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Mono-, Di-, and Triborylphosphine Analogues of Triarylphosphines

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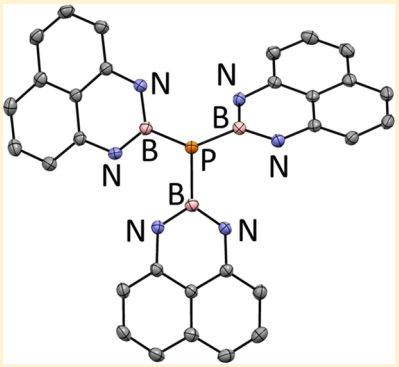
Supporting Information

ABSTRACT: Diazaborinylphosphines based on the 1,8-diaminonaphthylboronamide heterocycle are prepared by a chlorosilane-elimination reaction, and their structural and bonding properties are compared to those of PPh_3. The precursor chloroborane $ClB\{1,8\text{-}(NH)_2C_{10}H_6\}$ (**I**) is fully characterized including its crystal structure, which features intermolecular $\pi-\pi$ stacking, B···N interactions, and N−H···Cl hydrogen bonding. Treatment of **I** with $Ph_{3-n}P(SiMe_3)_n$ gave the corresponding $Ph_{3-n}P(B\{1,8\text{-}(NH)_2C_{10}H_6\})_n$, {$\mathbf{L_1}$ (n = 1), $\mathbf{L_2}$ (n = 2), and $\mathbf{L_3}$ (n = 3)}. The crystal structures of $\mathbf{L_{1-3}}$ reveal an increase in the planarity at P as a function of n, and the steric bulk of the diazaborinyl substituent $B\{1,8\text{-}(NH)_2C_{10}H_6\}$ is similar to that of a phenyl. Nucleus-independent chemical shift calculations were carried out that suggest that the 14 π-electron diazaborinyl substituent can be described as aromatic overall, though the BN_2-containing ring is slightly antiaromatic. The complexes *cis*-$[Mo(\mathbf{L_{1-3}})_2(CO)_4]$ (**1**−**3**) are prepared from $[Mo(nbd)(CO)_4]$ (nbd = norbornadiene) and $\mathbf{L_{1-3}}$. From the position of the $\nu(CO)$ (A_1) band in the IR spectra of **1**−**3**, it is deduced that the diazaborinyl substituent has a donating capacity similar to an alkyl group.

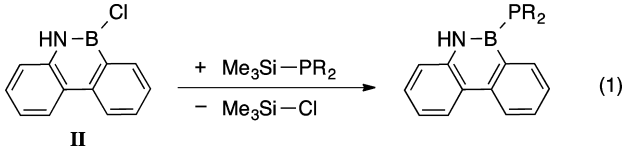


INTRODUCTION

Triphenylphosphine is one of the most important phosphorus(III) compounds. Its applications in synthetic chemistry range from coordination chemistry[1] to stoichiometric organic synthesis.[2] Its metal complexes ignited the field of homogeneous catalysis in the 1960s, and they remain the catalysts of choice for many processes.[3] More generally, arylphosphines, in all their guises (mono-, bi-, and tridentates) constitute a hugely important class of ligands whose properties (stereoelectronics, chirality, solubility) can be readily and systematically varied.

Dewar pioneered the incorporation of BN units in polycyclic aromatic hydrocarbons (PAHs),[4] and recently these compounds have garnered much academic interest in nanoscience and conducting materials due to their desirable photophysical properties.[5] We are interested in arylphosphines in which the aryl group contains BN units and the P is bonded to the B. The coordination chemistry of such borylphosphines and their potential use in homogeneous catalysis has been little explored.[6] Here we report ligands containing the 1,8-diaminonaphthylboronamide group $B\{1,8\text{-}(NH)_2C_{10}H_6\}$, which is derived from the chloroborane **I** (Scheme 1).

Recently we showed that the P−B ligands, derived from chloroborane **II**, by the route shown in eq 1, are powerful σ-donors and that Rh complexes with these ligands catalyze the hydrogenation of cyclohexene at least as efficiently as their arylphosphine analogues.[6]



II (1)

The route to borylphosphines shown in eq 1 is high-yielding and convenient since the only byproduct is the volatile Me_3SiCl; notably, attempts to make the borylphosphines using $LiPR_2$ were unsuccessful.[6] The silyl route (eq 1) has the potential to be the basis for a general method of making borylphosphines, and we report here its extension to the synthesis of the series of borylphosphines $\mathbf{L_{1-3}}$ derived from chloroborane **I** (Scheme 1). Monoborylphosphines that are analogues of $\mathbf{L_1}$ ($R_2BPR'_2$) have attracted much attention recently,[7] while diborylphosphines that are analogues of $\mathbf{L_2}$ ($\{R_2B\}_2PR'$) have been neglected since the work of Power[8] and Nöth[9] over 20 years ago. There has been just one triborylphosphine analogue of $\mathbf{L_3}$ reported, namely, $\{(NMe_2)_2B\}_3P$, which was isolated from the thermolysis of $(Me_2N)_2BP(SiHMe_2)_2$.[10]

RESULTS AND DISCUSSION

Diazaborinylphosphines. The 1,8-diaminonaphthylboronamide[11] group has been used extensively,[12] but surprisingly, the commonly used precursor chloroborane **I**, generated as shown in Scheme 1, has not been previously isolated. Sublimation of **I** gave crystals suitable for X-ray diffraction, which showed (see Figure 1) that the B−N bond lengths in **I** (1.4004(16) and 1.4018(16) Å) are shorter than those in typical borazine derivatives (e.g., 1.428(5)−1.449(4) Å for 2,4,6-trichloro-1,3,5-trimethylborazine),[13] but the B−Cl bond length (1.7947(14) Å) is within the normal range. The solid-state structure revealed several intermolecular interactions: offset $\pi-\pi$ arene stacking (interplanar separation, 3.47 Å),[14]

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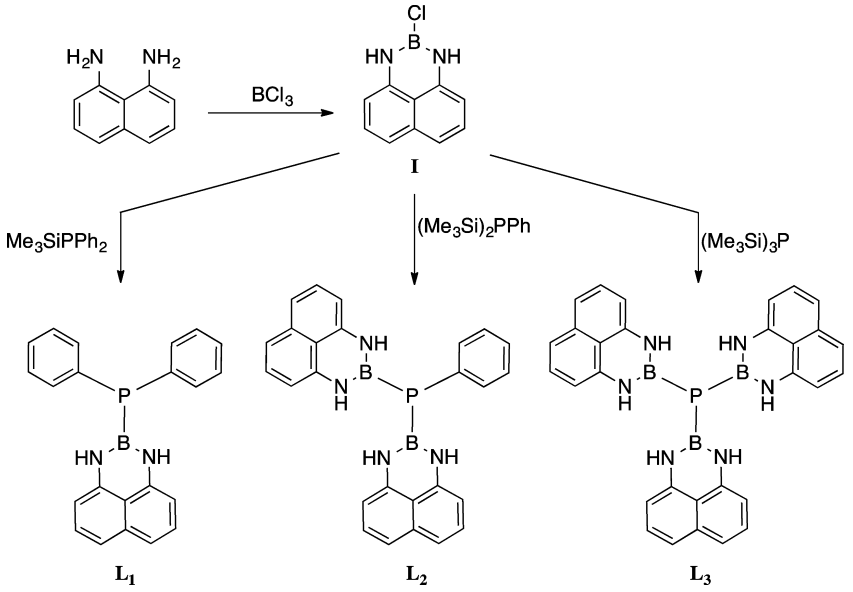
Scheme 1



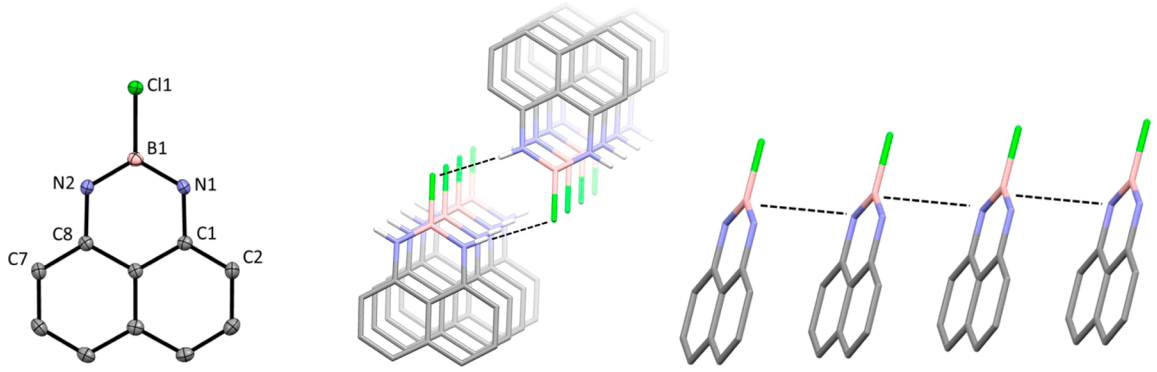


Figure 1. Thermal ellipsoid (50% probability) plot of **I**, omitting all hydrogen atoms and plots showing the intermolecular N-H···Cl hydrogen bonding and the arene−arene stacking. Selected bond lengths [Å]: Cl1−B1 1.7947(14), N1−B1 1.4004(16), N2−B1 1.4018(16), N1−C1 1.4092(15), N2−C8 1.4082(15).

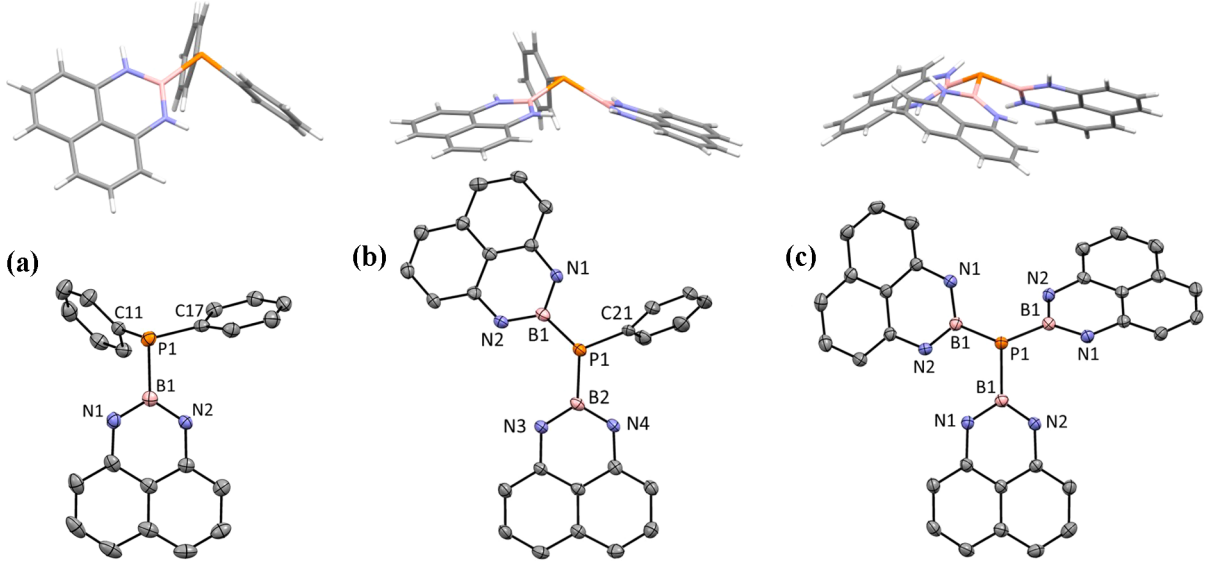


Figure 2. Thermal ellipsoid (50% probability) plot of (a) L_1, (b) L_2, and (c) L_3 omitting all hydrogen atoms with insets showing side-on views.

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Table 1. X-ray Structural Data for $Ph_{3-n}P(B\{1,8\text{-}(NH)_2C_{10}H_6\})_n$ (n = 0−3)

	PPh_3[18]	L_1	L_2	L_3
P−B, Å		1.9448(18)	1.917(4) (P1−B1) 1.927(3) (P1−B2)	1.9080(19)
P−C, Å	1.834(2)	1.8360(15) (P1−C11)	1.839(3)	
	1.828(2)	1.8309(15) (P1−C17)		
	1.832(2)			
B−N, Å		1.410(2) (B1−N1)	1.417(4) (B1−N1)	1.411(2) (B1−N1)
		1.414(2) (B1−N2)	1.422(5) (B1−N2)	1.429(2) (B1−N2)
			1.415(4) (B2−N3)	
			1.412(5) (B2−N4)	
Σ(angles), deg	308.3	307.6	316.7	322.2
θ_{cryst}, deg	154.8[19]	160.2	155.7	157.6

short B···N contacts (3.447 Å) between adjacent molecules, and N−H···Cl hydrogen bonding (N···Cl distances of 3.520 and 3.547 Å). The NH signal in the ^{1}H NMR spectra of **I** is broad and showed considerable variation in chemical shift with the solvent donicity (4.90 ppm in C_6D_6, 5.75 in $CDCl_3$, and 7.63 in deuterated tetrahydrofuran (d_8-THF)) consistent with hydrogen bonding involving the N−H persisting in solution (see Supporting Information for the ^{1}H NMR spectra).

The reaction between chloroborane **I** and the silylphosphines $(Me_3Si)_nPPh_{3-n}$ (n = 1−3) proceeded smoothly and quantitatively according to the in situ ^{31}P NMR spectra to afford the borylphosphines $\mathbf{L}_{1-3}$ (Scheme 1). The rate of formation of $\mathbf{L}_{1-3}$ decreased in the order $\mathbf{L}_1 > \mathbf{L}_2 > \mathbf{L}_3$. Thus, the reaction between Me_3SiPPh_2 and **I** to give $\mathbf{L}_1$ was complete in 30 min at ambient temperature, whereas after 30 min of the reaction between $(Me_3Si)_3P$ and **I**, the in situ ^{31}P NMR spectrum showed three signals at −245, −240, and −229 ppm, which were assigned to the mono- and diboryl intermediates and triborylphosphine $\mathbf{L}_3$. The preparation of $\mathbf{L}_3$, which is only sparingly soluble in the CH_2Cl_2 reaction solvent, was driven to completion by heating the reaction mixture for 18 h.

The chloroborane substituents are apparently critical to the success of the silyl route to B−P bond formation since we have found that, in an attempt to make the known[10] compound $P\{B(NMe_2)\}_3$, no reaction took place between $P(SiMe_3)_3$ and $ClB(NMe_2)$ under conditions (18 h, 40 °C) where $P(SiMe_3)_3$ reacted with chloroborane **I** to give $\mathbf{L}_3$ quantitatively.[15]

The crystal structures of all three borylphosphines $\mathbf{L}_{1-3}$ were determined (Figure 2a−c), which means that structural and spectroscopic comparisons can be made for the complete series $Ph_{3-n}P(B\{1,8\text{-}(NH)_2C_{10}H_6\})_n$ where n = 0−3 (see Table 1). The P−C bond lengths in PPh_3, $\mathbf{L}_1$, and $\mathbf{L}_2$ are not significantly different from each other, but the P−B bond lengths shorten in the order $\mathbf{L}_1 > \mathbf{L}_2 > \mathbf{L}_3$ and the planarization around the P atom increases in the same order $\mathbf{L}_1$ (308°) < $\mathbf{L}_2$ (317°) < $\mathbf{L}_3$ (322°). These features are consistent with P−B π overlap increasing with the number of boryl substituents. There are no obvious trends in the crystallographic cone angles θ_{cryst}, calculated according to literature methods[16] (Table 1), and all are within a narrow range of ca. 155−160°. The triborylphosphine $\mathbf{L}_3$ crystallized in the hexagonal space group $P6_3$, and the structure shows crystallographic C_3 symmetry (see Figure 2(c)).

There were no significant differences in the ^{11}B NMR spectra of all three compounds (each has $\delta_B \approx 32$ ppm). By contrast, the ^{31}P NMR signals shift markedly upfield upon going from PPh_3 (δ_P −6 ppm) to $\mathbf{L}_3$ (δ_P −237 ppm). The δ_P values for $\mathbf{L}_n$ (n = 1−3) are similar to the δ_P values for the corresponding $(Me_3Si)_nPPh_{3-n}$ and H_nPPh_{3-n} (see Figure 3). The electronic similarity between H and $SiMe_3$ is well-established,[17] and we have previously noted the ^{31}P NMR support for the B−Si diagonal relationship.[6]

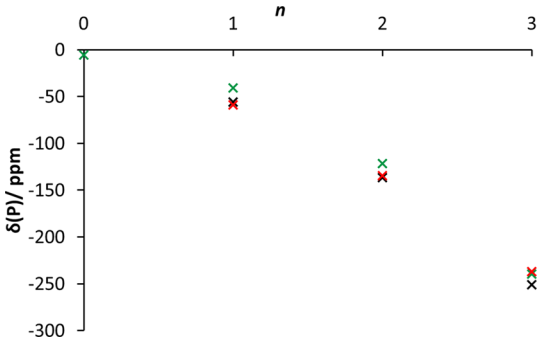
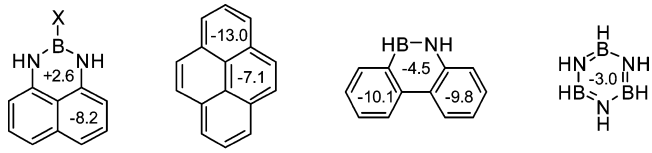


Figure 3. ^{31}P NMR chemical shifts for $Ph_{3-n}P(B\{1,8\text{-}(NH)_2C_{10}H_6\})_n$ (red ×); $Ph_{3-n}P(SiMe_3)_n$ (black ×); $Ph_{3-n}PH_n$ (green ×).

Aromatic Character of the Diazaborinylphosphines. In the crystal structures of **I** and $\mathbf{L}_{1-3}$, the $B\{1,8\text{-}(NH)_2C_{10}H_6\}$ rings in **A** (see Figure 4) are planar and the B−N bond lengths



A **B** **C** **D**

Figure 4. NICS-1 values (calculated at the B3LYP/6-311+G(2d) level). For **A**, the values shown correspond to the case where X = H.

(1.41−1.43 Å) are consistent with a bond order greater than 1; in borazine (**D**), the B−N bond length was determined to be 1.435(1) Å by electron diffraction.[20] Moreover the 14 π-electron count in **A** obeys the Huckel $4n + 2$ rule for aromaticity. There are no neutral hydrocarbons that are isoelectronic with **A**,[21] but pyrene (**B**) is related.

Nucleus-independent chemical shift (NICS) calculations have emerged as a simple way to assess the aromaticity of planar π-conjugated rings.[20] Placing a ghost atom 1 Å above the center of each ring and measuring its absolute chemical shielding provides information on the contributions to the aromaticity of the individual rings. These NICS-1 values were calculated at the B3LYP/6-311+G(2d) level from structures optimized at the B3LYP/6-31G(d) level. The NICS-1 values for **A** (X = H) were calculated to be +2.6 for the C_3BN_2 ring and −8.2 for the C_6 rings. Very similar values were calculated

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for X = PH_2 (+2.6 and −8.3) and X = Cl (+2.4 and −8.6) showing that the B-bound exocyclic group has little bearing on the aromaticity of the rings. Thus, the C_3BN_2 component of **A** is calculated to be slightly antiaromatic, but this is counterbalanced by the strongly aromatic contribution from the naphthalene component. NICS values have been previously calculated for pyrene (**B**),[22] B−N substituted phenanthrene (**C**),[23] and borazine (**D**),[24] but the sensitivity of NICS calculations to different basis sets and methods led us to calculate the NICS-1 values given in Figure 4 for internal consistency.

Molybdenum(0) Complexes of the Diazaborinylphosphines. To probe the ligand properties of $\mathbf{L_{1-3}}$, the *cis*-$[MoL_2(CO)_4]$ complexes **1**−**3** were prepared by the route shown in eq 2. The reactions were followed by ^{31}P NMR spectroscopy, which showed that the times for complex formation increased in the order of **1** < **2** < **3**. Intermediates of the type $[MoL(nbd)(CO)_4]$ (nbd = norbornadiene) would be expected but were not detected in the ^{31}P NMR spectra indicating that the coordination of the second borylphosphine is faster than the first. Crystals of **1** were grown from CH_2Cl_2/hexane, and the X-ray crystal structure (Figure 5) showed that the geometry around P in the coordinated $\mathbf{L_1}$ is little different from the free ligand.

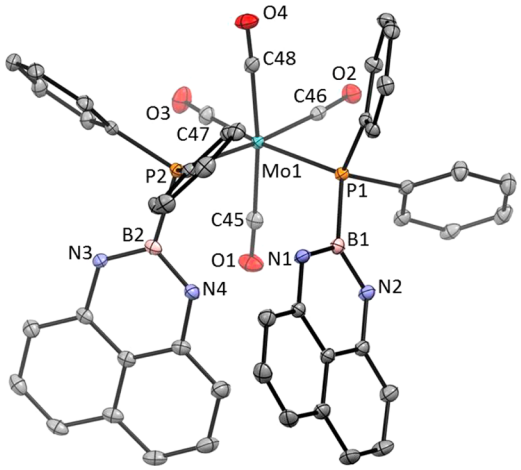
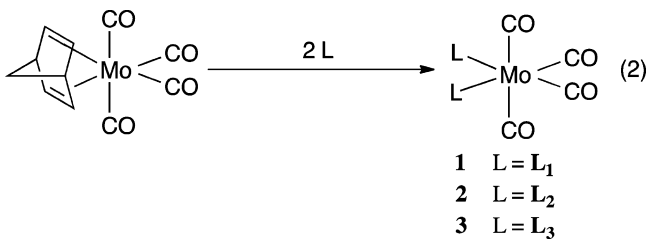


Figure 5. Thermal ellipsoid (50% probability) plot of **1**, omitting all hydrogen atoms. Selected bond lengths [Å]: N1−B1 1.413(2), N2−B1 1.409(2), N3−B2 1.409(2), N4−B2 1.408(2), P1−B1 1.9544(17), P2−B2 1.9378(17), Mo1−P1 2.5765(4), Mo1−P2 2.5680(4).



(2)

The position in the IR spectrum of the A_1 ν(CO) band in **1**−**3** provides a measure of the donor properties of $\mathbf{L_{1-3}}$. The IR data given in Table 1 show that, as the number of boryl groups on the P increases, the ν(CO) stretching frequency decreases, consistent with the electron-donating ability increasing in the order of $\mathbf{L_1}$ < $\mathbf{L_2}$ < $\mathbf{L_3}$. Crabtree[25] showed that the positions of the A_1 bands in $[MoL_2(CO)_4]$ and $[NiL(CO)_3]$ are linearly correlated according to eq 3.

$$\nu_{Ni} = 0.593 \times \nu_{Mo} + 871 \quad (3)$$

The calculated ν_{Ni} values, which are the Tolman electronic parameters (TEPs), for $\mathbf{L_{1-3}}$ are shown in Table 2. Comparing

Table 2. IR Data for Complexes 1−3 and Calculated TEP Values

	cis-$[MoL_2(CO)_4]$	$[NiL(CO)_3]$ (calc)
PPh_3	2022[25]	2068.9[26]
$\mathbf{L_1}$	2018.1	2067.7
$\mathbf{L_2}$	2015.8	2066.4
$\mathbf{L_3}$	2012.8	2064.6

these values to the TEPs given in Tolman's seminal paper[26] reveals that the TEP for $\mathbf{L_1}$ (2067.7 cm^{-1}) is close to that for $PPh(CH_2Ph)_2$ (2067.6 cm^{-1}), the TEP for $\mathbf{L_2}$ (2066.4 cm^{-1}) is close to that for $P(CH_2Ph)_3$ (2066.4 cm^{-1}), and the TEP for $\mathbf{L_3}$ (2064.6 cm^{-1}) is close to that for PMe_3 (2064.1 cm^{-1}). These comparisons are consistent with the boryl group having a net donating effect on the P akin to that of an alkyl group.

CONCLUSION

It has been shown that the chlorosilane-elimination route developed for azaborinylphosphines[6] can be applied to diazaborinylphosphines. The complete series of mono-, bis-, and tris-diazaborinyl phosphines $\mathbf{L_{1-3}}$, featuring the 14 π-electron, 1,8-diaminonaphthylboronamide heterocycle have been prepared, and each has been characterized by X-ray crystallography. The complexes *cis*-$[Mo(\mathbf{L_{1-3}})(CO)_4]$ have been prepared, and from their IR spectra it is concluded that the diazaborinyl group in $\mathbf{L_{1-3}}$ is as electron-releasing as an alkyl group. Further work is in progress to generalize the chlorosilane route to other BN analogues of arylphosphines and their applications in coordination chemistry and homogeneous catalysis.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all manipulations were carried out under a dry N_2 or argon atmosphere using standard Schlenk line and glovebox techniques. Toluene, *n*-hexane, and dichloromethane were purified by means of a Grubbs-type solvent system, deoxygenated by three successive freeze−pump−thaw cycles, and stored over 4 Å molecular sieves. THF was dried over Na/benzophenone. Deuterated benzene (C_6D_6) and chloroform ($CDCl_3$) were dried over CaH_2 and stored over 4 Å molecular sieves. NMR spectra were acquired on Jeol ECP (Eclipse) 300, Jeol ECS 300, Varian 400-MR, Jeol ECS 400, and Varian VNMRS500 spectrometers. Chemical shifts are referenced relative to high frequency of residual solvent (^1H and ^{13}C), 85% H_3PO_4 (^{31}P), and $BF_3{\cdot}OEt_2$ (^{11}B). Elemental analyses were carried out by the Microanalytical Laboratory at the University of Bristol. Mass spectrometry was carried out by the Mass Spectrometry Service at the University of Bristol. 1,8-diaminonaphthalene, Ph_2PSiMe_3 (containing 5−10% Ph_2PH), and BCl_3 (1 M solution in toluene) were purchased from Sigma-Aldrich and used as received. $P(SiMe_3)_3$ was purchased from Acros Organics and used as received. $ClSiMe_3$ was purchased from Sigma-Aldrich and distilled prior to use. $[Mo(nbd)(CO)_4]$ was prepared by a literature method.[27]

PhP(SiMe$_3$)$_2$. To a stirred solution of $PhPH_2$ (2.0 mL, 2.0 g, 18 mmol) in THF (40 mL), cooled to −78 °C, was added a 1.6 M solution of "BuLi in hexane (23.8 mL, 38.1 mmol) dropwise over 5 min. After complete addition of the "BuLi, extra THF (10 mL) was

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added to the resulting dark suspension to facilitate stirring. After 10 min stirring at −78 °C, the mixture was stirred at RT for 2 h. The mixture was cooled again to −78 °C, $ClSiMe_3$ (5.07 mL, 4.34 g, 40.0 mmol) was added over 10 min, and then the reaction mixture was allowed to warm to ambient temperature with stirring. After 16 h, the solution was filtered by filter cannula, the solvent was removed, and the product was distilled under vacuum (100 °C, 0.05 Torr) to give $PhP(SiMe_3)_2$ as a colorless liquid (3.32 g, 13.0 mmol, 72%). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ −136.9.

Chloroborane **I**. To a solution of 1,8-diaminonaphthalene (2.01 g, 12.7 mmol) in toluene (45 mL) was added a 1 M solution of BCl_3 in toluene (12.7 mL, 12.7 mmol) over 10 min. The reaction mixture was stirred at 80 °C for 16 h. All volatile compounds were then removed in vacuo, and the crude brown product was sublimed (70 °C, 0.05 Torr) to afford chloroborane **I** as off-white crystals (1.03 g, 5.09 mmol, 40%) suitable for X-ray diffraction. $^{11}B\{^1H\}$ NMR ($CDCl_3$, 96 MHz): δ 25.8 (br s). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.16−7.10 (m, 4H, *meta/para* C*H*), 6.35 (dd, 2H, J = 7.0, 1.4 Hz, *ortho* C*H*), 5.74 (br s, 2H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 140.1 (quat. *C*), 136.2 (quat. *C*), 127.6 (*meta/para* CH), 119.1 (quat. *C*), 118.9 (*meta/para* CH), 106.7 (*ortho* CH). High-resolution mass spectrometry (HR-MS) electron impact (EI) m/z calculated for $[C_{10}H_8BClN_2 - HCl]^+$ = 166.0702; obs.: 166.0705. Anal. Found (calcd for $C_{10}H_8BClN_2$): C, 59.01 (59.33), H, 4.00 (3.98), N, 13.63 (13.84)%.

Monoborylphosphine L_1. A solution of $Ph_2P(SiMe_3)$ (173.1 mg, 0.670 mmol) in CH_2Cl_2 (2 mL) was added to a solution of **I** (130 mg, 0.642 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred for 30 min. The volatiles were then removed in vacuo, and the white residue was scraped loose and ground to a fine powder. The powder was washed with hexane (4 × 2 mL) and then dried in vacuo to give $\mathbf{L_1}$ as a white powder (180 mg, 0.511 mmol, 80%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a 3:1 hexane/dichloromethane solution. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz,): δ −58.7 (br s). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ 32.3 (br s). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.52−7.46 (m, 4H, phenyl C*H*), 7.42−7.34 (m, 6H, phenyl), 7.10−7.03 (m, 4H, naphth. *meta/para* C*H*), 6.19 (dd, 2H, J = 6.9, 1.4 Hz, 2H, naphth. *ortho* C*H*), 5.66 (br s, 2H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 140.2 (d, J = 3.8 Hz, quat. *C*), 136.3 (quat. *C*), 134.9 (d, J = 17.8 Hz, phenyl *meta* CH), 134.2 (d, J = 7.5 Hz, quat. *C*), 129.1 (d, J = 7.3 Hz, phenyl *ortho/para* CH), 128.6 (phenyl *ortho/para* CH), 127.6 (naphth. *meta/para* CH), 120.0 (quat. *C*), 118.4 (naphth. *meta/para* CH), 106.2 (naphth. *ortho* CH). Anal. Found (calcd for $C_{22}H_{18}BN_2P$): C, 73.89 (75.03), H, 5.29 (5.15), N, 8.06 (7.95)%. Satisfactory C microanalysis was not obtained, despite several attempts and with crystalline samples;[28] ^1H, ^{13}C, ^{31}P, and ^{11}B NMR spectra are given in the Supporting Information.

Diborylphosphine L_2. A solution of $PhP(SiMe_3)_2$ (121.3 mg, 0.477 mmol, ∼92% pure) in CH_2Cl_2 (1 mL) was added to a solution of **I** (176.3 mg, 0.871 mmol) in CH_2Cl_2 (2 mL). After the solution was stirred at ambient temperature for 16 h, the volatiles were removed in vacuo. The white solid was washed with hexane (2 × 1 mL) and then dried in vacuo to give $\mathbf{L_2}$ as a white powder (184 mg, 0.416 mmol, 96%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a 3:1 hexane/CH_2Cl_2 solution. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ −135.0 (br s). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ 32.4 (br s). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.65 (m, 2H, phenyl *meta* C*H*), 7.43−7.40 (m, 3H, phenyl *ortho/para* C*H*), 7.12−7.05 (m, 8H, naphth. *meta/para* C*H*), 6.28 (dd, 4H, J = 7.2, 1.2 Hz, naphth. *ortho* C*H*), 5.79 (br s, 4H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 140.0 (d, J = 4.1 Hz, quat. *C*), 137.2 (d, J = 15.7 Hz, phenyl *meta* CH), 136.3 (quat. *C*), 130.2 (d, J = 2.0 Hz, quat. *C*), 129.5 (d, J = 7.8 Hz, phenyl *ortho/para* CH), 128.7 (d, J = 1.5 Hz, phenyl *ortho/para* CH), 127.7 (naphth. *meta/para* CH), 119.9 (quat. *C*), 118.6 (s, naphth. *meta/para* CH), 106.4 (naphth. *ortho* CH). Anal. Found (calcd for $C_{26}H_{21}B_2N_4P$): C, 70.55 (70.64), H, 4.84 (4.79), N, 13.04 (12.67)%.

Triborylphosphine L_3. To a solution of $P(SiMe_3)_3$ (79.6 mg, 0.318 mmol) in CH_2Cl_2 (1 mL) was added a solution of **I** (193.0 mg, 0.953 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was inserted into a sealed Young's tube and heated, without stirring, at 40 °C overnight. During this time, a white solid had crystallized. The supernatant was syringed off, and then the product was washed with CH_2Cl_2 (2 × 1 mL) and dried in vacuo to give $\mathbf{L_3}$ as a white crystalline solid (126.7 mg, 0.238 mmol, 75%). The product was soluble in THF. Crystals suitable for X-ray diffraction were obtained by layering a THF solution of $\mathbf{L_3}$ with hexane. $^{31}P\{^1H\}$ NMR (d_8-THF, 202 MHz): δ −236.8 (br s). $^{11}B\{^1H\}$ NMR (d_8-THF, 96 MHz): δ 32.6 (br s). ^1H NMR (d_8-THF, 500 MHz): δ 7.27 (br s, 6H, N*H*), 7.02−6.99 (m, 6H, *meta/para* C*H*), 6.91 (dd, 6H, J = 8.3, 1.0 Hz, *meta/para* C*H*), 6.38 (dd, 6H, J = 7.4, 1.0 Hz, *ortho* C*H*). $^{13}C\{^1H\}$ NMR (d_8-THF, 126 MHz): δ 142.7 (d, J = 4.9 Hz, quat. *C*), 137.6 (quat. *C*), 128.3 (*meta/para* CH), 121.2 (quat. *C*), 118.1 (*meta/para* CH), 106.5 (*ortho* CH). Anal. Found (calcd for $C_{30}H_{24}B_3N_6P$): C, 67.49 (67.74), H, 4.86 (4.55), N, 15.58 (15.80)%.

cis-[Mo(L_1*)$_2$(CO)$_4$] (1)*. A solution of $\mathbf{L_1}$ (34.0 mg, 0.0965 mmol) in CH_2Cl_2 (0.8 mL) was added to a solution of $[Mo(nbd)(CO)_4]$ (14.5 mg, 0.0483 mmol) in CH_2Cl_2 (0.8 mL) and left to stand for 30 min. Hexane (5 mL) was added, and the solution was stored at −20 °C overnight to precipitate the product as a yellow solid. The supernatant was filtered off, and the solid was dried in vacuo to give **1** as a pale yellow powder (31.5 mg, 0.0345 mmol, 71%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a 3:1 hexane/CH_2Cl_2 solution. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ −24.1. $^{11}B\{^1H\}$ NMR ($CDCl_3$, 96 MHz): δ 30.0 (br s). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.52−7.47 (m, 8H, phenyl C*H*), 7.39−7.35 (m, 4H, phenyl C*H*), 7.31−7.27 (m, 8H, phenyl C*H*), 7.03−6.97 (m, 8H, naphth. *meta/para* C*H*), 5.94 (dd, 4H, J = 6.5, 1.9 Hz, napth. *ortho* C*H*), 5.58 (br s, 4H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 215.2 (d, J = 15.0 Hz, *C*O groups trans to phosphines), 210.6 (t, J = 8.1 Hz, CO groups cis to phosphines), 139.4 (d, J = 5.3 Hz, quat. *C*), 136.2 (quat. *C*), 133.89 (d, J = 11.7 Hz, phenyl C*H*), 133.85 (d, J = 31.1 Hz, quat. *C*), 129.7 (phenyl C*H*), 129.1 (d, J = 8.9 Hz, phenyl C*H*), 127.6 (naphth. *meta/para* CH), 120.0 (quat. *C*), 118.9 (naphth. *meta/para* CH), 107.0 (naphth. *ortho* CH). Anal. Found (calcd for $C_{48}H_{36}B_2MoN_4O_4P_2$): C, 63.44 (63.19), H, 4.07 (3.98), N, 6.26 (6.14)%. IR spectrum (CH_2Cl_2): 2018.1 (A_1) and a broad signal with overlapping peaks at 1916, 1904, with a shoulder at ∼1880 cm^{-1}.

cis-[Mo(L_2*)$_2$(CO)$_4$] (2)*. A solution of $\mathbf{L_2}$ (31.3 mg, 0.0708 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of $Mo(nbd)(CO)_4$ (10.6 mg, 0.0354 mmol) in CH_2Cl_2 (0.5 mL). The solution was heated at 40 °C for 1.5 h, after which the volatiles were removed in vacuo to afford **2** as a yellow powder in quantitative yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 122 MHz): δ −111.8 (br s). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 96 MHz): δ 31.7 (br s). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.71 (m, 4H, phenyl C*H*), 7.47−7.43 (m, 2H, phenyl C*H*), 7.37−7.33 (m, 4H, phenyl C*H*), 7.07−7.00 (m, 16H, naphth. *meta/para* C*H*), 6.03 (dd, 8H, J = 7.1, 1.3 Hz, naphth. *ortho* C*H*), 5.81 (br s, 8H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 215.4 (d, J = 13.7 Hz, CO groups trans to phosphines), 210.5 (t, J = 7.1 Hz, CO groups cis to phosphines), 143.5 (quat. *C*), 139.1 (d, J = 4.9 Hz, quat. *C*), 136.2 (quat. *C*), 135.1 (d, J = 10.7 Hz, phenyl CH), 129.88 (d, J = 8.7 Hz, phenyl CH), 129.82 (d, J = 12.0 Hz, phenyl CH), 127.7 (naphth. *meta/para* CH), 120.0 (quat. *C*), 119.3 (naphth. *meta/para* CH), 107.2 (naphth. CH). Anal. Found (calcd for $C_{56}H_{42}B_4MoN_8O_4P_2$): C, 61.47 (61.59), H, 4.12 (3.88), N, 9.76 (10.26)%. IR spectrum (CH_2Cl_2): 2015.8 (A_1) and a broad signal with overlapping peaks at 1916, 1895 and a shoulder at lower frequency.

cis-[Mo(L_3*)$_2$(CO)$_4$] (3)*. A solution of $\mathbf{L_3}$ (23.0 mg, 0.0432 mmol) in THF (0.5 mL) was added to a solution of $Mo(nbd)(CO)_4$ (6.5 mg, 0.022 mmol) in THF (0.5 mL). In situ ^{31}P NMR showed ca. 50% conversion to the desired complex after 10 min. After a further 90 min heating at 60 °C, ca. 80% conversion was observed. The volatiles were removed in vacuo, CH_2Cl_2 (1 mL) was added, and the excess unreacted ligand was precipitated from solution by addition of hexane (∼5 mL). This was removed by filtration, and the product was obtained as a yellow powder (13.6 mg, 0.011 mmol, 49%) following removal of the volatiles in vacuo. $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz): δ −226.2 (br s). $^{11}B\{^1H\}$ NMR (C_6D_6, 96 MHz): δ ∼31 (br s). ^1H NMR (C_6D_6, 500 MHz): δ 6.97 (dd, 12H, J = 8.4, 0.9 Hz, C*H*), 6.80 (dd, 12H, J = 8.4, 7.4 Hz, C*H*), 6.17 (br d, 12H, J = 3.0 Hz, N*H*), 5.76 (dd, 12H, J = 7.4, 0.9 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, partial): δ

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215.7 (d, ~12 Hz, CO groups trans to phosphines), 211.8 (t, J = 6.8 Hz, CO groups cis to phosphines), 128.0 (CH, determined from HSQC data, masked by residual solvent signal), 119.9 (CH), 107.9 (CH). IR spectrum (CH_2Cl_2): 2012.8 (A_1) and a broad signal with overlapping peaks at 1913, 1887 and a shoulder at lower frequency. Complex **3** was not obtained in analytically pure form; ^{1}H, ^{13}C, ^{31}P, and ^{11}B NMR spectra are given in the Supporting Information.

Computational. Calculations were carried out using the Gaussian 03 software package.[29] All structures were optimized at the B3LYP/6-31G(d) level. NICS-1 values were obtained at the B3LYP/6-311+G(2d) level using the GIAO methodology[30] for ghost atoms located 1 Å above the centroids of each ring.

Crystallography. X-ray diffraction experiments on **I**, $\mathbf{L_1}$, $\mathbf{L_2}$, $\mathbf{L_3}$ and **1** were carried out at 100 K on a Bruker APEX II diffractometer using Mo Kα radiation (λ = 0.710 73 Å). Data collections were performed using a CCD area detector from a single crystal mounted on a glass fiber. Intensities were integrated[31] from several series of exposures measuring 0.5° in ω or φ. Absorption corrections were based on equivalent reflections using SADABS.[32] The structures were solved using SHELXS and refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXL.[33] Crystal structure and refinement data are given in the Supporting Information (Table S1). N−H protons were located in the difference map, refined with fixed distances, and assigned fixed isotropic parameters of 1.2 times that of the nitrogen.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data, NMR data for **I**, $\mathbf{L_1}$ and **3**, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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