Chemistry–A European Journal
Research Article
doi.org/10.1002/chem.202400592
Chemistry Europe
European Chemical Societies Publishing
www.chemeurj.org

Chemoselective Post-Synthesis Modification of Pyridyl-Substituted, Aromatic Phosphorus Heterocycles: Cationic Ligands for Coordination Chemistry

Lea Dettling[+],[a] Martin Papke[+],[a] Moritz J. Ernst,[a] Manuela Weber,[a] and Christian Müller*[a]

Triazaphospholes are potential polydentate ligands due to the presence of both phosphorus and nitrogen donor atoms within the aromatic 5-membered heterocycle. The incorporation of an additional pyridyl-substituent opens up the possibility of a post-synthesis modification *via* chemoselective and also stepwise alkylation exclusively of the nitrogen atoms. This can be controlled by the choice and by the stoichiometry of the electrophile and allows the targeted synthesis of a variety of novel mono- and dicationic ligands. Reaction with Cu(I)-halides causes the formation of cuprates of the type $[CuX_n]^{(n-1)-}$, which enables coordination of the π-acidic phosphorus donor to the negatively charged metal core, which is favored over the coordination by a strongly σ-donating nitrogen atom. The use of cationic triazaphosphole derivatives can be used as a strategy to enforce the coordination of the ligand to an electron rich metal solely *via* the phosphorus atom. However, there is a subtle balance between the formation of either coordination polymers or dimeric structures, as the substitution pattern on the heterocycle and the nature of the halide have a large influence on the coordination motifs formed.

Introduction

According to the isolobal relationship between a trivalent phosphorus atom and a C–H fragment, 3*H*-1,2,3,4-triazaphospholes (**A**, Figure 1) are the phosphorus analogues of the well-known 1,4-disubstituted 1,2,3-triazoles. These $\lambda^3\sigma^2$-phosphorus heterocycles are easily accessible *via* a [3+2] cycloaddition reaction of organic azides and phosphaalkynes, without the need of a catalyst.[1] First synthesized in 1984 by Carrié and Regitz independently,[2] triazaphospholes have recently gained more interest as continued studies, particularly on their coordination chemistry and reactivity, are currently carried out.[3] As ambidentate ligands, triazaphospholes can coordinate to a metal centre either *via* the low-coordinated phosphorus atom or *via* the nitrogen donors N^1 or N^2 (**B**, Figure 1). Since triazaphospholes, just as the aromatic phosphinines, have strong π-accepting properties, a coordination of the phosphorus atom to an electron-rich Pt(0) centre is enabled, as observed by Jones *et al.* (**C**, Figure 1).[4] In addition, the same group also reported on a Ag(I) complex (**D**, Figure 1),[5] in which the heterocycle binds *via* the N^1 atom to the metal centre. The functionalization of a triazaphosphole with a 2-pyridylmethyl-

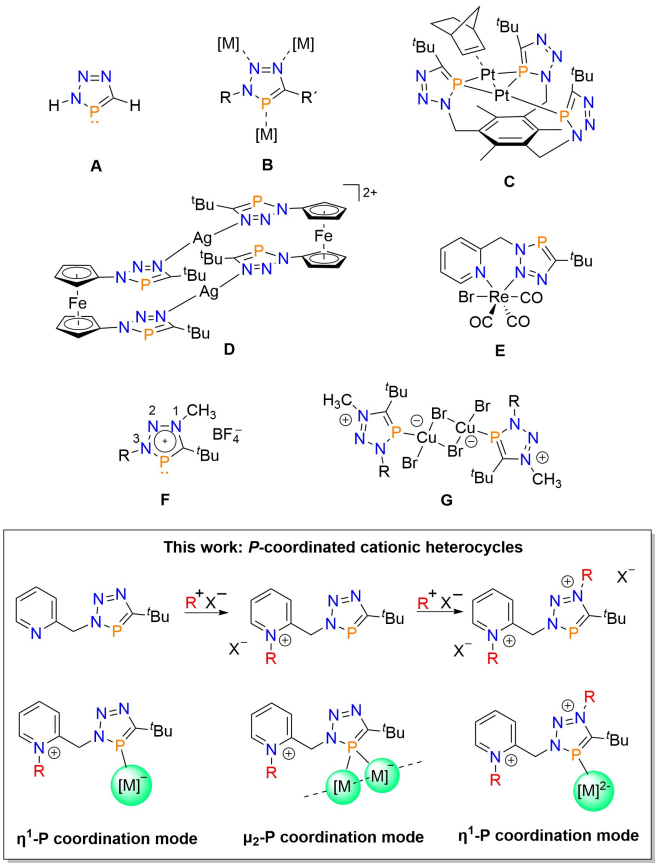


Figure 1. Triazaphosphole **A**, possible coordination modes **B**, triazaphospholenium salt (**F**) and coordination chemistry of triazaphospholes (**C**, **D**, **E**) and of triazaphospholenium salts (**G**).

[a] *M. Sc. L. Dettling,[+] Dr. M. Papke,[+] M. Sc. M. J. Ernst, M. Weber, Prof. Dr. C. Müller*
Freie Universität Berlin
Institut für Chemie und Biochemie
Fabeckstr. 34/36, 14195 Berlin, Germany
E-mail: c.mueller@fu-berlin.de

[+] *These authors have contributed equally.*

Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202400592

group at the 3-position of the heterocycle opens up the possibility of accessing potential chelating ligands.

So far, however, only examples are known in which the triazaphosphole acts as an N,N-chelating ligand, as observed in the octahedral $Re(CO)_3Br$-complex **E** (Figure 1).[6] In this case the bidentate triazaphosphole coordinates *via* N^2 and the pyridine nitrogen donor.

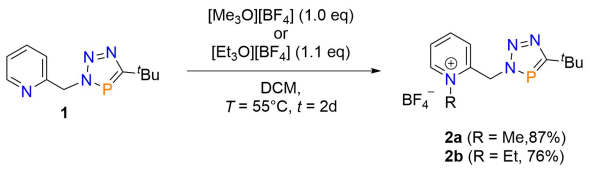
Recently, we reported the successful synthesis of a triazaphospholenium salt by selectively alkylating the N^1-atom of the $\{PCN_3\}$-heterocycle with Meerwein's reagents (**F**, Figure 1, R = benzyl).[7] In accordance with the isolobal principle, the cationic heterocycles can be regarded as phosphorus congeners of the well-known 1,2,3-triazolylidenes, which are also referred to as mesoionic carbenes.[8] In the presence of Cu(I) salts, a neutral coordination compound of type **G** is formed (Figure 1), which is the first example of the coordination chemistry of this new ligand class.[7]

Based on our previous work, we decided to investigate the reactivity of pyridylmethyl-functionalized triazaphospholes with respect to alkylation reactions with electrophiles. We anticipated that the different electron densities at the nitrogen atoms may open up the possibility of a post-synthesis modification, for example a chemoselective and also a stepwise quaternization of the triazaphosphole derivative. This would allow the targeted synthesis of a variety of new cationic ligands, which might show an interesting coordination chemistry (Figure 1).

Results and Discussion

Triazaphosphole **1** (Scheme 1) can be readily synthesized in high yield starting from *tert*-butylphosphaalkyne (^{t}Bu–C≡P) and 2-(azidomethyl)-pyridine.[6] These [3 + 2] cycloaddition reactions between phosphaalkynes and azides are known to proceed regioselectively without a Cu(I) catalyst, as first demonstrated by Rösch and Regitz in 1984.[2] In light of our recently reported successful alkylation of the N^1-atom of benzyl-triazaphosphole **F** (Figure 1; R = benzyl) with Meerwein's salt,[7] compound **1** was reacted with one equivalent of trimethyloxonium tetrafluoroborate ($[Me_3O][BF_4]$) or triethyloxonium tetrafluoroborate ($[Et_3O][BF_4]$), respectively (Scheme 1).

The $^{31}P\{^1H\}$ NMR spectrum of the reaction product **2a** reveals a single resonance at δ(ppm) = 178.4 (**2b**: δ(ppm) = 178.0). The rather small chemical shift difference compared to the starting material (**1**: δ(ppm) = 172.4) is a first indication that the alkylation did not take place at one of the nitrogen atoms of the phosphorus heterocycle, but instead at the pyridine nitrogen atom. Moreover, the ^{1}H NMR spectrum of **2a** show a new singlet resonance in the aliphatic region at δ(ppm) = 4.45 for one additional methyl group, while the ^{1}H NMR spectrum of **2b** displays a quartet resonance at δ(ppm) = 4.85 and a triplet resonance at δ(ppm) = 1.63, as expected for the presence of an ethyl-substituent. Both results indicate a single, selective and quantitative alkylation. The ^{1}H-^{13}C HMBC spectra (SI) of **2a/b** shows $^3J_{C\text{-}H}$ coupling between the carbon atoms of the pyridine ring and the protons of the methyl and ethyl groups, which is clear evidence for the alkylation of the nitrogen atom of the pyridine ring. Compounds **2a/b** were isolated as colourless solids and the molecular structure of **2b** was unambiguously confirmed by means of single crystal X-ray diffraction (Figure 2).



Scheme 1. Formation of the pyridinium-methyl-triazaphospholes **2a** and **2b**.

As expected, the alkylation of the nitrogen donor appears to have little effect on the bond lengths and angles within the molecule, which are comparable to those of the neutral pyridylmethyl-functionalized triazaphosphole derivatives.[6] The five-membered heterocycle is planar and the P(1)–C(1) bond length of 1.7205(12) Å is in-between the one of a P–C single bond (PPh_3: 1.83 Å)[9] and a P=C double bond ((diphenyl-methylene)-(mesityl)phosphane, $MesP{=}CPh_2$: 1.692 Å).[10] The N(1)–P(1)–C(1) angle of 86.33(5)° is close to 90°, which is also typical for neutral triazaphospholes.

The observation that the alkylation with Meerwein's salts takes place selectively at the pyridine nitrogen atom confirms the assumption that the electron density at the pyridine nitrogen atom is higher than that of all nitrogen atoms of the triazaphosphole.[7,8] In fact, a low basicity of the nitrogen atoms in the $\{PCN_3\}$-heterocycle has already been observed in the constitutional 1,2,4,3-isomers of triazaphospholes.[11]

Methyl iodide (MeI) is a frequently used reagent for the alkylation of 1,2,3-triazoles with the aim to access mesoionic carbenes.[12] Thus, reacting an excess of methyl iodide (4.0 eq) with compound **1** in acetonitrile at T = 80 °C leads to the formation of a light-yellow solid in very good yield (92%, Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum again shows a slightly shifted ($\Delta\delta$ = 5.0 ppm) new signal at δ(ppm) = 177.4, which is in the same region as observed for **2a** and **2b**. This indicates again, that the alkylation with MeI only takes place at the pyridine nitrogen atom. Further evidence is provided by the aliphatic region in the ^{1}H NMR spectrum as well as by the

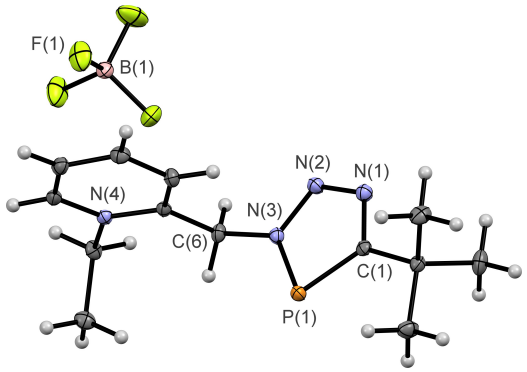
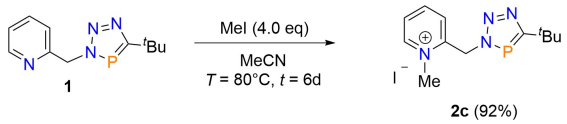


Figure 2. Molecular structure of **2b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angels (°): P(1)–N(3): 1.6908(11), P(1)–C(1): 1.7205(12), N(4)–C(12): 1.4926(15); N(3)–P(1)–C(1): 86.33(5).



Scheme 2. Formation of the pyridinium-methyl-triazaphosphole **2c**.

corresponding ^{1}H-^{13}C HMBC spectrum (Figure S18). We therefore assume that compound **2c** has been formed selectively.

Interestingly, even when using a high excess of methyl iodide, no reaction at one of the nitrogen atoms of the heterocycle was observed. This clearly contrasts the observation that triazoles generally react with MeI. However, it is consistent with the fact that MeI is a much weaker methylating reagent compared to trimethyloxonium tetrafluoroborate and is particularly used for the alkylation of "soft" donor centers.[13]

We therefore anticipated that the alkylation of the nitrogen atom N^{1} of the triazaphosphole, which is considered to show the highest electron density in accordance to the analogous triazoles, might be achieved by adding a second equivalent of Meerwein's salt.[7,14] Thus, 1.1 equivalents of trimethyloxonium tetrafluoroborate, respectively triethyloxonium tetrafluoroborate, were added to a solution of the triazaphosphole **2a** in dichloromethane (Scheme 3). After a reaction time of two days, the ^{31}P{^{1}H} NMR spectra of both reaction mixtures showed the formation of a new resonance with a chemical shift of δ(ppm) = 212.2 (**3a'**) and 210.5 (**3a''**). This is indeed characteristic for alkylated triazaphospholes, the so called triazaphospholenium salts, which were recently reported by us for the first time.[7] Moreover, the aliphatic region in the ^{1}H NMR spectra shows only an additional resonance for the second methyl group (**3a'**: δ(ppm) = 4.49), respectively two resonances for the ethyl group (**3a''**: δ(ppm) = 4.83 (q), 1.63 (t)). A similar reactivity can be observed starting from the ethylpyridinium-triazaphosphole **2b** and trimethyloxonium tetrafluoroborate, yielding the triazaphospholenium salt **3b'**. Remarkably, the yields for the second reaction are as good as for the first alkylation (81 % (**3a'**); 85 % (**3a''**), 89 % (**3b'**), Scheme 3a). A one-step synthesis of **3a'** and **3b''** directly from the **1** is also possible by adding two equivalents of the corresponding Meerwein's salt and extending the reaction time to 4 days (Scheme 3b).

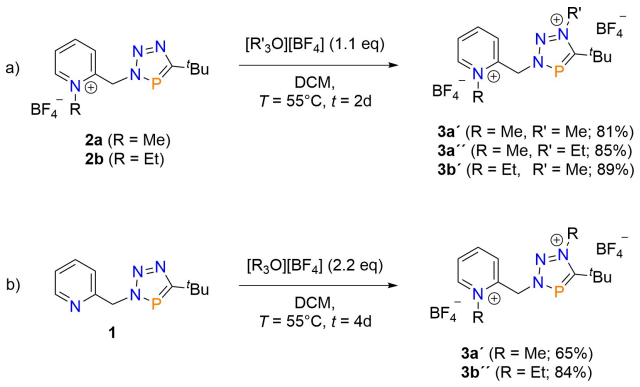
By diffusing dichloromethane into a concentrated solution of **3b''** in acetonitrile afforded single crystals of this compound, suitable for a crystallographic analysis (Figure 3). The solid-state structure of **3b''** clearly shows the presence of the anticipated dicationic heterocycle. Bond angles and lengths in the pyridine moiety are similar to the values found for **2b**. Likewise the bond lengths and angles of the triazaphospholenium ring are similar to the values observed for the benzyl-substituted triazaphospholenium salt (**3b''**: P(1)–C(1): 1.711(3), N(3)–P(1)–C(1): 86.56(16); **F**: P–C: 1.723(2), N–P–C: 86.81(10), Figure 1).[7] The planarity of the heterocycle still suggests a high degree of aromaticity within the phosphorus heterocycle, while the P(1)–C(1) bond length is in-between the one of a single and a double bond.

From these results it can be concluded that the alkylation of the nitrogen atoms in triazaphospholes is chemoselective and can be controlled by the choice of alkylation reagent as well as by the stoichiometry of the alkylation reagent.

We were further interested in exploring the coordination chemistry of the novel monocationic compounds **2** and the dicationic heterocycles **3**. It is apparent that **2** and **3** cannot function as a chelating ligand anymore as observed for 2-pyridylmethyl-functionalized triazaphospholes (**E**, Figure 1).

Consequently, we anticipated that **2a–c** will either coordinate *via* the nitrogen atom N^{1} and N^{2} of the heterocycle or, alternatively, *via* the π-acidic phosphorus donor. In metal complexes containing the dicationic ligands **3**, a coordination should consequently exclusively occur *via* the phosphorus atom, as observed for the benzyl-substituted triazaphospholenium salt **F** (Figure 1).

In analogy to the formation of **G** from **F** (Figure 1), **2a** was reacted with 3.0 equivalents of CuBr·SMe$_2$ in THF (Scheme 4a). The ^{31}P{^{1}H} NMR spectra recorded from the reaction mixture showed a slightly shifted resonance at δ(ppm) = 175.6 when compared to the staring material. Typically, only a marginal shift of the phosphorus resonance is observed upon coordination of a triazaphosphole to Cu(I) *via* the phosphorus atom.[7] After purification and removal of the byproduct CuBF$_4$, the new



Scheme 3. Formation of the pyridinium-methyl-triazaphospholium salts **3a'**, **3a''**, **3b'** and **3b''**.

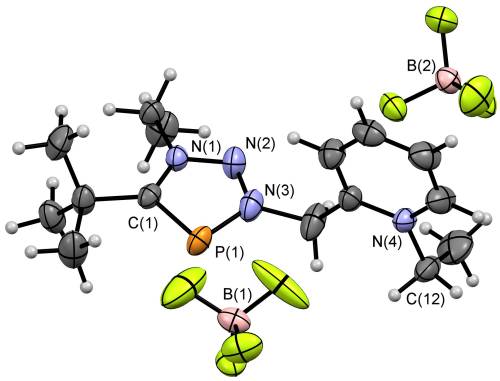
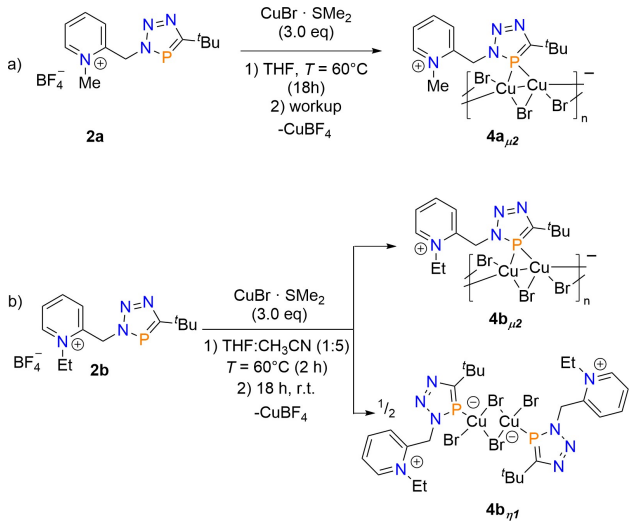


Figure 3. Molecular structure of **3b''** in the crystal. Displacement ellipsoids are shown at the 50 % probability level. Selected bond lengths (Å) and angels (°): P(1)–N(3): 1.698(4), P(1)–C(1): 1.711(3), N(1)–C(14): 1.492(4), N(4)–C(12): 1.507(5); N(3)–P(1)–C(1): 86.56(16).



Scheme 4. Formation of Cu(I) coordination compounds of triazaphospholes **2a** and **2b**.

coordination compounds $\mathbf{4a}_{\mu 2}$ was obtained as yellow solid. Recrystallisation by cooling a saturated solution of $\mathbf{4a}_{\mu 2}$ in acetonitrile to $T = -21\,^{\circ}C$ gave single crystals suitable for an X-ray crystal structure analysis. Recrystallisation from acetonitrile is, however, problematic as the products tend to decompose after some time under formation of $[Cu(CH_3CN)_4]BF_4$. Interestingly, the solid state structure of $\mathbf{4a}_{\mu 2}$ (Figure 4a) shows the formation of the neutral Cu(I) complex $[LCu_2Br_3]$, consisting of the cationic ligand L^+ and the cuprate $[Cu_2Br_3]^-$. The phosphorus atom bridges two different Cu(I) centres (Cu(1), Cu(2)) in a μ_2-P coordination mode. One bromido ligand acts as an additional bridging ligand for the two copper centres (Br(3)), while the two remaining bromido ligands (Br(1), (Br(2)) bridge

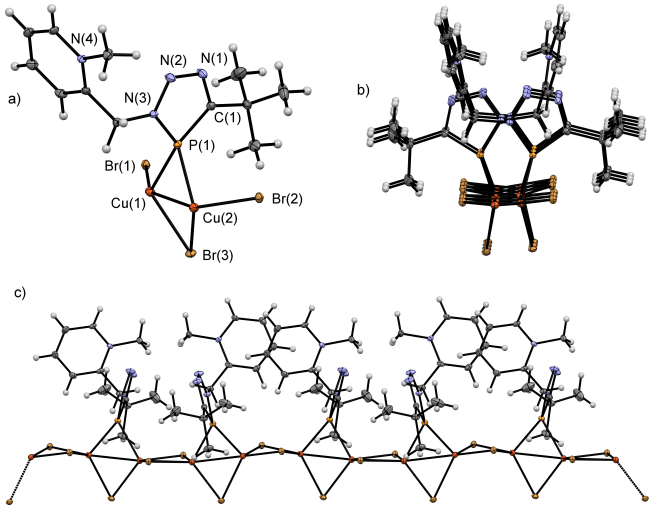


Figure 4. Molecular structure of $\mathbf{4a}_{\mu 2}$ in the crystal. Displacement ellipsoids are shown at the 50% probability level The solvent molecule (CH_3CN) is omitted for clarity. Selected bond lengths (Å) and angels (°): P(1)–N(3): 1.686(3), P(1)–C(1): 1.720(3), Cu(1)–P(1): 2.2476(9), Cu(2)–P(1): 2.3065(9), Cu(1)–Cu(2): 2.5499(6); N(3)–P(1)–C(1): 87.56(15), C(1)–P(1)–Cu(1): 135.26(12), Cu(1)–P(1)–Cu(2): 68.09(3).

$[LCu_2Br_3]$ units, forming a coordination polymer. Bond lengths of P(1)–Cu(1) = 2.2476(9) Å and P(1)–Cu(2) = 2.3065(9) Å are observed, while the Cu···Cu distance of 2.5499(6) Å is slightly shorter than the van der Waals distance $d(Cu, Cu)_{VDW} = 2.80$ Å.[15] The five-membered heterocycle is still planar and shows comparable bond lengths and angles with compound **2a**.

It should be mentioned here that the bridging μ_2-P coordination mode is common for low-coordinate phosphorus compounds. However, it has rarely been observed for triazaphospholes. To the best of our knowledge, only one example has been reported in literature, in which the heterocycle coordinates *via* the phosphorus atom in a bridging μ_2-P coordination mode to a metal centre (**C**, Figure 1, electron rich Pt(0) centre).[4]

However, when the reaction mixture of **2b** and $CuBr{\cdot}SMe_2$ was not worked up as described above for **2a** and $\mathbf{4a}_{\mu 2}$, two distinctive sets of crystals were directly formed from the solution at room temperature overnight. The X-ray crystallographic analysis of the yellow plates reveals a polymeric structure analogous to the one found for $\mathbf{4a}_{\mu 2}$, which is the coordination polymer $\mathbf{4b}_{\mu 2}$ (Scheme 4b, Table S4). On the other hand, the X-ray crystallographic analysis of the yellow blocks shows that a neutral Cu(I) dimer of the type $[LCu_2Br_4]$ ($\mathbf{4b}_{\eta 1}$) has been formed additionally, which is not surprising for coordination compounds of copper halides (Scheme 4b, Figure 5).[17b] In comparison to $\mathbf{4b}_{\mu 2}$ the phosphorus atoms in $\mathbf{4b}_{\eta 1}$ (P(1)) only coordinate to one copper centre(Cu(1)) of the $[Cu_2Br_4]^{2-}$ core in an η^1 coordination mode (P(1)–Cu(1) = 2.2300(5) Å. Compared to the neutral Cu(I) dimer **G** (Figure 1), formed from the benzyl substituted triazaphospholenium salt and $CuBr{\cdot}SMe_2$ (P(1)–Cu(1): 2.5251(5)), this bond is significantly shorter, suggesting a stronger P–Cu bond interaction in $\mathbf{4b}_{\eta 1}$.

Having synthesized the pyridinium-iodide **2c** (Scheme 2), we anticipated that this compound can directly be converted with $CuI{\cdot}SMe_2$ to the corresponding coordination compound, without formation of $CuBF_4$ as byproduct (Scheme 5). When reacting **2c** with a slight excess of $CuI{\cdot}SMe_2$, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows a single signal at

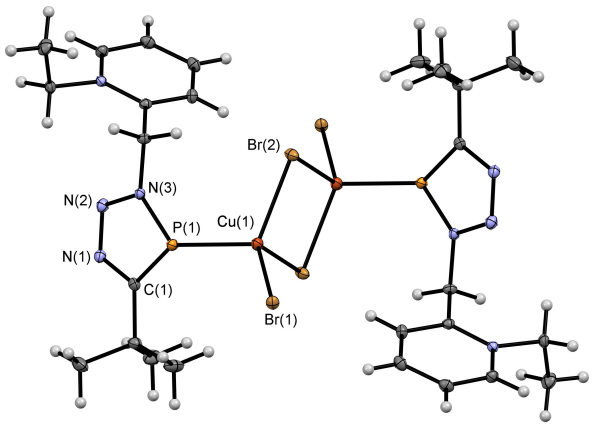
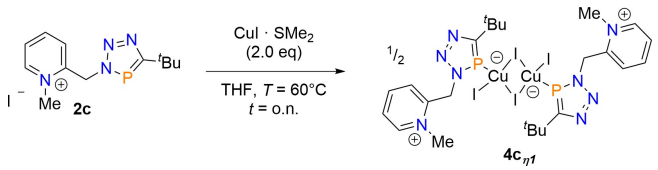


Figure 5. Molecular structure of $\mathbf{4b}_{\eta 1}$ in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angels (°): $\mathbf{4b}_{\eta 1}$: P(1)–N(3): 1.6931(13), P(1)–C(1): 1.7258(15), Cu(1)–P(1): 2.2300(5); N(1)–P(1)–C(1): 86.61(7), Br(1)–Cu(1)–P(1): 108.350(16).



Scheme 5. Formation of copper(I) compound of triazaphsophole **2c**.

δ(ppm) = 170.8, which is slightly shifted compared to the free ligand (**2c**: δ(ppm) = 177.4).

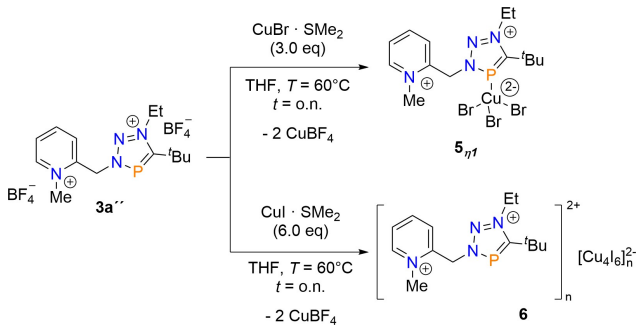
The crystallographic characterization of $\mathbf{4c}_{\eta 1}$ revealed, that indeed a dimer of the type $[L_2Cu_2I_4]$ had been formed, which is isostructural to $\mathbf{4b}_{\eta 1}$ (Figure 6). Surprisingly, the use of CuI·SMe_2 instead of CuBr·SMe_2 has little effect on the structural parameter.

The phosphorus atom P(1) coordinates to the Cu(1) centre in an η^1 fashion, while the P(1)–Cu(1) bond length is only slightly shorter than in $\mathbf{4b}_{\eta 1}$ ($\mathbf{4c}_{\eta 1}$: 2.2382(6) Å; $\mathbf{4b}_{\eta 1}$: 2.2300(5) Å). The trizaphosphole heterocycle is again planar and shows bond lengths and angles comparable to the ones observed in ligand **2c**.

Interestingly, in all coordination compounds described above, no coordination *via* one of the nitrogen atoms of the triazaphosphole ring is observed. This renders these compounds to one of the very few examples in which the coordination of the triazaphosphole heterocycle occurs *via* the π-acidic phosphorus atom. To the best of our knowledge, **4a–c** are the first Cu(I) complexes containing a triazaphosphole ligand with either a μ_2-P or an η^1 coordination mode. Our results demonstrate, that the use of cationic triazaphospholes can thus be used as a strategy to enforce the coordination of the triazaphosphole to an electron rich metal *via* the phosphorus atom. As cuprates of the type $[CuX_n]^{(n-1)-}$ are formed, the coordination of the π-acidic phosphorus donor to the cuprate core is evidently favored over the coordination of a strongly σ-donating nitrogen atom.

Having explored the coordination chemistry of the monocationic heterocycles in the salts **2a–c** in detail, we turned our attention to the reaction of the dicationic systems **3a'**–**3b"** with CuBr·SMe_2. We chose for using 3 equivalents of the Cu(I) precursor to allow the formation of two equivalents of $CuBF_4$ as a byproduct and to enforce the generation of a mononuclear compound containing a $[CuBr_3]^{2-}$ core. Dissolving **3a'** in dichloromethane or THF turned out to be difficult, and the presumed product precipitated out of solution as an orange-coloured solid. The NMR spectroscopic characterization of this compound in CD_3CN showed only decomposition of the ligand. However, using **3a"** as a starting material proved to be more straightforward (Scheme 6). Even though the NMR spectroscopic characterization of the product **5** turned out to be difficult due to solubility reasons, we were able to obtain single crystals of $\mathbf{5}_{\eta 1}$, suitable for crystallographic characterization, from a mixture of THF:CH_3CN (5:1). The molecular structure of $\mathbf{5}_{\eta 1}$ in the crystal and the corresponding structural parameters are depicted in Figure 7.

As proposed from the stoichiometry of the reagents used, the solid state structure of $\mathbf{5}_{\eta 1}$ reveals that a neutral mononuclear Cu(I) complex has indeed been formed, that shows that the phosphorus atom of the dicationic ligand coordinates in an η^1-fashion to a $[CuBr_3]^{2-}$ core.



Scheme 6. Formation of Cu(I) compound of triazaphospholenium salts **3a"**.

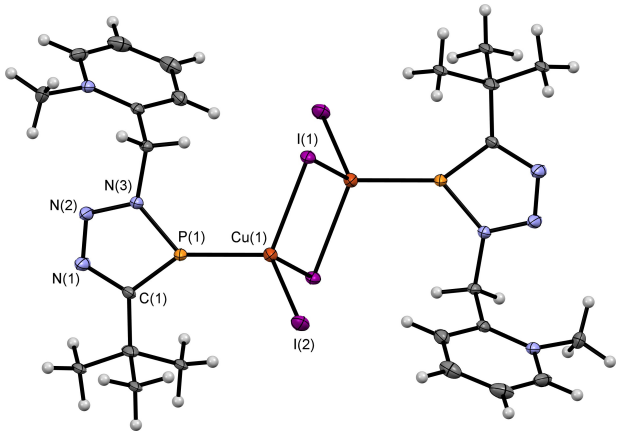


Figure 6. Molecular structure of $\mathbf{4c}_{\eta 1}$ in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angels (°): P(1)–N(3): 1.6816(19), P(1)–C(1): 1.725(2), Cu(1)–P(1): 2.2382(6); N(3)–P(1)–C(1): 87.11(10), I(2)–Cu(1)–P(1): 111.55(2).

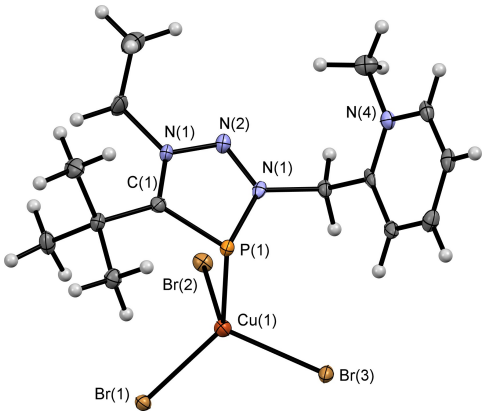


Figure 7. Molecular structure of $\mathbf{5}_{\eta 1}$ in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angels (°): P(1)–N(1): 1.703(4), P(1)–C(1): 1.730(5), Cu(1)–P(1): 2.4692(14); N(1)–P-(1)–C(1): 86.4(2), N(1)–P(1)–Cu(1): 96.48(14).

The triazaphospholenium heterocycle is planar, indicating that the aromaticity of the ligand is not disturbed. Nevertheless, the bonding situation in $\mathbf{5}_{\eta 1}$ deserves special attention, as the phosphorus atom adopts a pyramidal geometry and the Cu(I) is located below the plane of the heterocycle (N(1)–P(1)–Cu(1): 96.48(14)°). The P(1)–Cu(1) bond is with 2.4692(14) Å longer than observed in complexes $\mathbf{4a}_{\mu 2}$ (Cu(2)–P(1): 2.3065(9)) and $\mathbf{4b}_{\eta 1}$ (Cu(1)–P(1): 2.2300(5)) but shorter than the sum of the van der Waals radii of a phosphorus and a copper atom.[15] This arrangement is similar to the bonding situation observed in the previously reported Cu(I) complex of the benzyl substituted triazaphospholenium salt **G** (Figure 1). We therefore anticipate, that also in this case, the bonding situation in $\mathbf{5}_{\eta 1}$ can be described as an "inverse-dative" M→L donor-acceptor bond. Such a bonding situation has also been observed in Cu(I) coordination compounds of *N*-heterocyclic phosphenium cations.[15]

Furthermore, the reaction of CuI·SMe_2 with compound **3a"** afforded an orange solid (Scheme 6). The better solubility of the product compared to the $\mathbf{5}_{\eta 1}$ allowed for an NMR spectroscopic investigation. A new resonance in the $^{31}P\{^1H\}$ NMR spectrum of **6** was observed at δ(ppm) = 206.5 (**3a"**: δ(ppm) = 210.5). Single crystals suitable for a crystallographic characterization were obtained by cooling a saturated solution of **6** in acetonitrile to $T = -21$ °C. Surprisingly, the structural analysis of **6** reveals the presence of an ion pair in the asymmetric unit between the dicationic ligand and a $[Cu_4I_6]^{2-}$ core with no direct coordination of the phosphorus atom P(1) to one of the Cu(I)-ions (Figure 8).

Moreover, the dicationic ligands are located between parallelly oriented polymeric ribbons of the anions. This structural motif is one of the very few examples known in literature.[16] Taking a closer look at the infinite $[Cu_4I_6]^{2-}{}_n$ polymer, it consists of edge-shared $[Cu_2I_2]$ rhombohedrons with the copper atoms of every second rhombohedron being bridged by an additional iodido ligand. The bridging iodide anion conveys the copper atoms in proximity, changing the distance between the copper atoms from Cu(1)–$Cu(2)_{nonbridged}$: 2.6985(10) to Cu(2)–$Cu(3)_{bridged}$: 2.5083(9). This is in accordance with literature reports on the formation of this type of $[Cu_4I_6]_n$ polymers.[17]

Lastly, CuBr·SMe_2 was added to **3b"** yielding $\mathbf{7}_{\eta 1}$ as an orange solid (Scheme 7).

The $^{31}P\{^1H\}$ NMR spectrum of $\mathbf{7}_{\eta 1}$ shows the formation of a new species with a resonance at δ(ppm) = 200.9 (**3b"**: δ(ppm) = 210.1). Single crystals of $\mathbf{7}_{\eta 1}$, suitable for a crystallographic characterization, were obtained from an acetonitrile solution. In the solid state, $\mathbf{7}_{\eta 1}$ shows a polymeric zigzag chain of $[CuBr_2]$ units, while the coordination sphere of each Cu(I) centre is completed by a dicationic ligand, which is η^1-coordinated *via* the π-acidic phosphorus atom P(1), and an additional bromido ligand. The remaining $[BF_4]^-$ anion completes the structure of $\mathbf{7}_{\eta 1}$ (Figure 9). The ^{19}F and ^{11}B NMR spectra also confirm the presence of the $[BF_4]^-$ counterion.

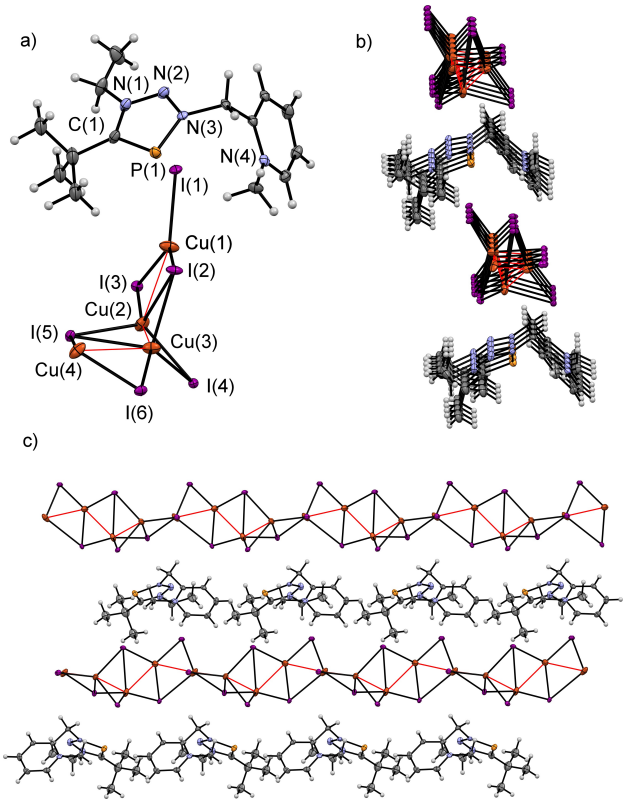
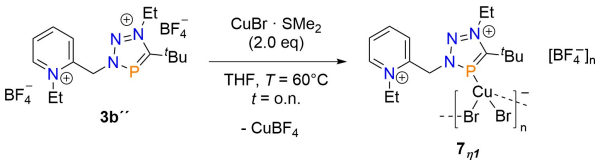


Figure 8. Molecular structure of **6** in the crystal. Displacement ellipsoids are shown at the 50 % probability level. Selected bond lengths (Å) and angels (°): P(1)–N(3): 1.698(4), P(1)–C(1): 1.716(5), Cu(1)–Cu(2): 2.6985(10)Cu(2)–Cu-u(3): 2.5083(9) ; N(1)–P(1)–C(1): 87.1(2).



Scheme 7. Formation of copper(I) compound of triazaphospholenium salts **3b"**.

Conclusions

We could demonstrate that pyridyl-functionalized triazaphospholes provide the possibility for a post-synthesis modification, affording a variety of mono- and dicationic species. This is achieved by a chemoselective and stepwise alkylation exclusively of the nitrogen atoms and can be controlled by the choice and by the stoichiometry of the used electrophile. This targeted synthesis opens up a fascinating coordination chemistry, as the reaction of the charged triazaphosphole derivatives with Cu(I)-halides causes the formation of cuprates of the type $[CuX_n]^{(n-1)-}$. Monocationic triazaphosphole derivatives from either coordination polymers containing $[Cu_2Br_3]^-$ cores, or dimeric structures with $[Cu_2Br_4]^{2-}$, respectively $[Cu_2I_4]^{2-}$ units. Dicationic triazaphospholenium salts, on the other hand, form mononuclear species containing a $[CuBr_3]^{2-}$ fragment, coordination polymers consisting of infinite *P*-coordinated

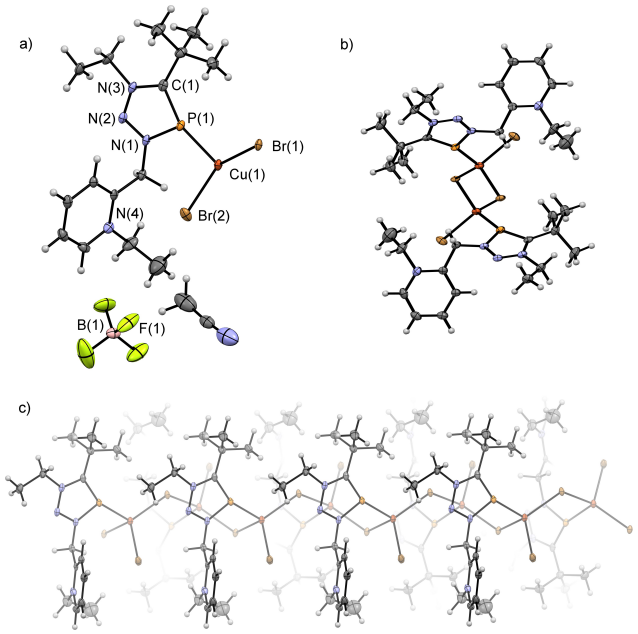


Figure 9. Molecular structure of $\mathbf{7}_{\eta 1}$ in the crystal. Displacement ellipsoids are shown at the 50% probability level. The BF_4 anion and a CH_3CN molecule is omitted for clarity in b) and c). Selected bond lengths (Å) and angels (°): P(1)–N(1): 1.688(3), P(1)–C(1): 1.718(3), Cu(1)–P(1): 2.2088(9), N(1)–P(1)–C(1): 87.57(14).

$[CuBr_2]^-$ chains with integrated $[BF_4]^-$ ions, as well as cuprates with no direct coordination of the ligand to the polymeric $[Cu_4I_6]^{2-}{}_n$ chain. The substitution pattern on the heterocycle and the nature of the halide have a large influence on the coordination motifs formed and, consequently, there is a subtle balance between the formation of either coordination polymers or dimeric structures. In case of a direct Ligand-Cu interaction, the coordination of the ligand to the negatively charged metal core takes exclusively place *via* the π-acidic phosphorus donor, which is apparently favoured over the interaction *via* a strongly σ-donating nitrogen atom. Consequently, the use of cationic triazaphosphole derivatives can be used as a strategy to enforce the coordination of the ligand to an electron rich metal solely *via* the phosphorus atom, thus enabling the access to new coordination compounds of five-membered, aromatic phosphorus heterocycles.

Experimental Section

General Remarks

All reactions were preformed using an MBRAUN glovebox under an argon atmosphere or standard Schlenk techniques. All common solvents and chemicals were commercially available. 2-(Azidomethyl)pyridine,[18] (2,2-Dimethylpropylidyn)phosphan and (*tert*-butylphosphaalkyne)[19] were prepared by methods described in the literature. The temperatures reported are oil bath temperatures. Commercially available chemicals were used without further purification. DCM, MeCN and *n*-pentane were prepared using an MBRAUN Solvent Purification System MB-SPS 800. THF was dried over K/benzophenone under argon and Et_2O was dried over Na under argon. ESIMS spectra were recorded on an Agilent 6210 ESI-TOF (4 kV) from Agilent Technologies. EI measurements were conducted with a modified device of a MAT 711 from Varian MAT. The intensities for the X-ray determinations were collected on a D8 Venture, Bruker Photon CMOS diffractometer with Mo/Kα or Cu/Kα radiation.[20] Semi-empirical or numerical absorption corrections were carried out by the SADABS or X-RED32 programs[21] Structure 535 solution and refinement were performed with the SHELX programs[22] included in OLEX2.[23] Hydrogen atoms were calculated for the idealized positions and treated with the 'riding model' option of SHELXL. Since some of the compounds crystallized together with disordered solvent molecules (partially close to special positions), the refinements of such structures were undertaken with the removal of the disordered solvent molecules using the solvent mask option of OLEX2. The representation of molecular structures was done using the Mercury 3.0 (2022).[24] Deposition Numbers https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/chem.202400592 2331037 (for **2b**), 2331035 (for **3b''**), 2331040 (for $\mathbf{4a}_{\mu 2}$), 2331042 (for $\mathbf{4b}_{\mu 2}$), 2331036 (for $\mathbf{4b}_{\eta 1}$), 2331038 (for $\mathbf{4c}_{\eta 1}$), 2331034 (for $\mathbf{5}_{\eta 1}$), 2331041 (for **6**), 2331039 (for $\mathbf{7}_{\eta 1}$) 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 http://www.ccdc.cam.ac.uk/structures. Details of the X-ray structure determinations and refinements are provided in Table S1–S9.

2-((5-(tert-Butyl)-3H-1,2,3,4-triazaphosphol-3-yl)methyl)pyridine (1)[6]

Triazaphosphole **1** was synthesized by condensing an excess of *tert*-butylphosphaalkyne into a solution of 2-(azidomethyl)pyridine (1.31 g, 9.75 mmol) in 60 mL THF. After stirring the reaction mixture for 12 hours at room temperature excess of the phosphaalkyne together with THF was condensed out of the reaction solution leaving an off white solid. Purification of the crude product was carried out by recrystallization from *n*-pentane. **1** was obtained as a colourless solid (1.97 g, 84%). **^{1}H NMR** (400 MHz, DCM-d_2): δ = 8.60–8.53 (m, 1H, H_{Ar}), 7.69 (t, J = 7.7 Hz, 1H, H_{Ar}), 7.29–7.17 (m, 2H, H_{Ar}), 5.82 (d, J = 6.8 Hz, 2H, methylen), 1.44 (s, 9H, C(CH3)3) ppm.**^{31}P{^{1}H} NMR** (162 MHz, DCM-d_2): δ = 172.4 ppm.

2-((5-(tert-butyl)-3H-1,2,3,4-triazaphosphol-3-yl)methyl)-1-methyl-pyridin-1-ium tetrafluoroborate (2a)

1 (385 mg, 1.64 mmol) and trimethyloxonium tetrafluoroborate (243 mg, 1.64 mmol) were added in a Schlenk flask and dissolved in DCM (10 mL). The reaction mixture was stirred at T = 55 °C for two days. Removal of the solvent in vacuum gave an off white solid. Washing of the solid with diethyl ether (3×10 mL) and subsequent drying in vacuum yielded **2a** (483 mg, 87%) as a colorless solid. **^{1}H NMR** (400 MHz, DCM-d_2): = 8.79 (d, J = 6.1 Hz, 1H, *H*Ar), 8.37 (t, J = 8.2 Hz, 1H, *H*Ar), 7.92 (t, J = 7.0 Hz, 1H, *H*Ar), 7.34 (d, J = 8.0 Hz, 1H, *H*Ar), 6.20 (d, J = 5.3 Hz, 2H, methylen), 4.45 (s, 3H, N-C*H*3), 1.43 (s, 9H, C(CH_3)$_3$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, DCM-d_2): δ = 200.4 (d, J = 57.6 Hz, C=P), 153.5 (CAr), 147.8 (CAr), 146.7 (CAr), 128.0 (CAr), 128.0 (CAr), 51.5 (d, J = 14.7 Hz, methylen), 46.7 (N-CH_3), 35.8 (d, J = 15.3 Hz, *C*(CH3)3), 31.7 (d, J = 7.7 Hz, C(CH_3)$_3$) ppm. **^{31}P{^{1}H} NMR** (162 MHz, DCM-d_2): δ = 178.4 ppm. **^{19}F NMR** (377 MHz, DCM-d_2): δ = −151.3 ppm. **^{11}B NMR** (129 MHz, DCM-d_2): δ = −1.3 ppm. **ESI-TOF** (m/z): 249.1295 g/mol (calculated: 249.1246 g/mol) $[M]^+$).

2-((5-(tert-Butyl)-3H-1,2,3,4-triazaphosphol-3-yl)methyl)-1-ethyl-pyridin-1-ium tetrafluoroborate (2 b)

1 (171 mg, 0.73 mmol) and triethyloxonium tetrafluoroborate (153 mg, 0.80 mmol) were added in a Schlenk flask and dissolved in DCM (5 mL). The reaction mixture was stirred at $T = 55\,^{\circ}C$ for two days. Removal of the solvent in vacuum gave an off white solid. Washing of the solid with diethyl ether (3×10 mL) and subsequent drying in vacuum yielded **2 b** (195 mg, 76%) as a colorless solid. **^{1}H NMR** (400 MHz, DCM-d_2): $\delta = 8.86$ (dd, $J = 6.2$, 1.2 Hz, 1H, *H*Ar), 8.41 (td, $J = 7.9$, 1.4 Hz, 1H, *H*Ar), 8.02 (ddd, $J = 7.7$, 6.3, 1.5 Hz, 1H, *H*Ar), 7.53 (d, $J = 8.0$ Hz, 1H, *H*Ar), 6.23 (d, $J = 5.2$ Hz, 2H, methylen), 4.82 (q, $J = 7.3$ Hz, 2H, CH_2CH_3), 1.60 (t, $J = 7.3$ Hz, 3H, CH_2CH_3), 1.45 (d, $J = 1.4$ Hz, 9H, C(*CH*3)3) ppm. **^{13}C{^{1}H} NMR** (101 MHz, DCM-d_2): $\delta =$ 200.4 (d, $J = 57.6$ Hz, C=P), 152.7 (CAr), 146.7 (CAr), 146.4 (CAr), 129.4 (CAr), 128.7 (CAr), 54.9 (CH_2CH_3), 51.3 (d, $J = 14.9$ Hz, methylen), 36.0 (d, $J = 15.4$ Hz, $C(CH_3)_3$), 31.7 (d, $J = 7.6$ Hz, $C(CH_3)_3$), 16.1 (CH_2CH_3) ppm. **^{31}P{^{1}H} NMR** (162 MHz, DCM-d_2): $\delta = 178.0$ ppm. **^{19}F NMR** (377 MHz, DCM-d_2): $\delta = -152.1$ ppm. **^{11}B NMR** (129 MHz, DCM-d_2): $\delta = -1.3$ ppm. ESI-TOF (m/z): 263.1432 g/mol (calculated: 263.1420 g/mol) $[M]^+$).

2-((5-(tert-butyl)-3H-1,2,3,4-triazaphosphol-3-yl)methyl)-1-methyl-pyridin-1-ium iodide (2 c)

1 (217 mg, 0.93 mmol) was dissolved in MeCN (15 mL) and methyl iodide (526 mg, 3.71 mmol) was added. The reaction mixture was stirred at $T = 80\,^{\circ}C$ for six days, then cooled to room temperature and the solvent was removed *in vacuo*. Washing of the solid with diethyl ether (3 x 10 mL) and subsequent drying in vacuum yielded **2 c** (345 mg, 92%) as a slightly yellow solid. **^{1}H NMR** (400 MHz, MeCN-d_3): $\delta = 8.78$ (ddt, $J = 6.2$, 1.5, 0.7 Hz, 1H, H_{Ar}), 8.42 (td, $J = 8.0$, 1.5 Hz, 1H, H_{Ar}), 7.95 (ddd, $J = 7.8$, 6.1, 1.5 Hz, 1H, H_{Ar}), 7.34 (d, $J =$ 7.8 Hz, 1H, H_{Ar}), 6.26 (d, $J = 5.6$ Hz, 2H, methylen), 4.38 (s, 3H, Py-CH_3), 1.47 (d, $J = 1.5$ Hz, 9H,$C(CH_3)_3$) ppm. **^{13}C{^{1}H NMR** (101 MHz, MeCN-d_3): $\delta = 200.3$ (d, $J = 56.8$ Hz, C=P), 154.3 (C_{Ar}), 148.1 (C_{Ar}), 147.4 (C_{Ar}), 128.3 (C_{Ar}), 128.1 (C_{Ar}), 52.3 (d, $J = 14.4$ Hz, methylen), 47.2 (Py-CH_3), 36.0 (d, $J = 15.6$ Hz, $C(CH_3)_3$), 31.6 (d, $J = 7.7$ Hz, $C(CH_3)_3$) ppm. **^{31}P{^{1}H} NMR** (162 MHz, MeCN- d_3): $\delta = 177.4$ ppm. **ESI-TOF** (m/z): 249.1293 g/mol (calculated: 249.1264 g/mol) $[M]^+$).

General procedure to synthesize the dications (3 a', 3a'', 3 b', 3 b'')

Method A: Trimethyloxonium tetrafluoroborate or triethyloxonium tetrafluoroborate (1.1 eq.) was added to a solution of the corresponding 3*H*-1,2,3,4-triazaphospholenium salt (1.0 eq.) in DCM (10 mL per 200 mg triazaphospholenium salt) and the reaction mixture was stirred at $T = 55\,^{\circ}C$ for two days. The solvent was then removed in vacuo, the residue was washed with diethyl ether (3 x 10 mL per 200 mg reactant) and dried in vacuo.

Method B: (only for **3 a'** and **3 b''**) Trimethyloxonium tetrafluoroborate or triethyloxonium tetrafluoroborate (2.2 eq.) was added to a solution of the corresponding 3*H*-1,2,3,4-triazaphosphol (1.0 eq.) in DCM (10 mL per 200 mg triazaphosphol) and the reaction mixture was stirred at $T = 55\,^{\circ}C$ for four days. The solvent was then removed in vacuo, the residue was washed with diethyl ether (3×10 mL per 200 mg reactant) and dried in vacuo.

2-((5-(tert-butyl)-1-methyl-3H-1,2,3,4-triazaphosphol-1-ium-3-yl)methyl)-1-methylpyridin-1-ium tetrafluoroborate (3 a')

Method A: The dication **3 a'** was synthesized from **2 a** (104 mg, 0.31 mmol) and trimethyloxonium tetrafluoroborate (50.0 mg, 0.34 mmol) in DCM (5 mL). **3 a'** was obtained as colorless solid (110 mg, 81%) **Method B**: The dication **3 a'** was synthesized from 1 (145 mg, 0.62 mmol) and trimethyloxonium tetrafluoroborate (201 mg, 1.36 mmol) in DCM (10 mL). **3 a'** was obtained as colorless solid (175 mg, 65%). **^{1}H NMR** (500 MHz, MeCN-d_3): $\delta = 8.80$ (d, J = 6.1 Hz, 1H, HAr), 8.55 (t, J = 8.0 Hz, 1H, HAr), 8.06 (t, J = 6.9 Hz, 1H, HAr), 7.91 (d, J = 8.1 Hz, 1H, HAr), 6.23 (d, J = 5.4 Hz, 2H, methylen), 4.49 (d, J = 1.0 Hz, 3H, N-CH_3), 4.36 (s, 3H, Py-CH_3), 1.61 (d, J = 2.5 Hz, 9H, $C(CH_3)_3$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, MeCN-d_3): $\delta = 193.4$ (d, J = 64.0 Hz, C=P), 150.6 (CAr), 149.0 (CAr), 147.9 (CAr), 130.2 (CAr), 129.5 (CAr), 55.2 (d, J = 12.2 Hz, methylen), 47.4 (Py-CH_3), 44.5 (N-CH_3), 36.3 (d, J = 11.2 Hz, $C(CH_3)_3$), 29.8 (d, J = 11.1 Hz, C(CH3)3) ppm. **^{31}P{^{1}H} NMR** (162 MHz, MeCN- d_3): $\delta = 212.3$ ppm. ^{19}F-NMR (377 MHz MeCN- d_3): $\delta = -151.6$ ppm. **^{11}B NMR** (129 MHz MeCN- d_3): $\delta = -1.3$ ppm. ESI-TOF (m/z): 249.1285 g/mol (cal.: 249.1264 g/mol) $[M-CH_3]^+$.

2-((5-(tert-butyl)-1-ethyl-3H-1,2,3,4-triazaphosphol-1-ium-3-yl)methyl)-1-methylpyridin-1-ium tetrafluoroborate (3 a'')

Method A: **2 a** (108 mg, 0.32 mmol) and triethyloxonium tetrafluoroborate (67.1 mg, 0.35 mmol) were dissolved in DCM (5 mL). **3 a''** was obtained as colorless solid (124 mg, 85%). **^{1}H NMR** (500 MHz, MeCN-d_3): $\delta = 8.81$ (d, $J = 6.0$ Hz, 1H, *H*Ar), 8.55 (t, $J = 7.9$ Hz, 1H, *H*Ar), 8.05 (t, $J = 7.0$ Hz, 1H, *H*Ar), 7.96 (d, $J = 8.2$ Hz, 1H, *H*Ar), 6.26 (d, $J = 5.2$ Hz, 2H, methylen), 4.83 (q, $J = 7.2$ Hz, 2H, N-CH_2CH_3), 4.38 (s, 3H, Py-CH_3), 1.63 (t, $J = 7.2$ Hz, 3H, N-CH2CH_3), 1.60 (d, $J = 1.9$ Hz, 9H, $C(CH_3)_3$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, MeCN-d_3): $\delta = 193.3$ (d, $J =$ 63.4 Hz, C=P), 150.0 (CAr), 149.1 (CAr), 147.9 (CAr), 130.5 (CAr), 129.6 (CAr), 55.3 (d, $J = 12.7$ Hz, Methylen), 53.6 (N-*C*H2CH3), 47.4 (Py-CH_3), 36.3 (d, $J = 11.4$ Hz, $C(CH_3)_3$), 30.23 (d, $J = 11.3$ Hz, $C(CH_3)_3$), 15.28 (N-CH_2CH_3) ppm. **^{31}P{^{1}H} NMR** (162 MHz, MeCN-d_3): $\delta =$ 210.5 ppm. **^{19}F NMR** (377 MHz MeCN-d_3): $\delta = -151.3$ (s) ppm. **^{11}B NMR** (129 MHz MeCN-d_3): $\delta = -1.3$ ppm. **ESI-TOF** (m/z): 139.0846 g/mol (calculated: 139.0825 g/mol) $[M]^{2+}$).

2-((5-(tert-butyl)-1-methyl-3H-1,2,3,4-triazaphosphol-1-ium-3-yl)methyl)-1-ethylpyridin-1-ium tetrafluoroborate (3 b')

Method A: **3 b'** was synthesized by adding trimethyloxonium tetrafluoroborate (76.0 mg, 0.51 mmol) to a solution of **2 b** (150 mg, 0.43 mmol) in DCM (5 mL). **3 b'** was obtained as colourless solid (173 mg, 89%). **^{1}H NMR** (500 MHz, MeCN-d_3): $\delta = 8.87$ (dd, $J = 6.2$, 1.5 Hz, 1H, H_{Ar}), 8.54 (td, $J = 8.0$, 1.5 Hz, 1H, H_{Ar}), 8.10 (ddd, $J = 7.8$, 6.1, 1.5 Hz, 1H, H_{Ar}), 7.93 (d, $J = 8.1$ Hz, 1H, H_{Ar}), 6.26 (d, $J = 5.3$ Hz, 2H, methylen), 4.70 (q, $J = 7.3$ Hz, 2H, Py-CH_2CH_3), 4.48 (d, $J = 1.0$ Hz, 3H, N-CH_3), 1.64 (t, $J = 7.3$ Hz, 3H, Py-CH_2CH_3), 1.60 (d, $J = 2.4$ Hz, 9H, $C(CH_3)_3$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, MeCN-d_3): $\delta = 193.4$ (d, J = 64.0 Hz, C=P), 150.0 (CAr), 149.1 (CAr), 147.9 (CAr), 130.3 (CAr), 129.6 (CAr), 55.2 (d, J = 12.1 Hz, methylen), 47.4 (Py-CH_3), 44.5 (N-CH3), 36.3 (d, J = 11.0 Hz, $C(CH_3)_3$), 29.81 (d, J = 11.2 Hz, $C(CH_3)_3$) ppm. **^{31}P{^{1}H} NMR** (162 MHz, MeCN-d_3): $\delta = 212.1$ ppm. **^{19}F NMR** (377 MHz MeCN-d_3): $\delta = -151.4$ (s) ppm. **^{11}B NMR** (129 MHz MeCN-d_3): $\delta = -1.3$ ppm. ESI-TOF (m/z): 139.0847 g/mol (calculated: 139.0825 g/mol) $[M]^{2+}$)

2-((5-(tert-butyl)-1-ethyl-3H-1,2,3,4-triazaphosphol-1-ium-3-yl)methyl)-1-ethylpyridin-1-ium tetrafluoroborate (3 b'')

Method B: **1** (236 mg, 1.01 mmol) was disolved in DCM (10 mL) and triethyloxonium tetrafluoroborate (402 mg, 2.12 mmol) was added to the reaction mixture. **3 b''** was obtained as colourless solid (395 mg, 84%). **^{1}H NMR** (500 MHz, MeCN-d_3): $\delta = 8.87$ (dd, $J = 6.2$, 1.5 Hz, 1H, *H*Ar), 8.55 (td, $J = 8.0$, 1.5 Hz, 1H, *H*Ar), 8.11 (ddd, $J = 7.9$, 6.2, 1.6 Hz, 1H, *H*Ar), 7.98 (dd, $J = 8.1$, 1.5 Hz, 1H, *H*Ar), 6.27 (d, $J =$

5.2 Hz, 2H, methylen), 4.82 (qd, J=7.2, 1.0 Hz, 2H, N-CH_2CH$_3$), 4.72 (q, J=7.3 Hz, 2H, Py-CH_2CH$_3$), 1.65 (t, J=7.3 Hz, 3H, Py-CH$_2$CH_3), 1.61 (d, J=2.4 Hz, 9H, C(CH_3)$_3$), 1.61 (t, J=7.2 Hz, 3H, N-CH$_2$CH_3) ppm. **^{13}C{^{1}H} NMR** (101 MHz, MeCN-d_3): δ=193.0 (d, J=63.6 Hz, C=P), 149.1 (CAr), 147.7 (CAr), 147.4 (CAr), 131.1 (d, J=0.9 Hz, (CAr)), 129.9 (CAr), 55.3 (Py-CH$_2$CH$_3$), 54.7 (d, J=12.2 Hz, methylen), 53.4 (N-CH$_2$CH$_3$), 36.2 (d, J=11.3 Hz, C(CH$_3$)$_3$), 30.0 (d, J=11.5 Hz, C(CH$_3$)$_3$), 16.0 (Py-CH$_2$CH$_3$), 15.1 (N-CH$_2$CH$_3$) ppm. ^{31}P{^{1}H}-NMR (162 MHz, MeCN-d_3): δ=210.1 ppm. **^{19}F NMR** (377 MHz MeCN-d_3): δ=−151.7 (s) ppm. **^{11}B NMR** (129 MHz MeCN-d_3): δ=−1.3 ppm. **ESI-TOF** (m/z): 263.1430 g/mol (calculated.: 263.1420 g/mol) [M–C$_2$H$_5$]$^+$.

Cu(I) complexes of triazaphosphole salts 2 a, 2 c

The corresponding the Cu(I) salt (3.0 eq) was added to a solution of the alkylated triazaphosphole (1.0 eq) in THF (3 mL per 20.0 mg triazaphospholenium salt) and stirred at T=60 °C for overnight. The solvent was reduced to half in vacuum and *n*-pentane (10 mL per 20.0 mg triazaphospholenium salt) was added to complete the precipitation of the product. The solid obtained was washed with n-pentane (3×10 mL per 20.0 mg reactant), dried in vacuo and recrystallized from acetonitrile.

[C$_{12}$H$_{18}$N$_4$P]$_n$ [Cu$_2$Br$_3$]$_n$ (4 a$_{\mu 2}$)

2 a (20.0 mg, 0.06 mmol) and CuBr·SMe$_2$ (37.1 mg, 0.18 mmol) were dissolved in THF (3 mL). **4a$_{\mu 2}$** was obtained quantitatively according to ^{31}P NMR spectroscopy as yellow solid. **^{1}H NMR** (400 MHz, MeCN-d_3): δ=8.70 (d, J=6.1 Hz, 1H, H-1), 8.41 (t, J=7.9 Hz, 1H, H-3), 7.94 (t, J=6.9 Hz, 1H, H-2), 7.34 (d, J=8.1 Hz, 1H, H-4), 6.20 (d, J=5.6 Hz, 2H, CH$_2$), 4.35 (s, 3H, N-CH$_3$), 1.48 (d, J=1.4 Hz, 9H, C(CH$_3$)$_3$) ppm. **^{31}P{^{1}H} NMR** (162 MHz, MeCN-d_3): δ=175.6 ppm.

[C$_{12}$H$_{18}$N$_4$P]$_2$ [Cu$_2$I$_4$] (4 c$_{\eta 1}$)

2 c (15.0 mg, 0.05 mmol) and CuI·SMe$_2$ (36.5 mg, 0.15 mmol) were dissolved in THF (3 mL). **4c$_{\eta 1}$** was obtained quantitatively according to ^{31}P NMR spectroscopy as orange solid. **^{1}H NMR** (400 MHz, MeCN-d_3): δ=8.72 (ddd, J=6.2, 1.4, 0.7 Hz, 1H, *H*Ar), 8.41 (td, J=7.7, 1.1 Hz, 1H, *H*Ar), 7.95 (ddd, J=7.8, 6.1, 1.5 Hz, 1H, *H*Ar), 7.33 (d, J=8.5 Hz, 1H, *H*Ar), 6.28 (d, J=5.7 Hz, 2H, methylen), 4.38 (s, 3H, Py-CH_3), 1.49 (d, J=1.4 Hz, 9H, C(CH_3)$_3$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, MeCN-d_3: δ=195.8 (d, J=63.1 Hz, C=P), 154.3 (CAr), 148.0 (CAr), 147.4 (CAr), 128.4 (CAr), 128.1 (CAr), 52.3 (d, J=13.6 Hz, methylen), 47.3 (Py-CH_3), 36.0 (d, J=15.8 Hz, C(CH$_3$)$_3$), 31.6 (d, J=7.7 Hz, C(CH$_3$)$_3$) ppm. **^{31}P{^{1}H} NMR** (162 MHz, MeCN-d_3): δ=170.8 ppm. **ESI-TOF** (m/z): 249.1261 g/mol (calculated: 249.1264 g/mol) [M]$^+$ (only cation detected).

Cu(I) complexes of triazaphosphole salt 2 b

[C$_{13}$H$_{20}$N$_4$P]$_n$ [Cu$_2$Br$_3$]$_n$ (4b$_{\mu 2}$) / [C$_{13}$H$_{20}$N$_4$P]$_2$ [Cu$_2$Br$_4$] (4 b$_{\eta 1}$)

2 b (30.0 mg, 0.09 mmol) and CuBr·SMe$_2$ (55.0 mg, 0.27 mmol) were dissolved in THF (3 mL) and acetonitrile (0.5 mL) and stirred at T= 60 °C for 2 h. The reaction mixture was allowed to stand at room temperature for overnight. Yellow crystals of **4b$_{\mu 2}$** and **4b$_{\eta 1}$** were obtained directly from the reaction mixture. **^{1}H NMR** (400 MHz, MeCN-d_3): δ=8.77 (dd, J=6.2, 1.2 Hz, 1H, HAr), 8.42 (td, J=7.9, 1.3 Hz, 1H, HAr), 7.99 (ddd, J=7.5, 6.2, 1.1 Hz, 1H, HAr), 7.49 (d, J= 8.1 Hz, 1H, HAr), 6.26 (d, J=3.9 Hz, 2H, methylen), 4.73 (q, J= 7.4 Hz, 2H, CH$_2$CH$_3$), 1.57 (t, J=7.2 Hz, 3H, CH$_2$CH$_3$), 1.47 (d, J= 1.4 Hz, 9H, C(CH$_3$)$_3$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, MeCN-d_3): δ= 198.7 (d, J=70.2 Hz, C=P), 152.8 (CAr), 147.3 (CAr), 146.7 (CAr), 129.4 (CAr), 128.8 (CAr), 54.9 (CH$_2$CH$_3$), 51.7 (d, J=14.0 Hz, methylen), 36.0 (d, J=15.4 Hz, C(CH$_3$)$_3$), 31.6 (d, J=7.8 Hz, C(CH$_3$)$_3$), 15.9 (CH$_2$CH$_3$) ppm. **^{31}P{^{1}H} NMR** (162 MHz, MeCN-d_3): δ= 174.0 ppm.

Cu(I) complexes of triazaphospholenium salts 3 a'', 3 b''

The corresponding dication (1.0 eq) and a Cu(I) salt (3.0 eq) were dissolved in THF (3 mL per 20.0 mg dication) and stirred at T=60 °C for overnight. The solvent was reduced to half in vacuum and *n*-pentane (10 mL per 20.0 mg triazaphospholenium salt) was added to complete the precipitation of the product. The solid obtained was washed with *n*-pentane (3×10 mL per 20.0 mg reactant), dried in vacuo and recrystallized from acetonitrile.

[C$_{14}$H$_{23}$N$_4$P][CuBr$_3$] (5$_{\eta 1}$)

3 a' (30.0 mg, 0.06 mmol) and CuBr·SMe$_2$ (40.9 mg, 0.20 mmol) were dissolved in a mixture of THF: acetonitrile 1:1 (4 mL). **5$_{\eta 1}$** was obtained as orange solid.

[C$_{14}$H$_{23}$N$_4$P]$_n$[Cu$_4$I$_6$]$_n$ (6)

3 a' (10.0 mg, 0.02 mmol) and CuI·SMe$_2$ (33.6 mg, 0.14 mmol) were dissolved in THF (3 mL). **6** was obtained quantitatively according to ^{31}P-NMR as orange solid. **^{1}H NMR** (400 MHz, MeCN-d_3): δ=8.79 (dd, J=6.4, 1.2 Hz, 1H, HAr), 8.55 (td, J=7.9, 1.6 Hz, 1H, HAr), 8.06 (ddd, J=7.6, 6.1, 1.1 Hz, 1H, HAr), 7.98 (d, J=8.3 Hz, 1H, HAr), 6.27 (d, J= 5.4 Hz, 2H, methylen), 4.82 (qd, J=7.2, 1.0 Hz, 2H, N-CH$_2$CH$_3$), 4.38 (s, 3H, Py-CH$_3$), 1.62 (d, J=2.6 Hz, 9H, C(CH$_3$)$_3$), 1.62 (t, J=7.2 Hz, 3H, N-CH$_2$CH$_3$) ppm. **^{31}P{^{1}H} NMR** (162 MHz, MeCN-d_3): δ=206.5 ppm. **ESI-TOF** (m/z): 263.1492 g/mol (calculated: 263.1420 g/mol) [M]$^+$ (only cation of the structure C$_{13}$H$_{20}$N$_4$P$^+$ could be detected).

[C$_{15}$H$_{25}$N$_4$P]$_n$[BF$_4$]$_n$[CuBr$_2$]$_n$ (7$_{\eta 1}$)

3 b'' (30.0 mg, 0.06 mmol) and CuBr·SMe$_2$ (24.5 mg, 0.12 mmol) were dissolved in a Mixture of THF: acetonitrile 1:1 (4 mL). 7$_{\eta 1}$ was obtained quantitatively according to ^{31}P NMR spectroscopy as orange solid. **^{1}H NMR** (400 MHz, MeCN-d_3): δ=8.86 (dd, J=6.3, 1.5 Hz, 1H, *H*Ar), 8.53 (td, J=7.9, 1.5 Hz, 1H, *H*Ar), 8.19–8.02 (m, 2H, *H*Ar), 6.46 (d, J=5.2 Hz, 2H, methylen), 4.78 (qd, J=7.3, 1.3 Hz, 2H, N-CH$_2$CH$_3$), 4.47 (q, J=7.5 Hz, 2H, Py-CH$_2$CH$_3$), 1.67 (d, J=7.3 Hz, 3H, Py-CH$_2$CH$_3$), 1.64 (d, J=2.4 Hz, 9H, C(CH$_3$)$_3$), 1.60 (t, J=7.2 Hz, 3H, N-CH$_2$CH$_3$) ppm. **^{31}P{^{1}H} NMR** (162 MHz, MeCN-d_3): δ=200.9 ppm. **^{19}F NMR** (377 MHz MeCN-d_3): δ=−151.7–−151.8 (m) ppm. **^{11}B NMR** (129 MHz MeCN-d_3): δ=−1.1–−1.3 (m) ppm.

Acknowledgements

Financial support by Freie Universität Berlin is gratefully acknowledged. 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: Heterocycles · Phosphorus · Ligands · Coordination Chemistry · X-ray Crystallography

[1] a) J. A. W. Sklorz, C. Müller, *Eur. J. Inorg. Chem.* **2016**, 595–606; b) K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy: From Organophosphorus to Phospha-Organic Chemistry*, John Wiley & Sons, **1998**.
[2] a) Y. C. Yeung, L. Y. Ko, R. Carrié, *Chem. Commun.* **1984**, 1640–1641; b) W. Rösch, M. Regitz, *Angew. Chem. Int. Ed.* **1984**, *23*, 900–901.
[3] a) E. Yue, L. Dettling, J. A. W. Sklorz, S. Kaiser, M. Weber, C. Müller, *Chem. Commun.* **2022**, *58*, 310–313; b) L. Dettling, M. Papke, J. A. W. Sklorz, D. Buzsáki, Z. Kelemen, M. Weber, L. Nyulászi, C. Müller, *Chem. Commun.* **2022**, *58*, 7745–7748; c) L. Dettling, N. Limberg, R. Küppers, D. Frost, M. Weber, N. T. Coles, D. M. Andrada, C. Müller, *Chem. Commun.* **2023**, *59*, 10243–10246.
[4] S. L. Choong, C. Jones, A. Stasch, *Dalton Trans.* **2010**, *39*, 5774–5776.
[5] S. L. Choong, A. Nafady, A. Stasch, A. M. Bond, C. Jones, *Dalton Trans.* **2013**, *42*, 7775–7780.
[6] J. A. W. Sklorz, S. Hoof, M. G. Sommer, F. Weißer, M. Weber, J. Wiecko, B. Sarkar, C. Müller, *Organometallics* **2014**, *33*, 511–516.
[7] M. Papke, L. Dettling, J. A. W. Sklorz, D. Szieberth, L. Nyulászi, C. Müller, *Angew. Chem. Int. Ed.* **2017**, *56*, 16484–16489.
[8] a) M. Heckenroth, E. Kluser, A. Neels, M. Albrecht, *Dalton Trans.* **2008**, 6242–6249; b) G. Guisado-Barrios, J. Bouffard, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 4759–4762.
[9] J. J. Daly, *J. Chem. Soc.* **1964**, 3799–3810.
[10] T. A. Van Der Knaap, T. C. Klebach, F. Visser, F. Bickelhaupt, P. Ros, E. J. Baerends, C. H. Stam, M. Konijn, *Tetrahedron Lett.* **1984**, *40*, 765–776.
[11] Y. Charbonnel, J. Barrans, *Tetrahedron Lett.* **1976**, *32*, 2039–2043.
[12] a) Y. Jeong, J. S. Ryu, *J. Org. Chem.* **2010**, *75*, 4183–4191; b) S. Hohloch, C. Y. Su, B. Sarkar, *Eur. J. Inorg. Chem.* **2011**, 3067–3075; c) Z. K. Reeder, A. M. Adler, K. M. Miller, *Tetrahedron Lett.* **2016**, *57*, 206–209.
[13] a) P. J. Stang, M. Hanack, L. R. Subramanian, *Synthesis* **1982**, 85–126; b) E. S. Lewis, S. Vanderpool, *J. Am. Chem. Soc.* **1977**, *99*, 1946–1949; c) D. N. Kevill, G. M. L. Lin, *Tetrahedron Lett.* **1978**, *11*, 949–952.
[14] A. Bastero, D. Font, M. A. Pericàs, *J. Org. Chem.* **2007**, *72*, 2460.
[15] S. Burck, J. Daniels, T. Gans-Eichler, D. Gudat, K. Nättinen, M. Nieger, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1403–1412.
[16] K. Wang, A. K. Chinnam, N. Petrutik, E. P. Komarala, Q. Zhang, Q. Yan, R. Dobrovetsky, M. Gozin, *J. Mater. Chem. A* **2018**, *6*, 22819–22829.
[17] a) T. E. Kokina, L. A. Glinskaya, D. A. Piryazev, A. M. Agafontsev, E. V. Vorontsova, A. S. Bogomyakov, A. V. Tkachev, S. V. Larionov, *Russ. Chem. Bull. Int. Ed.* **2018**, *67*, 1251–1260; b) G. Hu, E. M. Holt, *Acta Crystallogr.* **1994**, *C50*, 1578–1580; c) S. Anderson, S. Jagner, *Acta Chem. Scand.* **1985**, *A40*, 181–186; d) N. P. Rath, E. M. Holt, *Chem. Commun.* **1985**, *7*, 665–667.
[18] C. Pardin, I. Roy, W. D. Lubell, J. W. Keillor, *Chem. Biol. Drug Des.* **2008**, *72*, 189–196.
[19] G. Becker, H. Schmidt, G. Uhl, W. Uhl, M. Regitz, W. Rösch, U.-J. Vogelbacher, *Inorg. Synth.* **1990**, *27*, 249–253.
[20] Bruker (**2010**). APEX2, SAINT, SADABS and XSHELL. Bruker AXS Inc., Madison, Wisconsin, USA.
[21] a) Sheldrick, G. SADABS. University of Göttingen: Göttingen, Germany: **2014**; b) Coppens, P. The Evaluation of Absorption and Extinction in Single-Crystal Structure Analysis. Crystallographic Computing. Copenhagen, Muksgaard: **1979**.
[22] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122; b) G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.
[23] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.
[24] C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler, P. A. Wood, *J. Appl. Crystallogr.* **2020**, *53*, 226–235.

Manuscript received: February 13, 2024
Accepted manuscript online: April 10, 2024
Version of record online: May 8, 2024