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Main-Group Chemistry

Cycloadditions of Diazoalkenes with P_4 and *t*BuCP: Access to Diazaphospholes

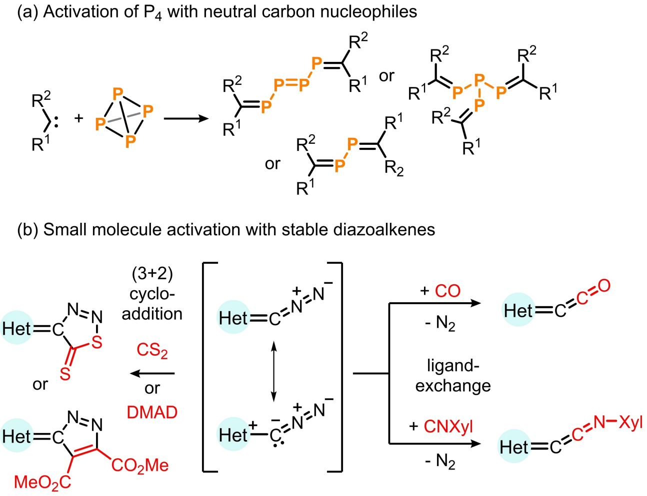
Sebastian Hauer, Justus Reitz, Taichi Koike, Max M. Hansmann, and Robert Wolf**

Dedicated to Professor Nikolaus Korber on the occasion of his 60th birthday

Abstract: Diazoalkenes readily react with *tert*-butylphosphaalkyne (*t*BuCP) and white phosphorus (P_4) to afford novel phosphorus heterocycles, 3*H*-1,2,4-diazamonophospholes and 1,2,3,4-diazadiphospholes. Both species represent rare examples of neutral heterophospholes. The mechanism of formation and the electronic structures of these formal (3+2) cycloaddition products were analyzed computationally. The new phospholes form structurally diverse coordination compounds with transition metal and main group elements. Given the growing number of stable diazoalkenes, this work offers a straightforward route to neutral aza(di-)phospholes as a new ligand class.

The activation of white phosphorus by main group and transition metal compounds is a powerful route to useful synthetic building blocks.[1] While the activation of P_4 with metalated carbon nucleophiles is well established to occur through P_4 butterfly opening, neutral carbon nucleophiles are much less investigated.[2] In pioneering work, Bertrand and co-workers have demonstrated that the use of stable carbenes affords organophosphorus species featuring P_1–P_4, P_8, and even P_{12} fragments (Scheme 1a).[3,4]

In 2021, the Hansmann and Severin groups independently described the first room temperature stable diazoalkenes ($R_2C{=}C{=}N_2$).[5] While the first diazoalkenes were based on imidazole backbones, 1,2,3-triazoles,[6] and 2-pyridines[7] were also reported.[8] Within the field of small molecule activation diazoalkenes can undergo ligand exchange reactions: N_2 can be exchanged with carbon monoxide,[6,9] or with isocyanides.[5a,6,10] Diazoalkenes also react with dipolarophiles via (3+2) cycloaddition, for instance with carbon disulfide or dimethylacetylene dicarboxylate (Scheme 1b).[5b,11] While diazoalkene chemistry is quickly expanding, most applications are in the area of transition metal chemistry.[8,12] Since last year, diazoalkenes have been utilized in main group chemistry, for instance in the combination with Ge-complexes,[13,14] their use as reagents for accessing tetrelavinylidenes of Si and Ge,[15] and in the reaction with a cobalt distibene complex.[16] Considering the ability of diazoalkenes to activate small molecules such as carbon monoxide, we were intrigued by the possibility to activate phosphorus compounds such as phosphaalkynes ($RC{\equiv}P$) and P_4.[17] Here, we describe the synthesis of diazadiphospholes and the corresponding diazamonophospholes, which feature aromatic properties and can be applied as ligands in transition metal and main group chemistry.


(a) Activation of P_4 with neutral carbon nucleophiles

(b) Small molecule activation with stable diazoalkenes

Scheme 1. (a) Activation products of P_4 with neutral carbon nucleophiles (carbenes); (b) (3+2) cycloaddition and ligand exchange reactivity of stable diazoalkenes. DMAD: Dimethyl acetylene dicarboxylate.

We initially investigated the reactivity of *t*BuCP towards diazoalkenes **1a–d** containing imidazole, triazole, and pyridine heterocyclic backbones (Scheme 2a; the synthesis of the new diazoalkene **1a** is described in the SI). ^{31}P{^{1}H} NMR spectroscopy revealed in all cases (**1a–d**) the quantitative formation of the elusive 3*H*-1,2,4-diazamonophospholes **2–5**. While isomeric 1*H*-1,2,4-diazamonophos-

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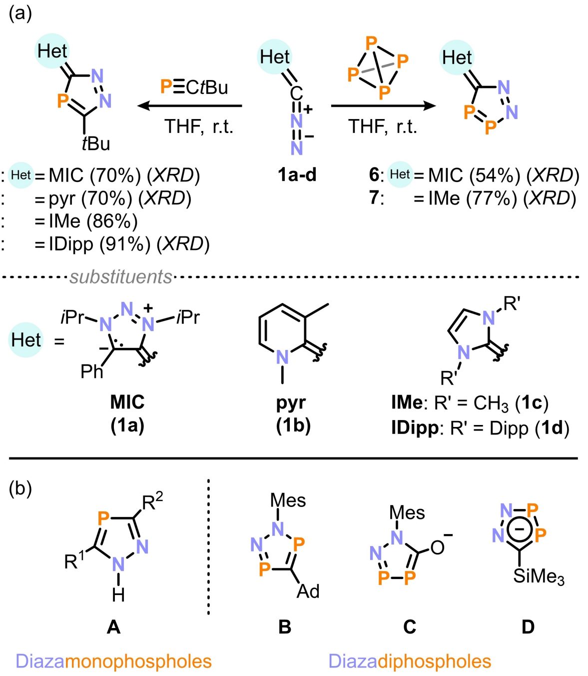
[*] Dr. S. Hauer, Prof. Dr. R. Wolf
University of Regensburg
Institute of Inorganic Chemistry
93040 Regensburg (Germany)
E-mail: robert.wolf@ur.de

J. Reitz, Dr. T. Koike, Prof. Dr. M. M. Hansmann
TU Dortmund
Faculty of Chemistry and Chemical Biology
44227 Dortmund (Germany)
E-mail: max.hansmann@tu-dortmund.de



Scheme 2. (a) (3+2) Cycloaddition reactions of diazoalkenes with tBuCP and P_4 affording **2**–**5** and **6**–**7**, respectively. (b) Selection of literature known 1,2,4-diazamonophospholes (**A**) and 1,2,3,4-diazadiphospholes (**B**–**D**); $R^1 \neq R^2$ = organic residue; MIC: mesoionic carbene. Mes: 1,3,5-trimethylphenyl.

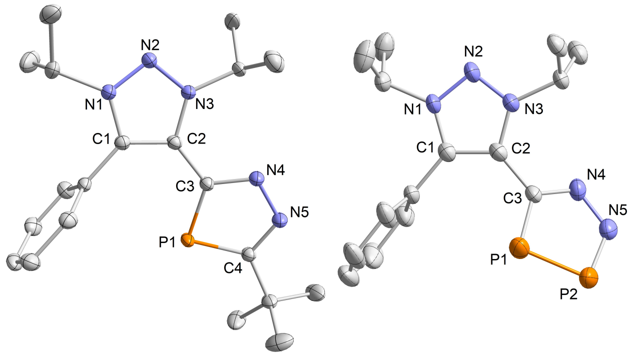


Figure 1. Solid-state molecular structures of **2** (left) and **6** (right). Hydrogen atoms and disorder are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: **2**: P1–C4 1.7542(1), P1–C3 1.7596(1), C4–N5 1.3393(1), N4–N5 1.3495(1), N4–C3 1.3478(1), C2–C3 1.4559(2), C3-P1-C4 84.97(5), P1-C4-N5 115.01(8); **6**: P1–P2 2.0877(1), P2–N5 1.669(4), P1–C3 1.752(4), N4–N5 1.336(4), N4–C3 1.347(5), C2–C3 1.466(5), C1–N1 1.339(5), C3-P1-P2 88.58(1), P1-P2-N5 97.64(1), P2-N5-N4 117.2(3).

pholes such as **A** (Scheme 2b) are known,[18,19] the here reported class of heterocycles **2**–**5** has been postulated as transient intermediates in cycloaddition reactions, which typically rapidly rearrange via [1,5]-shift.[20] **2** gives rise to a sharp singlet in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 79.6$ ppm, which is on the lower end of the typical range for heterophospholes ($\delta = 65$–178 ppm).[21] The reaction most likely proceeds via a (3+2) cycloaddition reaction selectively forming a single regioisomer.[22]

Compound **2** crystallizes as light-yellow needles in a good isolated yield of 70%. Single-crystal X-ray diffraction analysis (XRD) of **2** (Figure 1) revealed a nearly planar C_2N_2P unit with similar P1–C3 (1.759(6) Å) and P1–C4 (1.754(2) Å) bond lengths which lie between typical P–C single and P=C double bonds (Σr_{PC} 1.86 Å vs. 1.69 Å),[23] indicating π-delocalization.[24] In comparison to diazoalkene **1a** the C2–C3 bond is elongated (**1a**: 1.407(1) Å vs. **2**: 1.455(9) Å), thus exhibiting a higher single bond character. For the XRD structural data of **3** and **5**, see the SI.

We next selected P_4 as a substrate for the transfer of a formal [P≡P] fragment. **1a** and **1c** reacted with high selectivity at room temperature to give rare 5*H*-1,2,3,4-diazadiphospholes **6** and **7** as orange solids in 54% and 77% yield, respectively (Scheme 2a). Related 1,2,3,5-diazadiphosphole (**B**)[25] and 1,2,3,4-diazadiphosphole (**C**, **D**)[26,27] salts are known (Scheme 2b), however, their chemistry has remained poorly developed.[28] Isolated **6** exhibits two characteristic doublets at $\delta = 364.2$ ppm (P2) and $\delta = 217.5$ ppm (P1) with a large coupling constant of $^1J_{PP} = 444$ Hz, which was well reproduced by GIAO calculations (M06-L/def2-TZVP//B3PW91-D3(BJ)/def2-TZVP level of theory, $\delta = 359.0$ ppm (P2) and $\delta = 217.0$ ppm (P1). These resonances compare well with those reported for anionic **D**, ($\delta = 353$ (P2), 231 (P1) ppm), while the carbon-bound phosphorus signal for P1 is significantly shifted downfield in comparison to related anionic **C** ($\delta = 97$ ppm).[26,27] In the solid-state structure of **6** (Figure 1), the P1–P2 bond length of 2.087(7) Å indicates a fairly localized double bond and is between those reported for the anion **C** (2.102(8) Å) and protonated **D** (2.070(6) Å).[26,27] Contrary to coplanar **2**, the CN_2P_2 unit in **6** is tilted (43°) relative to the triazolium backbone.

DFT calculations suggest a P_4 activation step initiated by a (3+2) cycloaddition in which the C–P bond formation occurs simultaneously with N–P bond formation (see Figure S93), contrasting the ambiphilic carbene activation pathway. Following the (3+2) addition, an intermolecular P_2 transfer by another equivalent of **1** appears most likely. Importantly, we found a correlation between the nucleophilicity of the diazoalkene and the capability of P_4 activation. While the most nucleophilic diazoalkene (**1a**)[29] reacts rapidly and cleanly with P_4, the reactions involving **1c** and **1d** are significantly slower. Specifically, the reaction of sterically more demanding **1d** with P_4 yielded a mixture of several products, which could not be structurally characterized (see the Supporting Information for details). Moreover, the least polarized diazoalkene **1b** featuring the pyr-backbone did not give any conversion. These findings are significant for the design of P_4 activation strategies based on a (3+2) cycloaddition mechanism.

We conducted DFT calculations for the synthesized diazamonophospholes and -diphospholes (as well as model compounds **E** and **F**, Figure 2) to clarify the electronic effect of the π-electron donating *N*-heterocycles to the *P*-heterocycles. The Kohn–Sham HOMO-1 and HOMO exhibit π-electrons delocalized across the C_2N_2P-ring (Figure 2).[30] In fact, the energy level of the HOMO increases roughly in the

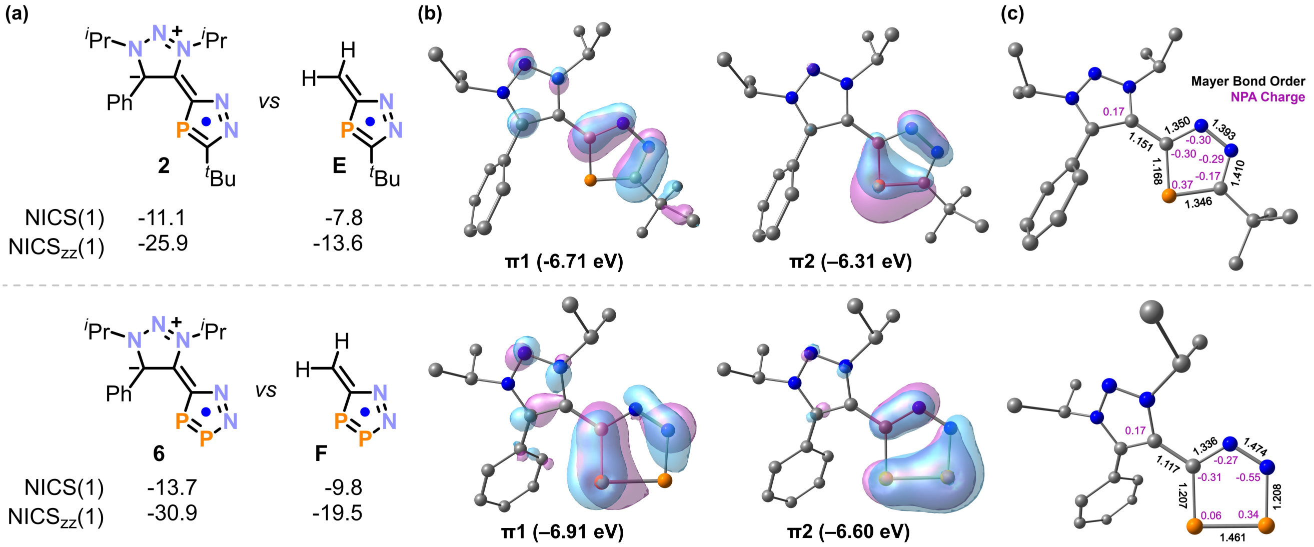


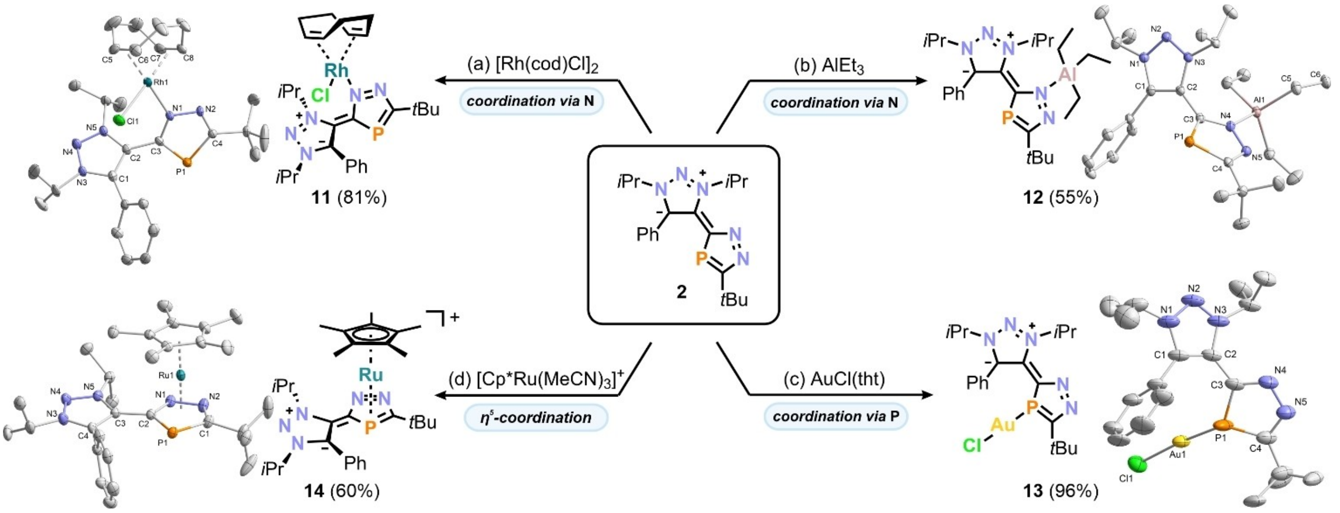
Figure 2. (a) Comparison of the NICS(1) and NICSzz(1) values of **MIC**-based diazaphospholes **2** and **6** with the parent methylene-diazaphospholes **E** and **F**. (b) Selected Kohn–Sham orbitals and energy levels of **2** and **6** calculated at the M06-2X/def2-TZVP[P,N,C]&def2-SVP[H]//B3PW91-D3(BJ)/def2-TZVP level of theory. (c) Mayer bond order and NPA charge of **2** and **6**.

order of **E** (−8.22 eV) < **3** (−6.81 eV) ≈ **4** (−6.81 eV) < **5** (−6.72 eV) < **2** (−6.31 eV) which correlates with the trend for the LP(π) orbitals in the corresponding diazoalkenes. A similar trend was seen for the diazadiphospholes [**F** (−8.58 eV) < **7** (−6.96 eV) < **6** (−6.60 eV)]. The high degree of π donation results in the polarization of the central C=C bond which is reflected in the small Mayer bond order (1.11–1.20) compared to the parent azaphospholes **E** (1.78) and **F** (1.76). Furthermore, the NPA charge analysis of **3** indicates higher negative charge on the N4 atom (−0.30e) compared to N5 (−0.29e) as well as N5 atom (−0.55e) compared to the N4 atom (−0.27e) for **6**. While no trend in the NICS or NICS_{zz} values could be seen depending either on the difference in the π donating ability among **pyr**, **IPh**, **IMe** and **MIC** or the twisting of the central C=C bonds, all exhibited similar degree of aromaticity (**2**–**4**, NICS(1): −12.3 to −11.1, NICS_{zz}(1): −29.2 to −25.9, **6**–**7**, NICS(1): −13.7 to −11.9, NICS_{zz}(1): −34.0 to −30.9; for details of the NICS calculations, see Figure S92 and Table S4). These values are significantly higher than those of the parent methylene-azaphospholes **E** (NICS(1) = −7.8, NICSzz(1) = −13.6) and **F** (NICS(1) = −9.8, NICSzz(1) = −19.5), which implies that the π donation from the *N*-heterocycles significantly increases the 6π-aromatic character of the P-heterocycles.

Cyclic voltammetry of the free ligand **2** shows an irreversible reduction ($E = -2.60$ V) and irreversible oxidation ($E = +0.74$ V; vs. Fc/Fc$^+$, Figures S64–66), which should feature a large stable redox-window for metal coordination. The calculated charges and frontier molecular orbitals of the new heterocycle **2** (Figure 2) indicate that both the nitrogen and phosphorus atoms are accessible for subsequent coordination. Indeed, we crystallographically identified three complexes $[\{W(CO)_5\}_2(\mathbf{2})]$ (**8**), $[W(CO)_3\{W(CO)_5(\mathbf{2})\}_3]$ (**9**) and $[W(CO)_5(\mathbf{2})]$ (**10**) from the reaction of **2** with $[W(CO)_5(thf)]$ (1–3 equiv.), which are obtained as a product mixture.[24] In these complexes, the phosphole coordinates the metal center via nitrogen and additionally via phosphorus (compounds **8** and **9**; see the Supporting Information for details of the characterizations). In contrast, reactions of **2** with $[Rh(cod)Cl]_2$ and $AlEt_3$ afforded complexes **11** and **12**, which show exclusive coordination of the N4 atom adjacent to the triazoliumyl substituent (Scheme 3a,b). Both complexes give rise to sharp singlets in the $^{31}P\{^1H\}$ NMR at δ = 86.7 ppm (**11**) and δ = 90.3 ppm (**12**), which is slightly downfield of uncoordinated **2** (δ = 79.6 ppm). Line broadening of the *i*Pr-groups and the cod signals in the ^1H NMR spectrum of **11** at room temperature indicates dynamic behavior, which was attributed to hindered rotation along the C2–C3 axis due to partial double bond character as well as a square planar rhodium center (Figure S27).

In order to achieve the targeted coordination only via phosphorus, we treated **2** with softer Lewis acids. In line with the HSAB concept, the addition of [AuCl(tht)] leads selectively to complex $[AuCl(\mathbf{2})]$ (**13**) in 96% yield (Scheme 3c). Thus so far only one related P-coordinated complex $[W(CO)_5(bdap)]$ (bdap = bis(1*H*-1,2,4-diazaphosphol-1-yl)methane) has been isolated from a mixture of multinuclear complexes.[31] **13** gives rise to a slightly broadened ($\Delta\nu_{1/2} = 136$ Hz) $^{31}P\{^1H\}$ NMR singlet at δ = 58.5 ppm, which is upfield of **2** (δ = 79.6 ppm) and $[W(CO)_5(bdap)]$ (δ = 80.7 ppm). In the solid-state structure **13** forms a dimer, due to the aurophilic Au–Au interaction (3.0705(4) Å).[32]

The preferred coordination via P or N donors is presumably determined by the HSAB principle, assuming that $W(CO)_5$ and AuCl are relatively soft Lewis acids in comparison with $[Rh(cod)Cl]_2$ and $AlEt_3$. Our calculations for **2** predict that two nitrogen atoms N4 and N5 have similar atomic charge charges (see the NPA charges in Figure 2 and the NRT analysis in Figure S94, SI). Thus, the coordination by N4 over N5 observed in **11** and **12** is likely favored for steric reasons. Steric effects also influence the



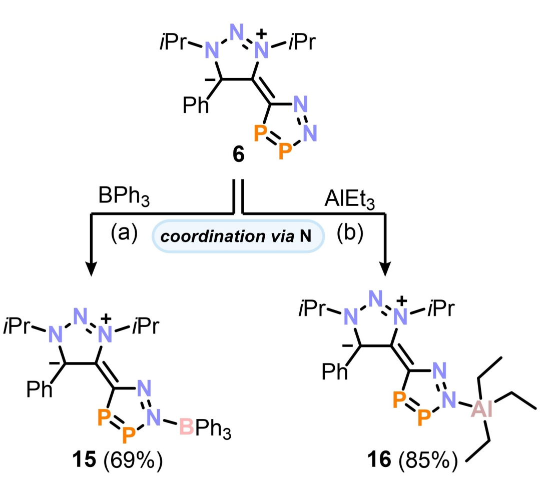
Scheme 3. Coordination of monophosphole **2**. Depending on the metal source, different coordination modes can be achieved; reagents/by-products and conditions: a) +0.5 eq. [Rh(cod)Cl]$_2$; toluene, r.t., 6 h; b) +1.0 eq. AlEt$_3$; THF, −35 °C to r.t., 2 h; c) +1.0 eq. [AuCl(tht)]/−tht; toluene, r.t., 7 h; d) +1.0 eq. [Cp*Ru(MeCN)$_3$]/−3 MeCN; THF, 65 °C, 1 d. In all cases, the corresponding X-ray solid-state structures are illustrated. Hydrogen atoms, PF_6^- (**14**) and disorder are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: **11**: Rh1–Cl1 2.3827(7), Rh1–N1 2.116(2), Rh1–$C_{56}^{centr.}$ 2.014(2), P1–C4 1.755(3), N1–N2 1.359(3), C2–C3 1.474(4), Cl1-Rh-N1 91.30(6); **12**: Al1–N4 1.9926(1), Al1–C5 1.9972(2), P1–C4 1.7608(2), N4–N5 1.3599(2), C2–C3 1.468(2), N1–N2 1.3217(2), Al1-N4-C3 136.12(1); **13**: Au1–P1 2.2232(1), Au1–Cl1 2.2841(9), P1–C3 1.735(3), P1–C4 1.739(4), N4–N5 1.370(5), C2–C3 1.449(5), P1-Au1-Cl1 173.18(5); **14**: Ru1–Cp*$^{centr.}$ 1.8189(1), Ru1–$C_2N_2P^{centr.}$ 1.8219(8), P1–C1 1.779(2), N1–N2 1.383(2), C2–C3 1.464(3), N3–N4 1.321(3), N4–N5 1.315(3), C1-P1-C2 85.11(1); cod = 1,5-cyclooctadiene, tht = tetrahydrothiophene, Cp* = η^5-C_5Me_5.

conformation of the ligand as shown by the twist angle between the monophosphole unit and the 1,2,3-triazolium backbone (56° for **11** and 74° for **12**).

We also investigated the reactivity of **2** towards precursors for sandwich complexes. On addition of [Cp*Ru(MeCN)$_3$]PF$_6$ (Cp*=C$_5$Me$_5$) to **2** in C$_6$D$_6$ a clean reaction was observed to give the ruthenocene analogue **14** (Scheme 3d). Monitoring via ^{31}P{^{1}H} NMR spectroscopy shows that the reaction most likely proceeds via a η^1-N coordinating intermediate (Figure S85). The proposed intermediate gives rise to a singlet at δ = 87.7 ppm, which compares well with the chemical shift of η^1-N coordinating complexes **11** and **12** (vide supra). Upon heating the reaction mixture (65 °C, 1 d), this intermediate signal disappears, and a new signal arises at δ = −48.9 ppm, which was attributed to isolated (60 %) **14**. To the best of our knowledge, only two related complexes [Cp*M(3,5-R$_2$C$_2$N$_2$P)] (M=Fe, Ru; R=H, *t*Bu, Ph) have been reported, starting from the corresponding 1H-diazaphospholide anions.[33] Structural analysis of **14** revealed a sandwich structure with two coplanar (179°) 6π-ligands in an eclipsed conformation (Figure S82).[24] Coordination results in an elongation of the bond lengths of the C$_2$N$_2$P moiety (see the SI).

Next, we focused on diazadiphosphole **6**, as no complexes have been reported for this heterocycle class so far. Surprisingly, attempted transition metal coordination (e.g. with [Rh(cod)Cl]$_2$, [AuCl(tht)], [Cp*Ru(MeCN)$_3$]PF$_6$) resulted in intractable suspensions which exhibited no observable signals in the ^{31}P{^{1}H} NMR spectra. However, when adding Lewis acids BPh$_3$ or AlEt$_3$ to a solution of **6**, we observed the clean formation of compounds **15** and **16** (Scheme 4).[24]

The coordination of boron in **15** is reflected by the observation of two doublets in the ^{31}P{^{1}H} NMR spectrum at δ = 216.4 and 380.9 ppm and an ^{11}B{^{1}H} NMR singlet at δ = 2.8 ppm. The ^{31}P{^{1}H} NMR spectrum of **16** features very similar doublet resonances at δ = 217.5 and 364.2 ppm. Structural analysis confirmed the presence of a CN$_2$P$_2$ unit with BPh$_3$ (**15**) and AlEt$_3$ (**16**) binding to the outer nitrogen N5 (Figure 3). The switch in coordination from N4 in **12** to



Scheme 4. Coordination of diphosphole **6** affording compounds **15** and **16**; reagents and conditions: a) +1.0 eq. BPh$_3$; THF, −35 °C to r.t., 1 h; b) +1.0 eq. AlEt$_3$; toluene, −35 °C to r.t., 2 h.

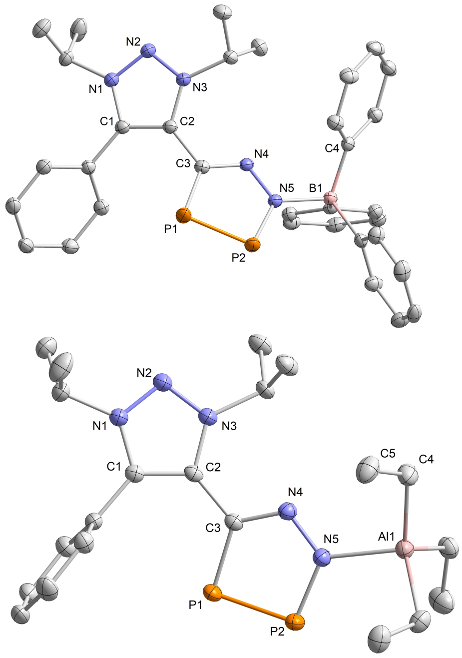


Figure 3. Solid-state molecular structures of **15** (top) and **16** (bottom). Hydrogen atoms omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: **15**: B1–N5 1.6191(2), B1–C4 1.6360(2), P1–P2 2.0809(5), P2–N5 1.6885(1), N4–N5 1.3406(1), B1-N5-N4 115.70(9), C3-P1-P2 89.64(4), P1-P2-N5 95.78(4); **16**: Al1–N5 1.9990(1), Al1–C4 1.9923(2), C5–C4 1.538(2), P1–P2 2.0739(6), P2–N5 1.6864(1), N4–N5 1.3395(2), Al1-N5-N4 120.17(9), C3-P1-P2 89.56(5), P1-P2-N5 96.44(5).

N5 in **15** and **16** is in line with our quantum chemical calculations, which predict a higher electronegativity of the N5 atom compared to the N4 atom in **6** (see Figure 2, NPA charge N5 −0.55e vs. N4 −0.27e, and the NRT analysis in Figure S94, SI). In **15**, the diphosphole plane is similarly twisted to the 1,2,3-triazole backbone (43°) as in the starting material **6** (43°), whereas in **16** the plane is twisted only 28°. The B1–N5 (1.6191(2) Å) bond length exceeds the sum of the covalent radii for a B–N (Σr_{BN} 1.56 Å) single bond, in line with a dative interaction.[23] In comparison, the Al1–N5 (1.9990(1) Å) bond length resembles that calculated for a Al–N(Σr_{AlN} 1.97 Å) single bond, suggesting a comparatively strong interaction.[23]

In conclusion, diazoalkenes are capable of activating *t*BuCP and P_4, thereby forming novel phospholes. The reaction of diazoalkenes with P_4 represents a rare example of P_4 activation by neutral, non-metalated carbon compounds. In contrast to the activation by carbenes, the products are formed through a (3+2) cycloaddition mechanism that correlates with the nucleophilicity of the diazoalkene. Strongly polarized (mesoionic) diazoalkenes are more effective in P_4 activation than weakly polarized diazoalkenes (e.g., those with a pyridine backbone). These findings provide straightforward design concepts for future small molecule activation processes. The resulting *3H*-1,2,4-diazamono-, and 1,2,3,4-diazadiphospholes were characterized by XRD and multinuclear NMR, and the analysis of their electronic properties was supported by DFT calculations. Significantly, we have investigated the donor capabilities and coordination modes of the new phospholes. By selecting different Lewis acids, we have demonstrated that the novel heterocycles successfully engage in distinct coordination sites (η^1-N-, η^1-P-, and η^5-coordination). The first boron and aluminium complexes of diazadiphospholes have been characterized. These findings augur well for a more comprehensive exploration of these new organophosphorus compounds in transition metal and main group chemistry.

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Conflict of Interest

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: Diazoalkenes · main-group chemistry · azaphospholes · transition-metal chemistry · nitrogen heterocycles

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