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Heterocycles

2-(Dimethylamino)phosphinine: A Phosphorus-Containing Aniline Derivative

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In memory of Professor Klaus Koch

***Abstract:** The yet unknown 2-amino-substituted λ^3,σ^2-phosphinines are phosphorus-containing aniline derivatives. Calculations show that the strong interaction of the π-donating NR_2 group with the aromatic system results in a high π-density at the phosphorus atom. We could now synthesize 2-$N(CH_3)_2$-functionalized phosphinines, starting from a 3-$N(CH_3)_2$-substituted 2-pyrone and $(CH_3)_3Si$-C≡P. Their reaction with $CuBr{\cdot}S(CH_3)_2$ affords Cu^I complexes with the first example of a neutral phosphinine acting as a rare bridging μ_2-P-4e donor-ligand between two Cu^I centers. Our experimental and theoretical investigations show that 2-aminophosphinines are missing links in the series of known 2-donor-functionalized phosphinines.*

After the successful synthesis of 2,4,6-triphenylphosphinine by Märkl in 1966 and the parent phosphinine C_5H_5P by Ashe III in 1971, several synthetic routes to access such intriguing aromatic phosphorus heterocycles have been developed.[1] For the use of λ^3,σ^2-phosphinines in more applied research fields, for example, as ligands in catalytically active metal complexes or in photoluminescent coordination compounds, their specific functionalization is particularly important in order to modify their stereoelectronic properties and coordination abilities.

While several polydentate phosphinines have been reported in the literature, additional donor substitution directly in 2-position of the heterocycle is relatively rare. These compounds can be considered as phosphorus-containing derivatives of triarylphosphine, phenol, and thiophenol (Figure 1 **A**, **B**).[2] Heterocycles of type **A** have been successfully used as chelating, small-bite angle diphosphorus ligands in several catalytic reactions.[3] Grützmacher and co-workers have recently accessed sodium salts of phosphinin-2-ols (**B**, E = O) (Figure 1, **C**).[4] While neutral phosphinin-2-ols show both the classical terminal 2e-donation via the lone pair and the less common μ_2-bridging 2e-lone-pair donation (μ_2-P-2e) to Cu^I centers (Figure 1, **D**), the anionic phosphinin-2-olate in **E** acts as a 4e-donor and bridges a cationic $[Au(PPh_3)]^+$ and a neutral [AuCl] fragment (μ_2-P-4e).[5–7,8] This unprecedented bonding mode of the anionic ligand was concluded from the strong coordination shift in the ^{31}P NMR spectrum to much lower frequencies compared to the uncomplexed ligand (strong negative Δ^{coord}),[8] and the significantly elongated PC distance in the complex as compared to the ligand itself.

Taking into account the literature on known donor-functionalized phosphinines **A**–**C**, it seems surprising that the corresponding phosphorus-containing aniline derivatives still remain elusive. Because nitrogen is less electronegative than oxygen, the lone pair at the nitrogen atom in a hypothetical 2-amino-substituted phosphinine should also exert a significant interaction with the π-accepting aromatic system

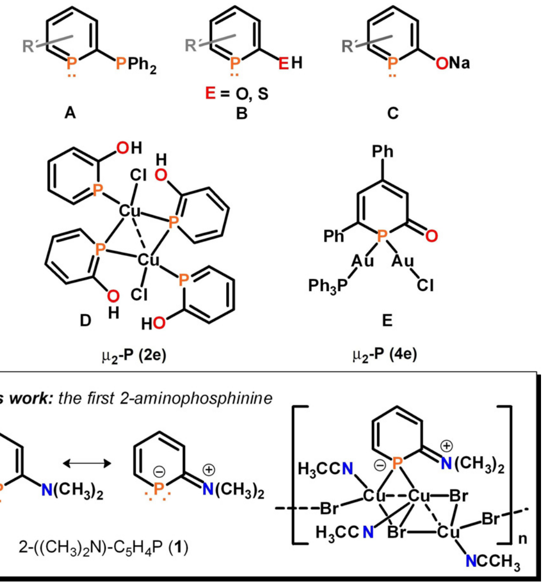

Figure 1. 2-Donor-substituted phosphinines **A**–**C** and selected coordination compounds **D**/**E**, illustrating the μ_2-P-2e and μ_2-P-4e coordination mode.

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of the heterocycle, with pronounced consequences for the coordination chemistry of the resulting P,N-ligand. It therefore appeared intriguing to us to start an investigation on the theoretical properties, the synthesis, and the coordination chemistry of hitherto unknown 2-aminophosphinines.

We first considered an evaluation of the electronic structure of amino-substituted P=C fragments. The π-orbital of a P=C building block is involved in conjugative interactions in a comparable manner to a C=C bond, as shown by the overall matching ionization energies of related P=C- and C=C-based compounds.[9] Accordingly, the aromaticity of phosphinine is similar to that of benzene.[10] While the P=C occupied orbitals show great similarity to the C=C orbitals, the unoccupied orbitals exhibit significant stabilization, rendering P=C units highly efficient π-acceptors as can be seen in the LUMO of the parent phosphinine (vide infra).[11] Consequently, the usual P=C bond polarity (phosphorus is positive) can be tuned significantly by additional π-electron pair donors, such as NR_2 substituents that are directly linked to the unsaturated carbon atom. This results in a 3c–4e interaction with a characteristic high energy orbital and a significant contribution at the phosphorus atom (Figure S1). In this way, an inversely polarized π-system with excess electrons at the phosphorus atom is formed.[12] The most prominent examples have two amino groups at carbon, that are involved in a 6 π-electron delocalization. Accordingly, in case of phosphinidene-imidazole-ylidene, it was shown that the zwitterionic (**F′**) and the P=C double-bonded (**F**) resonance structures have comparable contributions (Figure 2, S2).[13]

As a result, the phosphorus atom in **F**/**F′** is able to complex even two Lewis acids (e.g. boranes).[14] Heinicke et al. observed for the cyclic 1,3-benzazaphosphole **G** that the strong electron donation of a single amino group is sufficient to raise the energy of the polarized P=C bond to such an extent that a π-complex is formed with mercury, rather than the η^1-coordination to the metal center via the in-plane lone pair.[15] Moreover, the formation of polymeric or oligomeric μ_2-complexes with Cu^I or Ag^I were found as well.[16] In case of the 1,3-azaphosphole, the -P=C(*R*)-N∸ unit is incorporated into the aromatic π-system, while in 2-aminophosphinines of type **H** with the same PCN bonding motif, the electron pair of the nitrogen substituent acts externally and, consequently, the 3c–4e system is not entirely involved in the cyclic delocalization.[17] Thus, we were interested to evaluate the degree of interplay between the aromaticity and the polarizing effect of an external and strongly π-donating amino group. We focused primarily on the dimethylamino substituent, as a 2-(dimethylamino)phosphinine ($2\text{-}(CH_3)_2N\text{-}C_5H_4P$, **1**) should be synthetically feasible (vide infra).

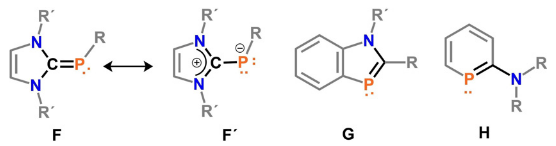


Figure 2. Phosphinidene-imidazole-ylidene system **F**/**F′** with zwitterionic resonance structure, benzazaphosphole **G**, and 2-amino-substituted phosphinine **H**, all having comparable >NC=P bonding motifs.

The B3LYP-D3/cc-pVTZ-optimized geometry shows that the dimethylamino group in **1** is fully planar, in contrast to the pyramidal nitrogen atom in *N*,*N*-dimethylaniline, indicating a strong interaction between the nitrogen lone pair and the π-system. We found that the 6.8 kcal mol^{-1} rotational barrier for the N−C bond in **1** is larger (2.4 kcal mol^{-1}) than in *N*,*N*-dimethylaniline. This can be attributed to the increased π-accepting property of phosphinine compared to benzene. Accordingly, the basicity of **1** is also reduced with respect to *N*,*N*-dimethylaniline, as shown by a decrease of the computed gas-phase basicities (220 vs. 225 kcal mol^{-1}). The interaction is also clearly visualized by the shape of the intrinsic bonding orbital in **1** (Figure S3e).[18] Accordingly, the PC(N) bond in the ring is longer by 0.051 Å with respect to C_5H_5P, while the other PC bond distance remains virtually unchanged (Figure S4). Altogether, these geometric changes result in a small reduction of the Bird index ($I_{6,C_5H_5P} = 96.5$ vs. $I_{6,2\text{-}(CH_3)_2N\text{-}C_5H_4P} = 79.0$). Likewise, the corresponding NICS(1) value changes from −10.2 to −8.9 ppm (Figure S5).[19,20] Thus, while the amino substituent acts polarizing on the neighboring PC bond, the aromaticity in the ring is only marginally decreased.

We further carried out Natural Resonance Theory (NRT) calculations on **1** (Figure 3, S6). Interestingly, it turned out that zwitterionic structures with C=N$^{(+)}$ bonds have a significant contribution of about 16.0 % in total, which exceeds the C=O$^{(+)}$ contribution in the neutral phosphinin-2-ol (8.7 %), while it is smaller than the C=O contribution in the anionic phosphinin-2-olate (40.3 %).[8] The non-ionic aromatic resonance structures contribute with 47.6 %. Again, this value is between the ones found for phosphinin-2-ol and phosphinin-2-olate (69.6 and 33.2 %, respectively).[8] Moreover, two resonance structures show two lone pairs at the phosphorus atom contributing with 12.9 % in total to the electronic ground state, again slightly exceeding the 12.5 % contribution in phosphinin-2-ol.[5,8]

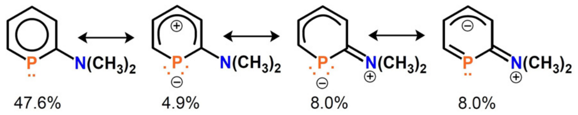


Figure 3. NRT analysis of $2\text{-}(CH_3)_2N\text{-}C_5H_4P$ (**1**).

The Kohn–Sham π-orbitals (Figure 4) show the n(N) contribution of the $(CH_3)_2N$-substituent, increasing the phosphinine HOMO energy (blue) by more than 1 eV, while the energy of the LUMO (green) with a nodal surface at the substituting position increases by 0.3 eV only.

Accordingly, **1** is a much stronger π-donor and somewhat weaker π-acceptor than the parent phosphinine C_5H_5P. The π-orbitals are delocalised throughout the ring, in accordance with the still significant aromaticity of the P-heterocycle (vide supra).[20] While the in-plane phosphorus lone-pair energy for 1-Me-1,3-azaphosphole is at about the same energy as for C_5H_5P (likewise the corresponding ionization energies[21]), the π-type HOMO (again in agreement with the ionization energies) and also the LUMO of the five-membered hetero-

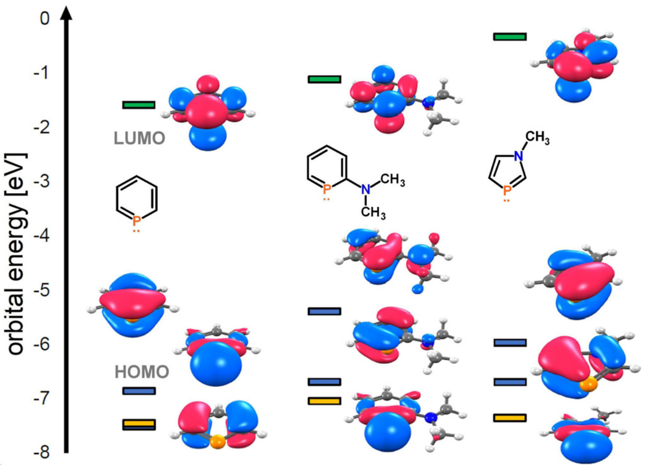


Figure 4. Kohn–Sham orbitals of C_5H_5P, 2-$(CH_3)_2$N-C_5H_4P (**1**), and 1-Me-1,3-azaphosphole. Energy level of the lone pair in yellow.

cycle are at much higher energy than in the six-membered ring, due to the presence of the donor nitrogen lone pair, which is integrated into the π-system. In case of **1**, the HOMO energy is even higher than in 1-Me-1,3-azaphosphole, while the LUMO is at much lower energy. This renders **1** a much "softer" ligand than 1-Me-1,3-azaphosphole.

A comparison of the electrostatic potential (EP) maps of C_6H_6, C_5H_5P, $(CH_3)_2N$-C_6H_5, and **1** reveals additional interesting information (Figure 5). From the top view it is apparent that C_5H_5P exhibits a more positive EP (blue) than benzene at an electron-density isosurface of 0.02 e/au^3, in accordance with its π-electron-accepting property. Amino substitution induces negative charge (red) accumulation in the ring's π-system, nevertheless, in *N*,*N*-dimethylaniline ($(CH_3)_2N$-C_6H_5) nitrogen (lone pair) shows the most negative EP. In case of **1**, however, the ring displays a rather negative EP compared to the substituent nitrogen, in full accordance with the basicity differences of the two compounds discussed above.

From the side view, it is obvious that the red (electron rich) area at the phosphorus atom has some ellipticity in the front part of the parent phosphinine C_5H_5P, in accordance with the high "s"-character of the in-plane lone pair. In case of **1** not only does the electron distribution become more asymmetric (elliptic), but also the negative charge (red color) increases compared to the parent phosphinine owing to the increased π-electron accumulation at the P-atom.

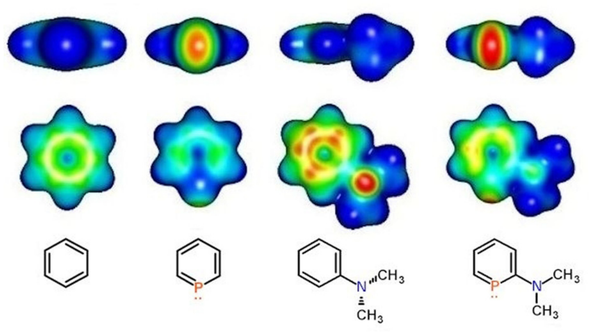
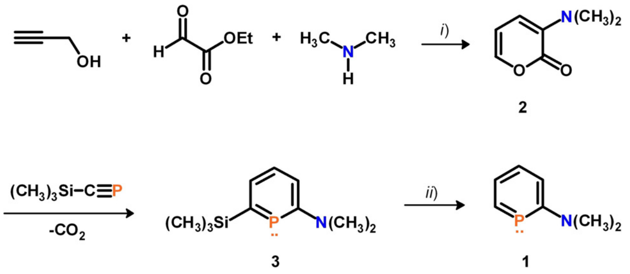


Figure 5. Electrostatic potential maps for C_6H_6, C_5H_5P, $(CH_3)_2N$-C_6H_5, and 2-$(CH_3)_2$N-C_5H_4P (**1**). The electrostatic potential (in a.u.), color-coded from −0.025 (red) to 0.050 (blue), is mapped on electron density isosurfaces of 0.02 e/au^3.

Having demonstrated that the amino group has an even stronger effect on the phosphinine π-system than the OH substituent, and that the perturbation approaches the anionic phosphinin-2-olate derivative, we turned our attention to the synthesis of **1**. We could already show that 3-bromo-2-pyrone reacts selectively with $(CH_3)_3$Si-C≡P to the corresponding 2-bromo-6-Si$(CH_3)_3$-functionalized phosphinine.[22] We thus anticipated that a [4+2] cycloaddition reaction of phosphaalkynes and 3-amino-substituted 2-pyrones might be a suitable synthetic route to access 2-aminophosphinines.[23] Fan and Ma only recently reported on the synthesis of a series of 3-amino-functionalized 2-pyrones.[24] After modification of their experimental procedure, we were able to access the hitherto unknown 3-$(CH_3)_2$N-2-pyrone **2** in reasonable yields (Scheme 1).



Scheme 1. Synthesis of dimethylamino-functionalized 2-pyrone **2**, Si$(CH_3)_3$-substituted 2-(dimethylamino)phosphinine **3** and 2-$(CH_3)_2$N-C_5H_4P **1**. *i*): a) CuBr (0.2 equiv), 3 Å MS, THF, 18 h, b) silica, toluene, 18 h; *ii*): a) HCl·Et_2O (2 M, 4.7 equiv), r.t., 12 h; b) triethylamine (exc.), r.t. 1 h.

2-pyrone **2** indeed undergoes a [4+2] cycloaddition with $(CH_3)_3$Si-C≡P under formation of a single product, according to ^{31}P{^{1}H} NMR spectroscopy (Scheme 1). As we could not find a $^2J_{(P-H)}$ coupling in the corresponding proton-coupled ^{31}P NMR spectrum, which could indicate the formation of a regiosomer with the amino group in 3-position of the phosphorus heterocycle, we were confident that 2-$(CH_3)_2$N-6-Si$(CH_3)_3$-phosphinine **3** had been formed selectively. The preferred formation of **3** over the possible regioisomer 2-Si$(CH_3)_3$-3-$(CH_3)_2$N-phosphinine **3′** could be confirmed by means of DFT calculations. Mainly electronic but also steric effects are responsible for the regioselectivity of this cycloaddition reaction (for details see Figures S7–S9).

Phosphinine **3** shows a resonance in the ^{31}P{^{1}H} NMR spectrum at δ(ppm) = 145.4. This value is very similar to the one found for 2-hydroxy-phosphinine **B** (Figure 1, δ = 149.1 ppm), while 2,4,6-triaryl-phosphinines show a chemical shift at $\delta \approx 190$ ppm in the ^{31}P{^{1}H} NMR spectrum.[1a] This observation is indicative of a pronounced interaction of the strongly π-donating amino group with the aromatic system of the phosphorus heterocycle, in accordance with the calculations. In analogy to our previous findings that 2-Si$(CH_3)_3$-phosphinine undergoes protodesilylation under formation of the parent phosphinine C_5H_5P, compound **3** can easily be converted to 2-$(CH_3)_2N$-C_5H_4P **1** in the presence of $HCl{\cdot}Et_2O$ and subsequent treatment with triethylamine (Scheme 1).[7] Phosphinine **1** represents the first phosphorus-containing *N*,*N*-dimethylaniline derivative and shows a single resonance at $\delta = 126.5$ ppm in the $^{31}P\{^1H\}$ NMR spectrum. This value is close to the calculated ^{31}P NMR shift of 2-phospha-aniline (2-H_2N-C_5H_4P) reported by Alkorta and Elguero ($\delta =$ 130.0 ppm[25]) and again reflects a significant interaction of the strong π-donating $(CH_3)_2N$ group with the π-system of the P-heterocycle. In contrast, the parent phosphinine C_5H_5P shows a chemical shift at $\delta = 206.6$ ppm in the $^{31}P\{^1H\}$ NMR spectrum.[7]

Calculations on Cu^I complexes of **1** further reveal that the phosphorus atom is the preferred coordination site. According to the discussion above, the μ_2-coordination mode should also be possible with more than one metal center (for details, see Figure S10). Therefore, **3** and **1** were reacted with $CuBr{\cdot}S(CH_3)_2$ in dichloromethane to afford single species **4** and [CuBr(**1**)] (that yields **5** in MeCN, see below), which show a resonance at $\delta = 120.6$ ppm, respectively at $\delta = 87.1$ ppm in the $^{31}P\{^1H\}$ NMR spectrum. Crystals of **4**, suitable for X-ray diffraction, could be obtained by slow crystallization from dichloromethane and, in case of **5**, by diffusion of *n*-pentane into a saturated solution of [CuBr(**1**)] in acetonitrile. The crystallographic characterization of **4** reveals the presence of an infinite $(CuBr)_x$ band with the two edges decorated with phosphinine ligands in an alternating manner (Figure 6 and S25).

The most striking feature of the structure of **4** is that the phosphorus atom of each $(CH_3)_2N$-substituted phosphinine bridges two Cu^I centers, in analogy to phosphinin-2-ol and phosphinin-2-olate (vide supra). In contrast, 2-$Si(CH_3)_3$-phosphinine itself forms Br^--bridged dinuclear Cu^I complexes with the classical η^1-P coordination mode of the phosphorus heterocycle upon reaction with $CuBr{\cdot}S(CH_3)_2$.[7] The nitrogen atom of each phosphinine in **4** is perfectly planar ($\Sigma_{C\text{-}N\text{-}C} = 360°$) and the rather short N-C_α bond of 1.331(5) Å indicates a significant N=C double bond character. The P−C_α(N) bond length is with 1.80 Å considerably longer than the average P−C bond in free phosphinines (1.70–1.73 Å) and in **D** (Figure 1, μ_2-P-2e), while it approaches the 1.82 Å found in **E** (μ_2-P-4e).[5,8] Furthermore, the alternation of the C−C bond lengths (between 1.358 and 1.422 Å, standard deviation 0.024 Å) is bracketed by the values found for **D** (μ_2-P-2e, between 1.384 and 1.390 Å, standard deviation 0.002 Å) and **E** (μ_2-P-4e, between 1.336 and 1.483 Å, standard deviation 0.064 Å).[5,8] These structural features indicate a considerable reduction of the aromaticity of the heterocycle **4**, in accordance with the rare bridging μ_2-P-4e coordination mode of the ligand, which is unprecedented for neutral phosphinines. However, the situation might be different in solution, as the coordination chemical shift difference of $\Delta^{coord} = -24.8$ ppm in the $^{31}P\{^1H\}$ NMR spectrum is more in line with the μ_2-P-2e mode, as reported for phosphinin-2-ol.[8] It is noteworthy that for the CuCl and CuBr complexes of 1,3-benzazaphosphole (with the -P=C-N< structural motif) a dynamic equilibrium has been detected between μ_1-P bound complexes in solution, and μ_2-P-2e bound complexes in the solid state.[16b] Thus, it can be expected that also an average ^{31}P NMR signal appears in solutions of **4**.

The solid-state structure of **5**, along with selected bond lengths and distances is depicted in Figure 7. The crystallographic characterization of **5** again reveals the presence of a Cu^I coordination polymer (Figure 6). Since **5** was generated from [CuBr(**1**)] in the presence of acetonitrile during crystallization, the two additional CuBr-moieties in the structure of **5** indicate the dissociation of the initially formed complex [CuBr(**1**)]. However, the NMR-spectroscopic investigation of the crystallization solution of **5** showed only one single resonance in the $^{31}P\{^1H\}$ NMR spectrum with a chemical shift of $\delta = 105.7$ ppm. This can be attributed to **5**, which might again be in a dynamic equilibrium with other

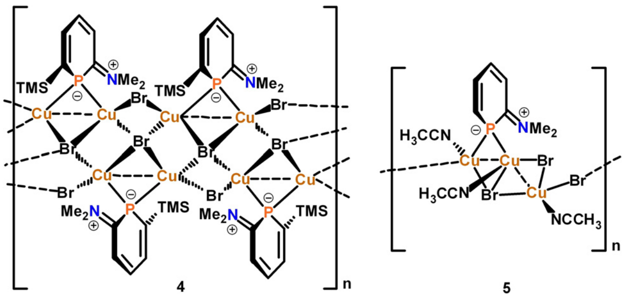


Figure 6. Cu^I coordination polymers **4** and **5**.

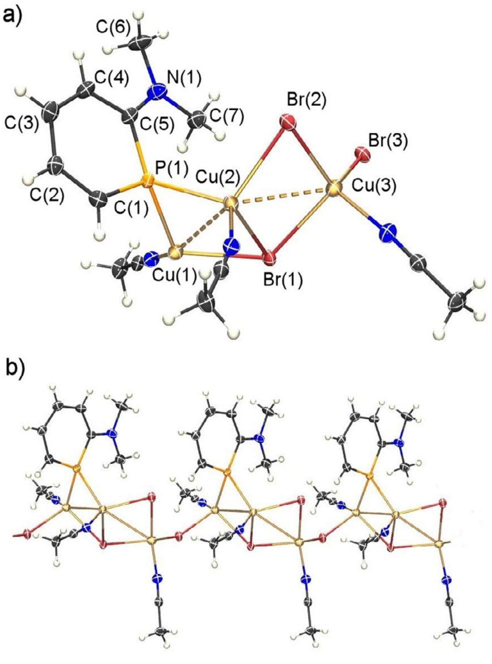


Figure 7. Molecular structure of **5** in the crystal.[27] Displacement ellipsoids are shown at the 50% probability level. a) Asymmetric unit. b) Representation of the infinite coordination polymer. Selected bond lengths [Å] and angles [°]: P(1)–Cu(1) 2.2778(17), P(1)–Cu(2) 2.3028(17), C(1)–C(2) 1.372(8), C(2)–C(3) 1.407(9), C(3)–C(4) 1.388(9); C(4)–C(5) 1.411(8), P(1)–C(5) 1.775(6), P(1)–C(1) 1.729(6), N(1)–C(5): 1.359(8), Cu(1)–Cu(2) 2.6077(10), Cu(2)–Cu(3) 2.9710(11); C(1)-P(1)-C(5) 104.2(3), Cu(1)-P(1)-Cu(2) 69.40(5).

complexes in solution as the resulting coordination chemical shift difference of $\Delta^{coord} = -21$ ppm is again more in line with a μ_2-P-2e coordination mode of the phosphinine.[8]

It should be mentioned that the parent phosphinine C_5H_5P forms infinite coordination polymers with $CuBr{\cdot}S(CH_3)_2$ with the classical terminal 2e-donation via the phosphorus lone pair.[7]

Similar to **4**, the phosphorus atom of each phosphinine ligand in **5** bridges two Cu^I centers of an unusual neutral $[Cu_3Br_3(CH_3CN)_3]$ unit, while the nitrogen atom is again perfectly planar ($\Sigma_{C\text{-}N\text{-}C} = 360°$). The 1.775 Å $P{-}C_\alpha(N)$ bond is longer than the average P−C bond length in free phosphinines (1.70–1.73 Å) but shorter than in **4**. Also the standard deviation of 0.016 Å for the ring C−C distances indicates somewhat less bond length alternation than in case of **4**, which is still considerably larger than observed for **D** (μ_2-P-2e). Thus, the π-system of ligand **1** is involved in the μ_2-P coordination, although this effect is larger in **3**, as shown by the comparison of the $P{-}C_\alpha(N)$ distances and the C−C bond length alternation in **4** and **5**. Clearly, the π-accepting $Si(CH_3)_3$ group facilitates the donation from the nitrogen lone pair of the amino group and increases the π-donor ability of the phosphorus atom. Accordingly, the electrostatic potential map of **3** (Figure S11) reveals a small depletion of the negative charge at the nitrogen atom in **3**, with some increase of negative charge at the phosphorus atom. Altogether, the μ_2-P-4e mode seems to be a general coordination motif of 2-aminophosphinines in the solid state, at least for Cu^I.

Interestingly, the Cu(1)–Cu(2) distance of 2.6077(10) Å suggests that the phosphinine ligand **1** enables cuprophilic interactions.[26] Similar Cu–Cu distances were reported for a Cu^I complex of a μ_2-P-2e coordinating 1,3-benzazaphosphole.[16c] Apparently, the μ_2-P complexation facilitates the close proximity of the Cu atoms.

In summary, we have synthesized the first phosphorus-containing 2-aniline derivatives—2-$(CH_3)_2N$-6-$Si(CH_3)_3$-phosphinine **3** and 2-$(CH_3)_2N$-phosphinine **1**—, starting from 3-(dimethylamino)-2-pyrone **2** and $(CH_3)_3Si{-}C{\equiv}P$. The amino substitution increases significantly the π-electron density at the phosphorus atom in the ring, as shown by the calculated electrostatic potential map of **1**, compared to the parent phosphinine C_5H_5P. Natural Resonance Theory calculations reveal resonance structures with two lone pairs at the phosphorus atom, contributing substantially to the electronic ground state of both **1** and **3**. Accordingly, both **1** and **3** form coordination polymers with $CuBr{\cdot}S(CH_3)_2$ in which the phosphorus atom of the phosphinine heterocycle bridges two Cu^I centers in a rare μ_2-P-4e coordination mode in the solid state, giving the first example for this bonding motif for a neutral substituted phosphinine. Our results show that 2-aminophosphinines are the most powerful neutral π-donating P,N-hybrid ligands, which can form interesting polynuclear coordination compounds. Furthermore, the strength of the π-donation can be further modified by additional substitution. Moreover, these novel phosphorus heterocycles provide a missing link in the series of known 2-donor-functionalized phosphinines. Further studies on the complexes of **1** and **3** with other transition metals are currently underway.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: crystallography · DFT calculations · heterocycles · P,N-ligands · phosphinine

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