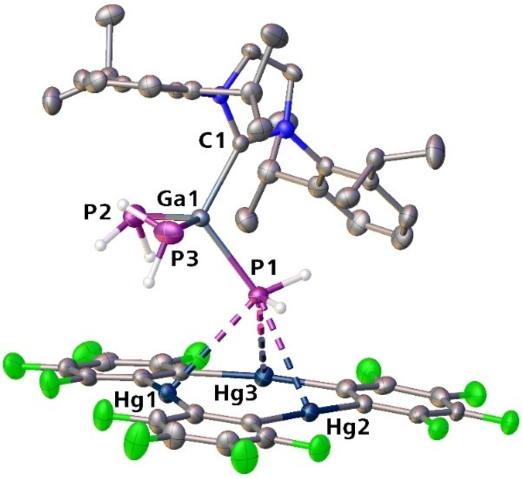


Figure 8. Molecular structure of **4** in the solid state. Anisotropic displacement ellipsoids are shown at 50 % probability level. Hydrogen atoms bound to carbon are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–Hg1 3.2547(13), P1–Hg2 3.1809(13), P1–Hg3 3.3169(13), Hg1–Hg2 3.5697(4), Hg2–Hg3 3.6002(4), Hg1–Hg3 3.5579(5, C1–Ga1 2.064(5), Ga1–P1 2.3809(14), Ga1–P2 2.3719(15), Ga1–P3 2.3310(15), C1–Ga1–P1 113.95(13), C1–Ga1–P2 105.74(12), C1–Ga1–P3 109.32(13), P1–Hg1–Hg2 55.33(2), P1–Hg2–Hg3 58.17(2), P1–Hg3–Hg2 56.38(2), Hg1–Hg2–Hg3 59.498(6), Hg2–Hg3–Hg1 59.823(6), Hg3–Hg1–Hg2 60.679(6).

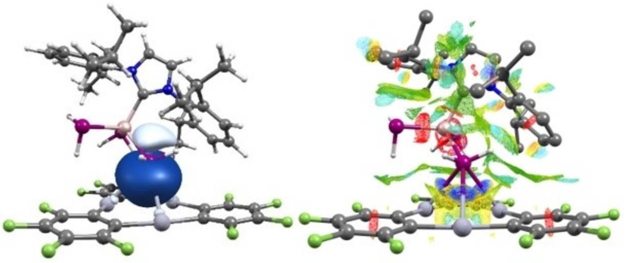


Figure 9. Occupied lone pair orbital (NBO) within **4** coordinating towards the $\{Hg\}_3$ unit (left) and plot of the calculated reduced density gradient of $[IDipp{\cdots}Ga(PH_2)_2(\mu_3\text{-}PH_2\{HgC_6F_4\}_3)]$ (right). Hydrogen atoms bound to carbon are omitted for clarity. The lined surfaces show regions of weak interactions within the molecule. Colour scheme: blue (strong electrostatic interaction), green (Van der Waals interaction), red (strong repulsion).

3.18109(13)–3.3168(13) Å. These distances are well below the sum of the Van der Waals radii of P and Hg (3.6 Å) and are indicative of at least weak attractive forces. Furthermore, the $Ga{-}P_{Hg}$ bond is slightly elongated with 2.3809(14) Å and the $C_{Carbene}{-}Ga{-}P_{Hg}$ bond angle is slightly widened towards 113.95(13)°. The lengthening of the Ga–P bond upon coordination might explain the pronounced instability and hence easy decomposition of the coordination compounds of **2 a** (see above).

The loose coordination mode of the ligand raised the question as to whether the bonding situation could still be described by covalent bonds or not. Therefore, quantum chemical calculations were performed (ZORA–B3LYP–D4/ZORA-def2-TZVPP (SARC on Hg)[24–28,38] //BP86-D4/def2-SVP[26–28,35,36] level of theory, Figure 9). The calculated structure is in good agreement with the solid-state structure. The *Wiberg Bond Indices* for the P–Hg bonds lie between 0.0243–0.0264 and do not indicate covalent bonding between these atoms. This is further supported by an *atoms-in-molecules* analysis[39] with no bond-critical points being found along the P–Hg coordination paths. By a *non-covalent interaction* analysis (NCI), a surface of the reduced density gradient between the three Hg atoms and the phosphorus atom indicates strong electrostatic interactions (Figure 9, right).[40] Furthermore, an NBO analysis (TPSSh/def2-TZVPP)[28,31] shows that the lone pair (orbital contributions from P: *s* 0.42, *p* 0.58) of the respective phosphorus atom points directly towards the centre of the mercury ring system (Figure 9, left). Overall, the applied computational methods suggest an electrostatic attraction based on the interactions of the three mercury atoms with the electron density around an occupied, nearly sp^2-hybridised orbital of the phosphorus atom.

Conclusion

In summary, we were able to complete the series of NHC-stabilised pentelylgallanes and alanes by synthesizing the first branched tripnictogenyl-substituted NHC adducts IDipp · $Ga(PH_2)_3$ (**1 a**), IDipp · $Ga(AsH_2)_3$ (**1 b**), IDipp · $Al(PH_2)_3$ (**2 a**) and IDipp · $Al(AsH_2)_3$ (**2 b**) by triple salt metathesis reactions. All these products decompose at ambient temperatures under strictly inert conditions and display extraordinary sensitivity towards air. In addition, the first NHC-stabilised triphosphanylindiumane IDipp · $In(PH_2)_3$ (**3**) was accessible by this pathway, as evident from its NMR spectroscopic features. Investigations on the reactivity of these compounds proved difficult due to very weak bonding between the group 13 and group 15 elements, resulting in bond cleavage in most cases. However, coordination towards $(HgC_6F_4)_3$ could be realised in [IDipp · $Ga(PH_2)_2(\mu_3\text{-}PH_2\{HgC_6F_4\}_3)$] (**4**) where one arm of the ligand is simultaneously coordinated to three Hg atoms by weak interaction. Electronic structure calculations confirm mainly electrostatic bonding within **4** and point out the highly polarised bonding between the group 15 and 13 elements in the obtained NHC-stabilised tripentelyltrielanes. In view of the instability of the presented compounds, these could not act as multidentate ligands so far, as bond breakage was observed. By decreasing the size of the NHC and using alkylated compounds instead of the parent compounds, this reaction behaviour might be improved. Future studies will also investigate catenation with suitable electrophiles and the use of these compounds as single-source precursors in chemical vapor deposition processes (CVD) towards the synthesis of thin layers of 13/15 materials.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the project Sche 384/41-1. R.S. is grateful to the Fonds der Chemischen Industrie (FCI) for a PhD fellowship. Christoph Riesinger is acknowledged for fruitful discussions. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Deposition Numbers 2218931 (**A**), 2218932 (**1 a**) 2218933 (**1 b**), 2218934 (**2 a**), 2218935 (**2 b**), 2218936 (**4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Keywords: aluminium · gallium · indium · N-heterocyclic carbene · phosphorus

[1] a) A. B. Burg, H. I. Schlesinger, *J. Am. Chem. Soc.* **1937**, *59*, 780–787; b) J. Gay-Lussac, J. Thenard, *Mem. Phys. Chim. Soc. d'Arcueil* **1809**, *2*, 210–211; c) A. Stock, E. Pohland, *Chem. Ber.* **1926**, *59*, 2210–2215.

[2] C. E. Housecroft, A. Sharpe, *Inorganic Chemistry*, 4. Aufl., Pearson, New York, **2012**, p. 859–860.

[3] S. Schulz, *Adv. Organomet. Chem.* **2003**, *49*, 225–317.

[4] a) A. C. Jones, P. O'Brien, *CVD of Compound Semiconductors: Precursor Synthesis Development and Applications*, VCH, Weinheim, **1996**; b) M. R. Leys, *Chemtronics* **1987**, *2*, 155–164; c) G. B. Stringfellow, *Rep. Prog. Phys.* **1982**, *45*, 469–525; d) R. A. Fischer, J. Weiß, *Angew. Chem. Int. Ed.* **1999**, *38*, 2830–2850; *Angew. Chem.* **1999**, *111*, 3002–3022; e) J. D. Masuda, A. J. Hoskin, T. W. Graham, C. Beddie, M. C. Fermin, N. Etkin, D. W. Stephan, *Chem. Eur. J.* **2006**, *12*, 8696–8707; f) R. D. Wells, W. L. Gladfelter, *J. Cluster Sci.* **1997**, *8*, 217–238; g) T. J. Clark, K. Lee, I. Manners, *Chem. Eur. J.* **2006**, *12*, 8634–8648; h) B. Neumüller, E. Iravani, *Coord. Chem. Rev.* **2004**, *248*, 817–834; i) S. Schulz, *Coord. Chem. Rev.* **2001**, *215*, 1–37; j) A. Y. Timoshkin, *Coord. Chem. Rev.* **2005**, *249*, 2094–2131; k) A. Staubitz, A. Presa Soto, I. Manners, *Angew. Chem. Int. Ed.* **2008**, *47*, 6212–6215; *Angew. Chem.* **2008**, *120*, 6308–6311.

[5] a) A. Adolf, M. Zabel, M. Scheer, *Eur. J. Inorg. Chem.* **2007**, *2007*, 2136–2143; b) C. A. Jaska, A. J. Lough, I. Manners, *Inorg. Chem.* **2004**, *43*, 1090–1099; c) M. Bodensteiner, A. Y. Timoshkin, E. V. Peresypkina, U. Vogel, M. Scheer, *Chem. Eur. J.* **2013**, *19*, 957–963; d) K.-C. Schwan, A. Y. Timoskin, M. Zabel, M. Scheer, *Chem. Eur. J.* **2006**, *12*, 4900–4908; e) C. Marquardt, A. Adolf, A. Stauber, M. Bodensteiner, A. V. Virovets, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2013**, *19*, 11887–11891; f) U. Vogel, P. Hoemensch, K.-C. Schwan, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2003**, *9*, 515–519.

[6] U. Vogel, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2001**, *40*, 4409–4412; *Angew. Chem.* **2001**, *113*, 4541–4544.

[7] A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534.

[8] M. A. K. Weinhart, A. S. Lisovenko, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2020**, *59*, 5541–5545; *Angew. Chem.* **2020**, *132*, 5586–5590.

[9] M. A. K. Weinhart, M. Seidl, A. Y. Timoshkin, M. Scheer, *Angew. Chem.* **2021**, *133*, 3850–3855; *Angew. Chem. Int. Ed.* **2021**, *60*, 3806–3811.

[10] F. Dankert, C. Hering-Junghans, *Chem. Commun.* **2022**, *58*, 1242–1262.

[11] a) M. K. Sharma, P. Dhawan, C. Helling, C. Wölper, S. Schulz, *Chem. Eur. J.* **2022**, *28*, e202200444; b) M. K. Sharma, C. Wölper, G. Haberhauer, S. Schulz, *Angew. Chem. Int. Ed.* **2021**, *60*, 6784–6790; *Angew. Chem.* **2021**, *133*, 6859–6865; c) A. Bücker, C. Wölper, G. Haberhauer, S. Schulz, *Chem. Commun.* **2022**, *58*, 9758–9761; d) C. Helling, C. Wölper, S. Schulz, *J. Am. Chem. Soc.* **2018**, *140*, 5053–5056; e) C. Helling, C. Wölper, Y. Schulte, G. E. Cutsail III, S. Schulz, *Inorg. Chem.* **2019**, *58*, 10323–10332; f) C. Ganesamoorthy, C. Helling, C. Wölper, W. Frank, E. Bill, G. E. Cutsail, S. Schulz, *Nat. Commun.* **2018**, *9*, 87; g) S. Ghosh, E. Glöckler, C. Wölper, J. Linders, N. Janoszka, A. H. Gröschel, S. Schulz, *Eur. J. Inorg. Chem.* **2022**, *2022*; h) C. Helling, C. Ganesamoorthy, C. Wölper, S. Schulz, *Dalton Trans.* **2022**, *51*, 2050–2058; i) C. Helling, C. Wölper, S. Schulz, *Eur. J. Inorg. Chem.* **2020**, *2020*, 4225–4235; j) C. Helling, C. Wölper, S. Schulz, *Dalton Trans.* **2020**, *49*, 11835–11842; k) J. Krüger, C. Wölper, G. Haberhauer, S. Schulz, *Inorg. Chem.* **2022**, *61*, 597–604; l) J. Krüger, C. Ganesamoorthy, L. John, C. Wölper, S. Schulz, *Chem. Eur. J.* **2018**, *24*, 9157–9164; m) J. Krüger, C. Wölper, S. Schulz, *Angew. Chem. Int. Ed.* **2021**, *60*, 3572–3575; *Angew. Chem.* **2021**, *133*, 3615–3618; n) B. Li, B. L. Geoghegan, H. M. Weinert, C. Wölper, G. E. Cutsail, S. Schulz, *Chem. Commun.* **2022**, *58*, 4372–4375; o) B. Li, C. Wölper, G. Haberhauer, S. Schulz, *Angew. Chem. Int. Ed.* **2021**, *133*, 2014–2019; p) J. Schoening, L. John, C. Wölper, S. Schulz, *Dalton Trans.* **2019**, *48*, 17729–17734; q) M. K. Sharma, C. Wölper, S. Schulz, *Dalton Trans.* **2022**, *51*, 1612–1616; r) H. M. Weinert, C. Wölper, S. Schulz, *Chem. Sci.* **2022**, *13*, 3775–3786.

[12] D. W. N. Wilson, J. Feld, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2020**, *132*, 21100–21104.

[13] B. Li, S. Bauer, M. Seidl, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2019**, *25*, 13714–13718.

[14] S. Schneider, S. Ivlev, C. von Hänisch, *Chem. Commun.* **2021**, *57*, 3781–3784.

[15] a) N. J. Hardman, B. E. Eichler, P. P. Power, *Chem. Commun.* **2000**, 1991–1992; b) S. Schneider, C. Hänisch, *Eur. J. Inorg. Chem.* **2021**, *2021*, 4655–4660.

[16] A. Ordyszewska, N. Szynkiewicz, J. Chojnacki, R. Grubba, *Inorg. Chem.* **2022**, *61*, 4361–4370.

[17] A. Y. Timoshkin, G. Frenking, *Inorg. Chem.* **2003**, *42*, 60–69.

[18] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

[19] V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709; *Angew. Chem.* **2005**, *117*, 5851–5855.

[20] a) D. F. Shriver, A. E. Shirk, J. A. Dilts, *Inorg. Synth.* **1977**, *17*, 42–45; b) G. W. Schaeffer, E. R. Anderson, *J. Am. Chem. Soc.* **1949**, *71*, 2143–2145; c) J. K. Ruff, M. F. Hawthorne, *J. Am. Chem. Soc.* **1960**, *82*, 2141–2144.

[21] N. Marion, E. C. Escudero-Adán, J. Benet-Buchholz, E. D. Stevens, L. Fensterbank, M. Malacria, S. P. Nolan, *Organometallics* **2007**, *26*, 3256–3259.

[22] H. Schäfer, G. Fritz, W. Hölderich, *Z. Anorg. Allg. Chem.* **1977**, *428*, 222–224.

[23] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, 3. Aufl., **1975**, Vol. 1, p. 516–517.

[24] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[25] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[26] E. Caldeweyher, C. Bannwarth, S. Grimme, *J. Chem. Phys.* **2017**, *147*, 34112.

[27] E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth, S. Grimme, *J. Chem. Phys.* **2019**, *150*, 154122.

[28] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–305.

[29] a) F. Neese, *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78; b) F. Neese, *WIREs Comput. Mol. Sci.* **2018**, *8*, e1327; c) F. Neese, *WIREs Comput. Mol. Sci.* **2022**, *12*, e1606; d) F. Neese, F. Wennmohs, U. Becker, C. Riplinger, *J. Chem. Phys.* **2020**, *152*, 224108.

[30] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.

[31] V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew, *J. Chem. Phys.* **2003**, *119*, 12129–12137.

[32] P. Sartori, A. Golloch, *Chem. Ber.* **1968**, *101*, 2004–2009.

[33] a) M. Fleischmann, C. Heindl, M. Seidl, G. Balázs, A. V. Virovets, E. V. Peresypkina, M. Tsunoda, F. P. Gabbaï, M. Scheer, *Angew. Chem. Int. Ed.* **2012**, *51*, 9918–9921; *Angew. Chem.* **2012**, *124*, 10056–10059; b) M. Fleischmann, J. S. Jones, G. Balázs, F. P. Gabbaï, M. Scheer, *Dalton Trans.* **2016**, *45*, 13742–13749; c) O. Loveday, J. Jover, J. Echeverría, *Inorg. Chem.* **2022**, *61*, 12526–12533; d) M. Tsunoda, M. Fleischmann, J. S. Jones, N. Bhuvanesh, M. Scheer, F. P. Gabbaï, *Dalton Trans.* **2016**, *45*, 5045–5051.

[34] M. Fleischmann, J. S. Jones, F. P. Gabbaï, M. Scheer, *Chem. Sci.* **2015**, *6*, 132–139.

[35] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.

[36] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824.

[37] a) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995–2001; b) L. Goerigk, S. Grimme, *J. Chem. Theory Comput.* **2011**, *7*, 291–309.

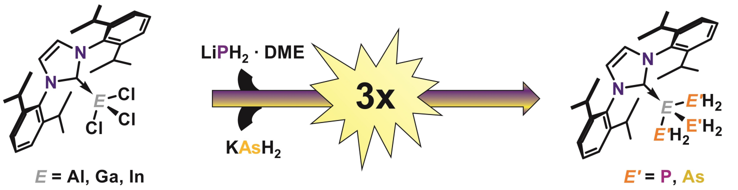
[38] a) D. A. Pantazis, X.-Y. Chen, C. R. Landis, F. Neese, *J. Chem. Theory Comput.* **2008**, *4*, 908–919; b) E. van Lenthe, J. G. Snijders, E. J. Baerends, *J. Chem. Phys.* **1996**, *105*, 6505–6516.

[39] R. F. W. Bader, *Acc. Chem. Res.* **1985**, *18*, 9–15.

[40] a) T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592; b) A. Otero-de-la-Roza, E. R. Johnson, J. Contreras-García, *Phys. Chem. Chem. Phys.* **2012**, *14*, 12165–12172; c) J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan, W. Yang, *J. Chem. Theory Comput.* **2011**, *7*, 625–632.

Manuscript received: February 1, 2023
Accepted manuscript online: February 21, 2023
Version of record online: ■■, ■■

RESEARCH ARTICLE



Three times the fun! The synthesis and characterisation of NHC-stabilised parent tripentelyltrielanes IDipp · E-(*Pn*H$_2$)$_3$ (E = Al, Ga; *Pn* = P, As) and triphosphanylindiumane IDipp · In(PH$_2$)$_3$ are presented (IDipp = 1,3-bis-(2,6-diisopropylphenyl)-imidazolin-2-ylidene), which were obtained by triple salt metathesis from IDipp · ECl$_3$ and alkali metal pnictogenides. Coordination towards (HgC$_6$F$_4$)$_3$ gave evidence of a first coordination compound.

*R. Szlosek, Dr. M. A. K. Weinhart, Dr. G. Balázs, Dr. M. Seidl, L. Zimmermann, Prof. Dr. M. Scheer**

1 – 9

NHC-Stabilised Parent Tripentelyltrielanes