

Characterization of the Ligand Properties of Donor-stabilized Pnictogenyltrielanes

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A general synthesis and the characterization of novel alkyl-substituted NHC-stabilized pnictogenylboranes NHC-BH₂ER₂ (NHC = N-heterocyclic carbene, E = P, As; R₂ = Me₂, Ph₂, ^tBuH, Cy₂, (SiMe₃)₂) are reported. These compounds were reacted with Ni(CO)₄ to the corresponding complexes of the type [(NHC-BH₂ER₂)Ni(CO)₃] to determine their donor strength by Tolman Electronic Parameters (TEPs) and their steric demand as ligands compared to classical phosphines, superbasic phosphines and other commonly applied donor systems. The results

show that the NHC-stabilized pnictogenyltrielanes can be considered as being highly basic, while their steric influence depends strongly on the organic residues as well as the donor attached to the {BH₂} moiety. Although weaker than commonly used superbasic phosphines, the donor strength of pnictogenyltrielanes in general can be classified as of similar strength as NHCs. The steric and electronic properties can easily be modified by alkyl substitution as evident from the TEP trends.

Introduction

Phosphines and especially trivalent phosphorus ligands have become ubiquitous compounds in synthetic chemistry and homogeneous catalysis.^[1,2] Compared to amines or arsines, phosphines offer versatile advantages that make them ideal ligands in many cases. By strong σ -donation and moderate π -acceptor abilities, the soft phosphines bind excellently to soft metal centers and their ligand properties can readily be modified by adjusting the attached organic residues.^[1] In that regard, chiral phosphines play a significant role especially in asymmetric catalysis, as the high inversion barrier prevents their racemization.^[1,3] Furthermore, the highly abundant ³¹P nucleus allows for facile reaction monitoring by NMR spectroscopy.^[4] The sterics and electronics of phosphines can easily be modified by varying the organic substituents. Although disputed nowadays,^[5] the traditional and still highly relevant classification

of donor strength is represented by the Tolman Electronic Parameter (TEP), formally introduced by C. Tolman as the magnitude of the A₁ vibration mode in [Ni(CO)₃L].^[6,7,8] Due to the dangerous toxicity of the required Ni(CO)₄, alternative carbonyl complexes of Rh, Cr, Au and Ir were used in the past.^[9] Today, however, computational methods are able to provide reliable theoretical values for any ligands by frequency analysis of the respective carbonyl complexes.^[10]

In many applications, phosphines were replaced by N-heterocyclic carbenes (NHCs)^[11] or cyclic (alkyl)(amino)carbenes (CAACs)^[12] as stronger σ -donors.^[13] However, during more recent years, new and highly basic classes of phosphines have been developed that are often referred to as “superbasic phosphines”.^[14] An overview of selected examples of mono-substituted “superbasic” phosphines is given in Figure 1. In general, electron-donating substituents are introduced to increase the basicity of the P atom.^[15,16]

Most commonly, amine- or imine-based substituents are used (e.g. PyAPs I, IAPs II),^[17–20] but it is also possible to increase

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202303603>

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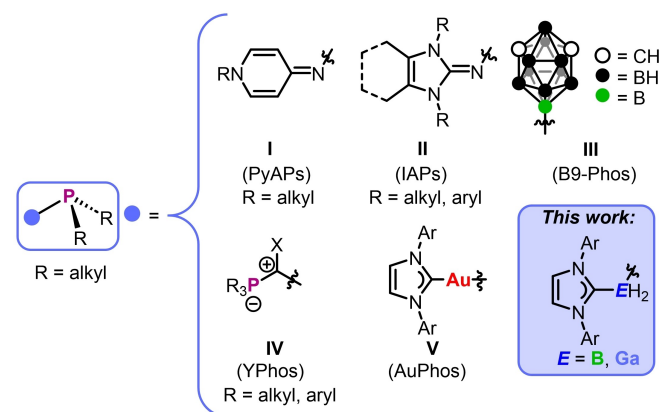


Figure 1. Selected examples of mono-substituted “superbasic” phosphines (L)PR₂.

the basicity with e.g. carborane residues (B9-Phos, III).^[21] Furthermore, the Gessner group developed phosphines carrying an ylidic substituent (YPhos, IV), finding broad application as ligands in transition metal-catalyzed cross coupling reactions.^[22] Alternatively, [(NHC)Au]-substituted terminal phosphines were developed by the groups of Toste, Bergman, Corrigan and Liu (AuPhos, V).^[23,24] Based on a π -repulsion between d_{Au} and p_P orbitals, AuPhos ligands are highly electron-rich and can be further tuned regarding the steric and electronic nature at the NHC or by having multiple [(NHC)Au] substituents surrounding the P atom.^[23] The d-p repulsion is further enhanced as NHCs only show comparatively low π -acceptor capabilities. Significant contributions to the field of superbasic phosphines were also made by the Dielmann group who developed several novel types of superbasic phosphines including pyridinylideneaminophosphines (PyAPs, I),^[20] imidazolin-2-ylideneaminophosphines (IAPs, II),^[17–19] 1,2,5 trimethylpyrrolyl-phosphines $P(\text{tmp})_3$ ^[25] and tris(1,1,3,3-tetramethylguanidiny)l-phosphine (Ptmg)₃.^[26] These compounds have shown remarkable reactivity and basicity while still being easy to access in larger quantities. Typically, these superbasic phosphines are used as ligands in catalysis including reactions such as hydroaminations, coupling reactions, decarbonylations, and many more.^[14,27] As shown by Dielmann and co-workers, however, by the splitting of CO_2 , the superbasic phosphines are powerful enough to activate small molecules.^[19]

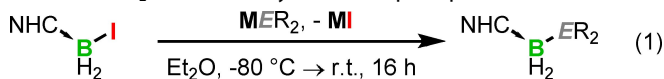
A different class of phosphines is represented by phosphines containing a $\{D\cdot\text{BH}_2\}$ ($D = \text{NHC}, \text{NMe}_3$) residue, namely phosphanylboranes.^[28–31] The same accounts for the heavier homolog containing arsenic $D\cdot\text{BH}_2\text{AsR}_2$.^[32–34] In recent years, the stabilization of 13/15 monomers containing the heavy group 13 homologs Ga, Al and In by an NHC could be reported in several studies as well.^[35,36] These monomers have been the subject of numerous studies and proved to be suitable building blocks towards 13/15 oligo- and polymeric compounds induced by thermal or transition metal-catalyzed pathways.^[37] Furthermore, the reactivity towards main group electrophiles, nucleophiles and transition metals was extensively investigated, as well as the oxidation of the pnictogen atom with chalcogens.^[28,29,31–33,38]

Despite known for almost two decades, neither a clear determination of the electronic and steric properties of these 13/15 compounds nor a comparison towards classic phosphines and modern superbasic phosphines have been reported so far. Herein, we report the first systematic study of the donor strength and steric demand of NHC- and NMe_3 -stabilized pnictogenyltrielanes by the evaluation of the TEPs of the corresponding Ni carbonyl complexes which have been synthesized by the reactions with $\text{Ni}(\text{CO})_4$. Furthermore, a general synthetic access towards E-alkyl ($E = \text{P}, \text{As}$)-substituted NHC-stabilized pnictogenylboranes $\text{NHC}\cdot\text{BH}_2\text{ER}_2$ is described, and the effects of the substitution are discussed.

Results and Discussion

Prior to the determination of TEPs, a suitable substrate scope was needed. As the NHC-stabilized 13/15 monomers display the

highest stability and accessibility, these compounds were chosen as the first candidates for the reactions with $\text{Ni}(\text{CO})_4$. However, since substituted $\text{NHC}\cdot\text{BH}_2\text{ER}_2$ ($E = \text{P}, \text{As}; \text{R} = \text{alkyl}$) were not reported in the literature, the aim was to synthesize a broad scope of alkyl-substituted NHC-stabilized pnictogenylboranes. By salt metathesis reactions of $\text{NHC}\cdot\text{BH}_2$ with alkalimetal-phosphanides and arsanides, several novel NHC-stabilized pnictogenylboranes were obtained in moderate to good yields (eq. 1). Surprisingly, in these reactions, the choice of solvent played a crucial role, when, for example, tetrahydrofuran was used instead of Et_2O under the same reaction conditions, only intractable product mixtures were obtained as oily residues. Therefore, Et_2O is necessary to isolate pure products.



- 1a:** NHC = SiDipp, $E = \text{P}$, $R = \text{H}$ (62%)
1b: NHC = IDipp, $E = \text{P}$, $R = \text{Ph}$ (72%)
1c: NHC = IDipp, $E = \text{P}$, $R = \text{Me}$ (57%)
1d: NHC = IDipp, $E = \text{P}$, $R_2 = \text{H}^t\text{Bu}$ (54%)
1e: NHC = IDipp, $E = \text{P}$, $R = \text{Cy}$ (60%)
1f: NHC = IDipp, $E = \text{P}$, $R = \text{SiMe}_3$ (15%)
2: NHC = IDipp, $E = \text{As}$, $R = \text{Ph}$ (37%)

Compounds **1a–2** were obtained as colorless to yellowish solids which could be stored under an inert atmosphere for at least several months without any signs of decomposition. Characteristic heteronuclear NMR data are summarized in Table 1. It was possible to crystallize compounds **1a**, **1d**, **1e** and **2** as single crystals suitable for X-ray diffraction studies and determine their solid-state structure (Figure 2, top row). The B–E bond lengths lie within the range of regular single bonds and the bond angles reveal (pseudo)tetrahedral geometries at the atoms of the element 13/15 core motifs. Remarkably, **1d**, containing a chiral P atom, crystallizes as a racemic mixture with both (*R/S*) enantiomers present in the asymmetric unit (cf. Supporting Information).

Table 1. Heteronuclear NMR chemical shifts [ppm], coupling constants [Hz] and signal multiplicities of compounds **1a–f** and **2** (298 K, C_6D_6 ; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad).

Entry	$^{31}\text{P}\{^1\text{H}\}$ NMR	^{31}P NMR	$^{11}\text{B}\{^1\text{H}\}$ NMR	^{11}B NMR
1a	–213.2 (s, br)	–213.2 (t, br)	–34.3 (s, br)	–34.3 (t, br)
1b	–38.1 (m, br)	–38.1 (m, br)	–26.9 (s, br)	–26.9 (t, br)
1c	–104.0 (q, br)	–104.0 (q, br)	–24.8 (d, br)	–24.8 (td, br)
1d	–67.3 (s, br)	–67.3 (d, br)	–33.0 (s, br)	–33.0 (t, br)
1e	–37.8 (m, br)	37.8 (m, br)	–30.0 (s, br)	–30.0 (t, br)
1f	–265.0 (s, br)	–265.0 (s, br)	–33.3 (s, br)	–33.3 (t, br)
2	–	–	–26.7 (s, br)	–26.7 (t, br)

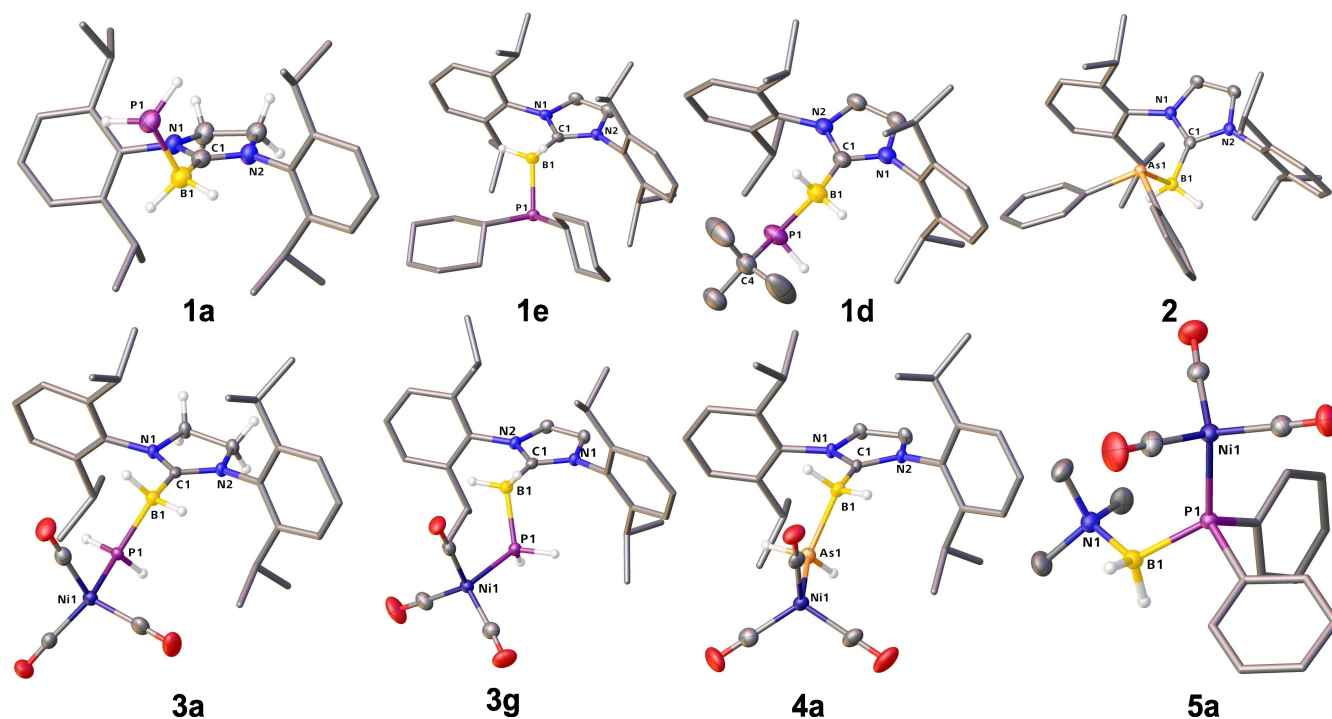
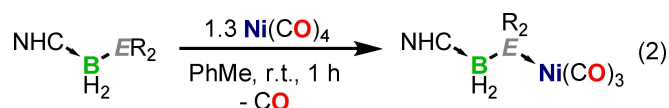


Figure 2. Molecular structures of **1a**, **1e**, **1d**, **2** and **3a**, **3g**, **4a**, **5a** in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability level. Hydrogen atoms bound to carbon are omitted for clarity. Dipp groups are displayed as stick models for clarity. Selected bond lengths [Å] and angles [°]: **1a**: N1-C1 1.356(6), N2-C1 1.340(6), C1-B1 1.579(8), B1-P1 2.038(6), N1-C1-N2 108.6(4), C1-B1-P1 111.6(4); **1e**: N1-C1 1.361(2), N2-C1 1.362(2), C1-B1 1.605(2), B1-P1 1.9944(19), N1-C1-N2 104.12(14), N1-C1-B1 126.97(15), N2-C1-B1 128.69(14), C1-B1-P1 115.45(12); **1d** (only one enantiomer shown): N1-C1 1.360(4), N2-C1 1.360(4), C1-B1 1.596(4), B1-P1 1.993(3), P1-C4 1.867(4), N1-C1-N2 104.2(2), N1-C1-B1 126.7(3), N2-C1-B1 128.9(3), C1-B1-P1 112.3(2), B1-P1-C4 102.85(15); **2**: N1-C1 1.3556(17), N2-C1 1.3594(16), C1-B1 1.5957(19), B1-As1 2.1109(14), N1-C1-N2 104.19(11), N1-C1-B1 128.64(11), N2-C1-B1 127.16(11), C1-B1-P1 108.94(9); **3a**: N1-C1 1.344(2), N2-C1 1.336(2), C1-B1 1.598(2), B1-P1 1.966(2), P1-Ni 2.2500(5), N1-C1-N2 104.19(11), N1-C1-B1 126.87(14), N2-C1-B1 124.32(14), C1-B1-P1 111.70(11), B1-P1-Ni1 115.56(6); **4a**: N1-C1 1.359(4), N2-C1 1.355(4), C1-B1 1.597(4), B1-As1 2.072(4), As1-Ni 2.3445(6), N1-C1-N2 105.1(2), N1-C1-B1 128.6(2), N2-C1-B1 126.3(3), C1-B1-As1 113.3(2), B1-As1-Ni1 116.03(10); **3g**: N1-C1 1.356(2), N2-C1 1.360(2), C1-B1 1.597(2), B1-P1 1.966(2), P1-Ni 2.2605(5), N1-C1-N2 104.21(14), N1-C1-B1 128.96(14), N2-C1-B1 126.82(14), C1-B1-P1 114.48(12), B1-P1-Ni1 115.59(6); **5a**: N1-B1 1.611(2), B1-P1 1.977(2), P1-Ni1 2.2581(5), N1-B1-P1 116.21(12), B1-P1-Ni1 121.12(6).



- 3a**: NHC = SIDipp, $E = \text{P}$, $R = \text{H}$ (28%)
3b: NHC = IDipp, $E = \text{P}$, $R = \text{Ph}$ (39%)
3c: NHC = IDipp, $E = \text{P}$, $R = \text{Me}$ (29%)
3d: NHC = IDipp, $E = \text{P}$, $R_2 = \text{H}^t\text{Bu}$ (54%)
3e: NHC = IDipp, $E = \text{P}$, $R = \text{Cy}$ (55%)
3f: NHC = IDipp, $E = \text{P}$, $R = \text{SiMe}_3$ (25%)
3g: NHC = IDipp, $E = \text{P}$, $R = \text{H}$ (24%)
4a: NHC = IDipp, $E = \text{As}$, $R = \text{H}$ (49%)
4b: NHC = IDipp, $E = \text{As}$, $R = \text{Ph}$ (24%)

Following the successful synthesis of suitable substrates, reactions with $\text{Ni}(\text{CO})_4$ were carried out to prepare the corresponding $[(\text{NHC} \cdot \text{BH}_2\text{ER}_2)\text{Ni}(\text{CO})_3]$ complexes and determine the TEPs. Thus, $\text{Ni}(\text{CO})_4$ was added to solutions of **1a–2** in toluene and the solutions stirred for one hour (eq. 2). According to NMR spectroscopic investigations of the reaction mixtures, full conversion is already achieved after one hour in all cases. Noteworthy, no evidence of sequential CO substitutions at $\text{Ni}(\text{CO})_4$ can be found, as no product mixtures are observed, which can largely be attributed to the bulkiness of IDipp

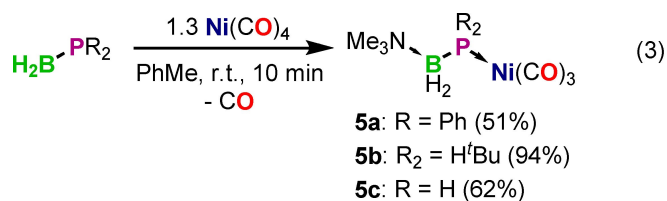
preventing a second substitution step of CO. After work-up, the complexes **3a–4** were isolated in moderate yields as brown powders. The brown color can likely be attributed to the presence of Ni nanoparticles which could not be fully separated by filtration.^[45] Characteristic heteronuclear NMR data are summarized in Table 2. Compounds **3a–3h** show a characteristic large downfield shift in the $^{31}\text{P}\{^1\text{H}\}/^{31}\text{P}$ NMR spectra compared to their uncoordinated counterparts. Furthermore, it was possible to crystallize compounds **3a**, **3g** and **4a** and determine their structure by single-crystal X-ray structure determination (Figure 2, bottom row). The compounds crystallized from $\text{Et}_2\text{O}/n\text{-hexane}$ (**3a**, **3g**) or toluene/ $n\text{-hexane}$ (**4a**) mixtures at -30°C as clear colorless blocks (**3a**, **3g**) or plates in the monoclinic space group $P2_1/c$. All structures show a regular tetrahedral coordination of the Ni atom by three CO molecules and one pnictogenylborane. All bonds within the compounds are within the expected range of the respective single bonds.

To address the influence of the donor molecule attached to boron, the same reactions were performed with the NMe_3 -stabilized compounds $\text{Me}_3\text{N} \cdot \text{BH}_2\text{PR}_2$ ($R_2 = \text{Ph}_2$, H^tBu , H_2). As NMe_3 significantly decreases the steric bulk of the reactants, the reaction principle was reversed by adding the phosphanylboranes dropwise to solutions of $\text{Ni}(\text{CO})_4$ (eq. 3). After 10 min, all

Table 2. Heteronuclear NMR chemical shifts and multiplicities of compounds **3a–5c** [ppm] (298 K, C₆D₆; d = doublet, t = triplet, q = quartet, m = multiplet, br = broad).

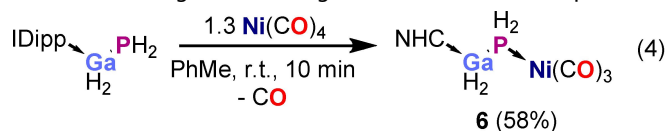
Entry	³¹ P{ ¹ H} NMR	³¹ P NMR	¹¹ B{ ¹ H} NMR	¹¹ B NMR
3a	−164.5 (q, br)	−164.5 (tq, br)	−32.2 (d, br)	−32.2 (td, br)
3b	−11.1 (q, br)	−11.1 (m, br)	−26.8 (m, br)	−26.8 (br)
3c	−68.9 (m, br)	−68.9 (m, br)	−24.8 (d, br)	−24.8 (dt, br)
3d	−38.7 (q, br)	−38.7 (dm, br)	−30.4 (d, br)	−30.4 (dt, br)
3e	−37.8 (m, br)	−37.8 (m, br)	−30.0 (s, br)	−30.0 (t, br)
3f	−241.8 (m, br)	−241.8 (m, br)	−33.2 (m, br)	−33.2 (m, br)
3g	−163.5 (q, br)	−163.5 (tq, br)	−32.2 (d, br)	−32.2 (m, br)
4a	–	–	−32.0 (s, br)	−32.0 (t, br)
4b	–	–	−26.9 (s, br)	−26.9 (t, br)
5a	−20.7 (q, br)	−20.7 (m, br)	−4.09 (d, br)	−4.09 (m, br)
5b	−47.2 (q, br)	−47.2 (dm, br)	−7.3 (d, br)	−7.3 (td, br)
5c	−155.6 (q, br)	−155.6 (tq, br)	−7.8 (d)	−7.8 (d, br)

volatiles were removed and the reaction outcomes investigated by multinuclear NMR spectroscopy. The reactions showed full conversion and small amounts of the inseparable side products [(Me₃N·BH₂PR₂)_xNi(CO)_{4−x}] (x = 2, 3; cf. Supporting Information). After filtration, **5a–c** were obtained as brown solids or oils in moderate yields, respectively. Characteristic heteronuclear NMR data for **5a–c** are given in Table 2.



Compound **5a** also crystallized from a saturated toluene solution at −30 °C as colorless blocks suitable for X-ray structure determination (Figure 2). **5a** crystallizes in the monoclinic space group *P2₁/n*. The solid-state structure of **5a** shows a tetrahedral coordination of the phosphanylborane to the {Ni(CO)₃} unit with a B–P–Ni angle of 121.12(6)°. The bond lengths of 2.2581(5) Å (P–Ni) and 1.977(2) (B–P) lie within the range of usual single bonds.

In this context, the question arose if it was also possible to synthesize the corresponding Ni complex of NHC-stabilized phosphanyl-gallanes and determine the donor strength, despite the high sensitivity of the compound due to the lability of the Ga–P bond. Thus, freshly prepared IDipp·GaH₂PH₂^[36] was reacted with Ni(CO)₄ (eq. 4). The reaction mixture showed full conversion already after 10 minutes with a downfield shift of the ³¹P resonance signal of +55 ppm. After work-up, [(IDipp·GaH₂PH₂)Ni(CO)₃] (**6**) is obtained in moderate yields as a brown powder. **6** represents the first example of a coordination compound of the highly unstable parent compound IDipp·GaH₂PH₂. The ³¹P NMR spectrum of **6** shows a distinct sharp triplet of triplets at −222.5 ppm (¹J_{HP} = 172 Hz, ³J_{HP} = 19 Hz) that merges into a singlet in the ³¹P{¹H} NMR spectrum.



After the successful synthesis of the complexes **3a–5a**, IR spectra of the solid products were recorded to evaluate the TEPs and compare the donor strength of the different

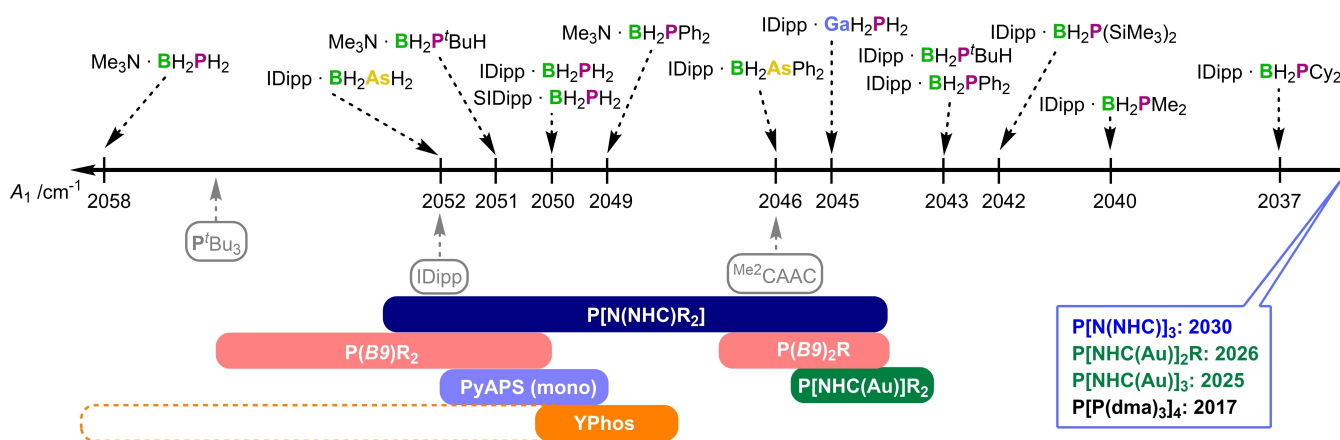


Figure 3. Schematic representation of the determined TEPs [cm^{−1}] in this work and comparison to selected phosphines and NHCs. TEPs were determined by the magnitude of the A₁ vibration mode in the corresponding IR spectra (ATR diamond crystal). TEPs of substance classes are represented by averaged areas. As the YPhos ligand system can vary strongly depending on the substituents, the region of the highest donor strength is given in bold print.

Table 3. Calculated averaged TCA [°] ^[40] and percent buried volumes %V _{bur} [%] ^[41,42] from the solid-state structures of 3a , 3g , 4a and 5a and comparison to selected phosphines. ^[7] %V _{bur} values of 3a , 3g , 4a and 5a were calculated from the solid-state structures (<i>r</i> = 3.5 Å, bond radii scaled by 1.17).							
	3a	3g	4a	5a	PH ₃ ^[6a]	PMe ₃ ^[6a]	PMePh ₂ ^[6a]
TCA	94	95	93	135	87	118	136
%V _{bur}	22.5	23.0	14.8	31.0	–	22.2	–
		PCy ₃ ^[6a]		P(tmp) ₃ ^[25]		P(9- <i>m</i> Cb) ^b Bu ₂ ^[21]	P(Ni ⁱ Pr) ₃ ^[19]
TCA		170		163	178		178
%V _{bur}		31.8		36.1	41.8		38.7

compounds by evaluating the A₁ vibration modes (Figure 3). In line with regular phosphines, the alkyl substituents on the pnictogen atom generally increase the donor strength. Compared to their substituted counterparts, the parent compounds reveal the weakest donor strength of the herein investigated compounds. Moreover, the group 13 element also strongly influences the donor strength with e.g. phosphanylgallanes, as they generally are stronger donors than phosphanylboranes (cf: **6**: 2045 cm⁻¹, **3g**: 2050 cm⁻¹). Just as arsines and phosphines, arsanylboranes show higher TEPs and can be considered slightly weaker donors than the respective phosphanylboranes (**4a**: 2052 cm⁻¹, **3g**: 2050 cm⁻¹). In general, exchanging NMe₃ for a stronger donor such as an NHC increases the overall donor strength, as the 13/15 monomer becomes more electron-rich (cf. **5c**: 2059 cm⁻¹ → **3g**: 2050 cm⁻¹).

With the common trend towards donor strength based on the composition of the 13/15 monomer now established, a comparison towards classic phosphines and other commonly used 2e-σ-donors is now addressed. All compounds **3a**–**5b** (except for **5c**) show lower TEPs and thus higher donor strength than regular phosphines PR₃ (cf. P^tBu₃: 2056 cm⁻¹), even the measured arsanylboranes. Based on the magnitude of the measured TEPs, a donor strength similar to that of NHCs can be attributed to **3a**–**5c** with some of them being significantly stronger donors. Although modern superbasic phosphines such as Sundermayer's phosphazenyphosphines (2017 cm⁻¹),^[16] Dielmann's tris(imidazolol-2-ylidenamino)phosphine (2030 cm⁻¹),^[19] Liu's AuPhos ligands P[(NHC)Au]₂R (2026 cm⁻¹) and P[(NHC)Au]₃ (2025 cm⁻¹) commonly achieve higher donor strengths,^[23] a remarkable value for the pnictogenyltrielanes is set by IDipp·BH₂PCy₂ (**3e**) with a TEP as low as 2037 cm⁻¹, which is comparable to P(NIMes)₂ⁱPr (2039 cm⁻¹),^[17] and P(tmp)₃ (2037 cm⁻¹)^[26] making **3e** the strongest donor within the herein presented series of pnictogenyltrielanes.^[39] This is especially intriguing, as **3e** displays such a high donor strength while having only one {NHC·BH₂} unit attached, which greatly simplifies the synthesis of **3e**.

With the solid-state structures of [(SIDipp·BH₂PH₂)Ni(CO)₃] (**3a**), [(IDipp·BH₂PH₂)Ni(CO)₃] (**3g**), [(IDipp·BH₂AsH₂)Ni(CO)₃] (**4a**) and [(Me₃N·BH₂PPh₂)Ni(CO)₃] (**5a**) at hand, it was also possible to calculate the Tolman Cone Angles (TCAs) and percent buried volumes (%V_{bur})^[41,42] directly from them to evaluate the steric demand of the ligands (Table 3).^[40] The TCAs for the parent phosphanyl- and arsanylboranes (**3a**, **3g**, **4a**) are only slightly larger than the value of PH₃ and thus show that the steric

demand at the pnictogen atom is comparatively low. The TCA for **5a** (135°) is comparable to the one for PMePh₂ (136°). This is further supported by comparably low %V_{bur} values for all compounds. Thus, the pnictogenyltrielanes can be considered as significantly stronger donors than regular phosphines while being sterically less hindered at the pnictogen atom. In

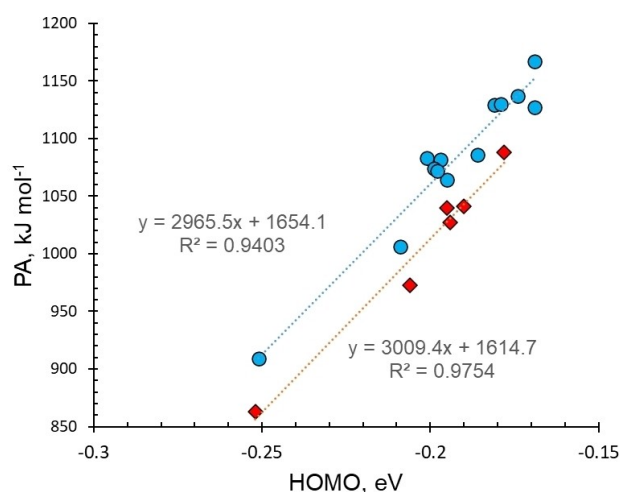


Figure 4. Correlation between the HOMO energy of the ligand L [eV] and PA [kJ mol⁻¹]. Blue: P-containing L; red: As-containing L.

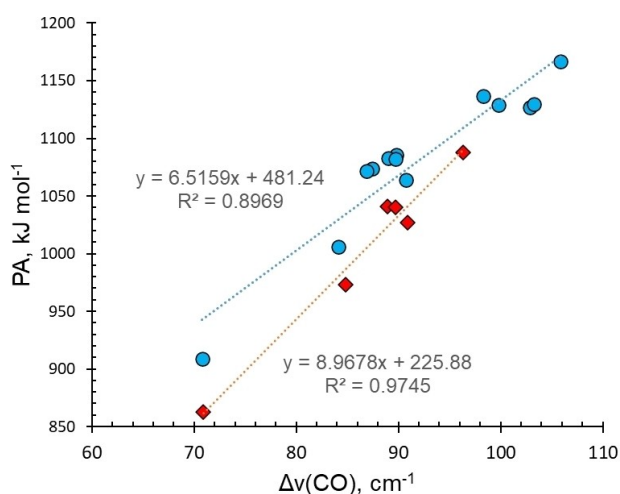
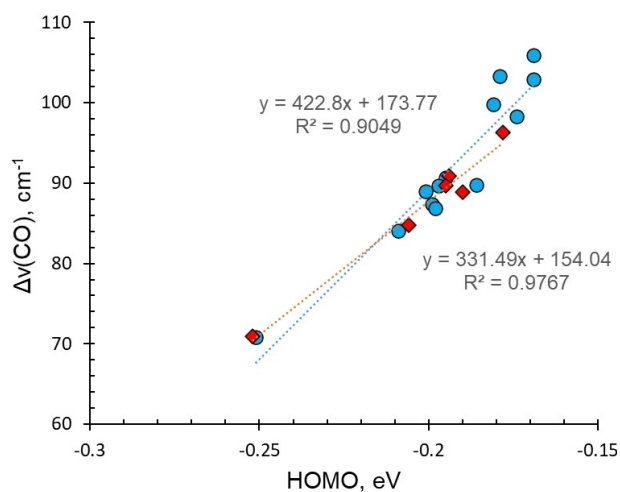


Figure 5. Correlation between the Tolman electronic parameter of the ligands L Δν(CO) [cm⁻¹] and the PA (in kJ mol⁻¹). Blue: P containing L; red: As containing L.

Table 4. Proton affinities (PA), HOMO energies (E_{HOMO}), Mulliken charges on the donor atom $q(\text{P/As})$, the shift in the symmetric stretching CO vibration upon complex formation with $\{\text{Ni}(\text{CO})_3\}$ ($\Delta\nu(\text{CO})$) with respect to free CO, dissociation enthalpies ($\Delta_{\text{diss}}H^\circ_{298}$), dissociation constants ($\text{p}K_{\text{diss}(298)}$) and the donor-acceptor bond distance ($R(\text{Ni}-\text{P/As})$) for complexes of ligands L with $\{\text{Ni}(\text{CO})_3\}$ (B3LYP/def2-TZVP level of theory).

L	PA/kJ mol ⁻¹	E_{HOMO} /eV	$q(\text{P/As})$	$\Delta\nu(\text{CO})/\text{cm}^{-1}$	$\Delta_{\text{diss}}H^\circ_{298}/\text{kJ mol}^{-1}$	$\text{p}K_{\text{diss}(298)}$	$R_{\text{Ni-P/As}}/\text{\AA}$
Me ₃ CCH ₂ PH ₂	909	-0.251	-0.068	70.8	53.9	2.01	2.2769
Me ₃ N·BH ₂ PH ₂	1006	-0.209	-0.297	84.1	74.5	4.54	2.3179
Me ₃ N·BH ₂ PH ^t Bu	1064	-0.195	-0.216	90.7	69.1	3.18	2.3500
Me ₃ N·BH ₂ PPH ₂	1086	-0.186	-0.104	89.8	74.6	3.47	2.3390
SIDipp·BH ₂ PH ₂	1083	-0.201	-0.217	89.0	78.4	6.33	2.3058
IDipp·BH ₂ PH ₂	1082	-0.197	-0.217	89.7	79.6	6.05	2.3057
IDipp·AlH ₂ PH ₂	1074	-0.199	-0.310	87.4	70.1	4.96	2.3252
IDipp·GaH ₂ PH ₂	1072	-0.198	-0.345	86.9	67.2	4.24	2.3191
IDipp·BH ₂ PH ^t Bu	1129	-0.181	-0.156	99.8	66.5	1.50	2.3311
IDipp·BH ₂ PPH ₂	1137	-0.174	-0.061	98.3	50.9	-1.51	2.3320
IDipp·BH ₂ PMe ₂	1127	-0.169	-0.015	102.9	80.4	4.15	2.3260
IDipp·BH ₂ PCy ₂	1167	-0.169	-0.030	105.9	51.8	0.34	2.3591
IDipp·BH ₂ P(SiMe ₃) ₂	1130	-0.179	-0.283	103.3	43.7	-2.53	2.4156
Me ₃ CCH ₂ AsH ₂	863	-0.252	-0.005	70.9	43.1	-0.50	2.4168
Me ₃ N·BH ₂ AsH ₂	973	-0.206	-0.221	84.8	63.8	3.18	2.4412
Me ₃ N·BH ₂ AsH ^t Bu	1027	-0.194	-0.107	90.9	64.9	3.03	2.4636
Me ₃ N·BH ₂ AsPh ₂	1041	-0.190	0.066	88.9	68.5	3.51	2.4488
IDipp·BH ₂ AsH ₂	1040	-0.195	-0.166	89.7	64.2	3.68	2.4341
IDipp·BH ₂ AsPh ₂	1088	-0.178	0.172	96.3	45.2	-1.96	2.4529

**Figure 6.** Correlation between the HOMO energy of the ligands L [eV] and the Tolman electronic parameter $\Delta\nu(\text{CO})$ [cm^{-1}]. Blue: P containing L; red: As containing L.

comparison, other superbasic phosphines of comparable donor strength such as $\text{P}(\text{tmp})_3$, $\text{P}(\text{9-}m\text{Cb})^t\text{Bu}_2$ and $\text{P}(\text{Ni}^i\text{Pr})_3$ reveal a higher steric demand (cf. Table 3).

To further investigate the electronic properties of the compounds, quantum chemical calculations were performed (B3LYP/def2-TZVP level of theory).^[43] The prominent values of computationally considered ligands L are summarized in Table 4. There are satisfactory correlations between E_{HOMO} , $\Delta\nu(\text{CO})$ and proton affinity (PA) values (Figures 4–6). In contrast,

there is no correlation between the charges on the P and As atoms and the PA values and dissociation enthalpies $\Delta_{\text{diss}}H^\circ_{298}$ and $\text{p}K_{\text{diss}(298)}$ values for the studied complexes.

When considering $\text{Me}_3\text{N}\cdot\text{BH}_2\text{PH}_2$ and $\text{Me}_3\text{N}\cdot\text{BH}_2\text{AsH}_2$ with the isoelectronic carbon compounds neopentylphosphine and neopentylarsine ($\text{Me}_3\text{CCH}_2\text{PH}_2$ and $\text{Me}_3\text{CCH}_2\text{AsH}_2$), the higher HOMO energy of the $\{\text{Me}_3\text{N}\cdot\text{BH}_2\}$ derivative leads to much larger PA (by 97 and 110 kJ mol^{-1}), which is also reflected in the Tolman electronic parameter (Table 4).

The substitution of the H atom in the EH_2 group by ^tBu and two hydrogen atoms by two phenyl substituents further increases the HOMO energy and the PA by 58–82 kJ mol^{-1} for $\text{E}=\text{P}$ and 54–68 kJ mol^{-1} for $\text{E}=\text{As}$. Despite the PA of the $\text{Me}_3\text{N}\cdot\text{BH}_2\text{EPH}_2$ derivatives being larger than the PA of $\text{Me}_3\text{N}\cdot\text{BH}_2\text{EH}^t\text{Bu}$, the Tolman electronic parameter is smaller for $\text{E}=\text{P}$ and As, which may be attributed to the steric demand of tertiary phosphines and arsines. Replacing NMe₃ by an NHC generally increases the PA by 51–77 kJ mol^{-1} ; the values of the PA for SIDipp and IDipp are very close. The substitution of the boron atom in IDipp·BH₂PH₂ by aluminium and gallium leads to a decrease of the PA by 8–10 kJ mol^{-1} .

Overall, the computed order of the PA of the studied phosphines is: $\text{Me}_3\text{CCH}_2\text{PH}_2 < \text{Me}_3\text{N}\cdot\text{BH}_2\text{PH}_2 < \text{Me}_3\text{N}\cdot\text{BH}_2\text{PH}^t\text{Bu} < \text{IDipp}\cdot\text{GaH}_2\text{PH}_2 < \text{IDipp}\cdot\text{AlH}_2\text{PH}_2 < \text{IDipp}\cdot\text{BH}_2\text{PH}_2 < \text{SIDipp}\cdot\text{BH}_2\text{PH}_2 < \text{Me}_3\text{N}\cdot\text{BH}_2\text{PPH}_2 < \text{IDipp}\cdot\text{BH}_2\text{PMe}_2 < \text{IDipp}\cdot\text{BH}_2\text{PH}^t\text{Bu} < \text{IDipp}\cdot\text{BH}_2\text{P}(\text{SiMe}_3)_2 < \text{IDipp}\cdot\text{BH}_2\text{PPH}_2 < \text{IDipp}\cdot\text{BH}_2\text{PCy}_2$, with the NHC-stabilized phosphanylboranes displaying the highest PA. The computed order of the PA of the studied arsines reveals an analogous trend in this regard:

Me₃CCH₂AsH₂ < Me₃N·BH₂AsH₂ < Me₃N·BH₂AsH^tBu <
IDipp·BH₂AsH₂ < Me₃N·BH₂AsPh₂ < IDipp·BH₂AsPh₂.

Conclusions

In summary, we expanded the range of NHC-stabilized pnictogenylboranes by synthesizing novel compounds of the type NHC·BH₂ER₂ (**1a**: NHC = SIDipp, ER₂ = PH₂; **1b**: NHC = IDipp, ER₂ = PPh₂; **1c**: NHC = IDipp, ER₂ = PMe₂; **1d**: NHC = IDipp, ER₂ = PH^tBu; **1e**: NHC = IDipp, ER₂ = PCy₂; **1f**: NHC = IDipp, ER₂ = P(SiMe₃)₂, **2**: NHC = IDipp, ER₂ = AsPh₂). The convenient general synthetic procedure allows for easy fine tuning of the donor properties of the compounds. Alongside the respective parent compounds, these compounds were reacted with Ni(CO)₄ to give the mono-substitution complexes [(NHC·BH₂ER₂)Ni(CO)₃] (**3a**: NHC = SIDipp, ER₂ = PH₂; **3b**: NHC = IDipp, ER₂ = PPh₂; **3c**: NHC = IDipp, ER₂ = PMe₂; **3d**: NHC = IDipp, ER₂ = PH^tBu; **3e**: NHC = IDipp, ER₂ = PCy₂; **3f**: NHC = IDipp, ER₂ = P(SiMe₃)₂, **3g**: NHC = IDipp, ER₂ = PH₂; **4a**: NHC = IDipp, ER₂ = PH₂; **4b**: NHC = IDipp, ER₂ = AsPh₂). Similarly, the reaction of IDipp·GaH₂PH₂ with Ni(CO)₄ yielded the unprecedented complex [Ni(CO)₃(IDipp·GaH₂PH₂)] (**6**) which represents the first example of stable coordination of IDipp·GaH₂PH₂ to a metal center. Analogous reactions of Me₃N·BH₂PR₂ yielded the corresponding compounds [(Me₃N·BH₂PR₂)Ni(CO)₃] (**5a**: R₂ = Ph₂; **5b**: R₂ = H^tBu, **5c**: R₂ = H₂). Evaluation of the Tolman Electronic Parameters and percent buried volumes %V_{bur} showed that **3a–5c** can in general be considered as of similar donor strength as NHCs, albeit weaker than modern superbasic phosphines. **3a–5c** reveal similar trends compared to phosphines, with the alkyl substitution strongly increasing the donor strength. Exchanging boron for gallium increases the donor strength, while replacing phosphorus with arsenic decreases it accordingly. Analysis of the Tolman Cone Angles revealed the steric demand of the pnictogen atoms within the pnictogenyltrielanes to be comparatively low, with the parent compounds exhibiting a similar steric demand at the pnictogen atom as to PH₃. Quantum chemical calculations highlight the electronic nature and explain the observed trends in donor strength by examining the theoretical TEPs and comparison with the proton affinities.

Experimental Section

Experimental procedures, full analytical data and details regarding quantum chemical calculations are described in the Supporting Information.

Deposition numbers CCDC 2304605 (**1a**), 2304606 (**1e**), 2304607 (**1d**), 2304608 (**2**), 2304609 (**3a**), 2304610 (**3g**), 2304611 (**4a**), and 2304612 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information

The authors have cited additional references within the Supporting Information.^[44]

Acknowledgements

This work was supported by a joint DFG-RSF project (DFG Sche 384/41-1, RSF grant 21-43-04404). The use of computational resources of the research center “Computing Center” of the St. Petersburg State University is acknowledged. R.S. is grateful to the Fonds der Chemischen Industrie (FCI) for a PhD fellowship. Lisa Zimmermann and Sophie Woick are acknowledged for assistance in IR measurements. Stephan Reichl (KASPh₂), Martin Weber (LiPMe₂), and Matthias T. Ackermann (NaPPh₂) are acknowledged for the preparation of the corresponding reagents. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: 13/15 compounds · ligand properties · pnictogen · tolman electronic parameter · triels

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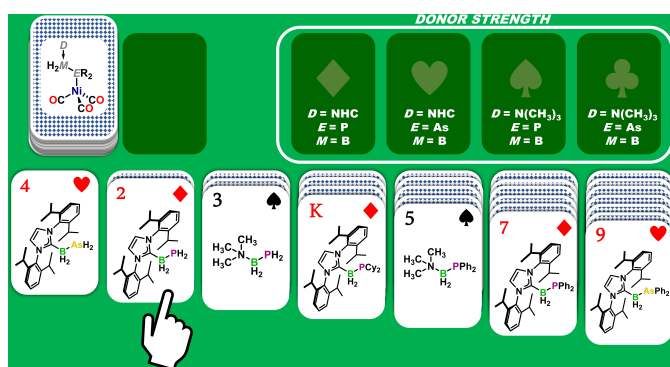
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[45] Further attempts by the amalgamation of the Ni particles by treating the solutions with elemental Hg followed by filtration did not provide a complete separation of the Ni particles either.

Manuscript received: October 31, 2023

Accepted manuscript online: December 22, 2023

Version of record online: ■■, ■■



The syntheses and characterizations of alkyl-substituted compounds $\text{IDipp} \cdot \text{BH}_2\text{ER}_2$ ($\text{E} = \text{P}, \text{As}; \text{R} = \text{alkyl}$) are presented. Together with other donor-stabilized pnicto-genyltrielanes, these compounds were reacted with $\text{Ni}(\text{CO})_4$ and their ligand properties evaluated regarding the steric and

electronic nature of this class of compounds. According to the corresponding Tolman Electronic Parameters, the compounds are significantly more electron-rich than regular phosphines and their steric and electronic demands can be modified easily.

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1 – 10

Characterization of the Ligand Properties of Donor-stabilized Pnicto-genyltrielanes

