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Au(I)-mediated N₂-elimination from triazaphospholes: a one-pot synthesis of novel N₂P₂-heterocycles†

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Novel tosyl- and mesitylsulfonyl-substituted triazaphospholes were synthesized and structurally characterized. In an attempt to prepare the corresponding Au(I)-complexes with stoichiometric amounts of AuCl-S(CH₃)₂, cyclo-1,3-diphospha(III)-2,4-diazane-AuCl-complexes were obtained instead. Our here presented results offer a new strategy for preparing such coordination compounds selectively in a one-pot approach.

According to the isolobal relationship between a trivalent P-atom and a C-H fragment, the 3,5-disubstituted 3*H*-1,2,3,4-triazaphosphole derivatives of type **B** are the phosphorus congeners of the well-studied 1,2,3-triazoles **A** (Chart 1).

These λ³σ² phosphorus heterocycles can be prepared in a modular [3+2] cycloaddition reaction, starting from organic azides and phosphalkynes, as first reported independently by Carrié and Regitz in 1984.¹ Generally, only one regioisomer is formed thermally and selectively, without the need of a copper-catalyst. 3*H*-1,2,3,4-triazaphosphole derivatives have a conjugated π-system with a high degree of aromaticity.² Typically, a whole variety of alkyl- and aryl-substituted as well as donor-functionalized azides (*R*-N₃) can be used for the preparation of triazaphospholes, but also TMS-N₃ or even H-N₃.³ On the other hand, the substituent *R*' can only be varied to some extent due to the limited availability of the corresponding phosphalkynes, although less sterically demanding phosphalkynes can be generated *in situ* prior to the cycloaddition reaction.⁴

The first few reports on the coordination chemistry of triazaphospholes have only appeared in literature as recently as 2010.⁵ As ambidentate ligands the coordination to a metal center can proceed either *via* the phosphorus atom or the nitrogen donors N(1) or N(2) (Chart 1, C).⁶

Despite the few reported examples on the coordination chemistry of 3*H*-1,2,3,4-triazaphosphole derivatives, very little is known about their reactivity.⁷ *N*-Aryl/alkyl-substituted triazaphospholes are thermally robust and do not show any sign of reactivity upon irradiation with UV light (λ ≥ 280 nm).^{7a} We therefore anticipated that the hitherto unknown introduction of an electron-withdrawing substituent at the N(3)-atom might change the coordination properties and reactivity of the corresponding heterocycle considerably. As a matter of fact, the phosphorus-lacking *N*-sulfonyl-1,2,3-triazoles show interesting chemical transformations in the presence of [Rh₂(OAc)₄].^{8,9} Inspired by this fascinating reactivity, we started to transfer the chemistry of *N*-sulfonyl-1,2,3-triazoles to their phosphorus congeners and report here on our first results into this direction.

4-Methylbenzenesulfonylazide (**1a**) and mesitylsulfonylazide (**1b**) were prepared according to literature procedures.¹⁰ As anticipated, the 1,3-dipolar cycloaddition reaction of **1a/b** with ^tBuC≡P afforded the desired *N*-arylsulfonyl-substituted triazaphospholes **2a/b**, which were obtained as white solids in up to 85% yield after recrystallization from pentane (Scheme 1). Both compounds do not show any sign of decomposition when stored under inert conditions for several weeks.

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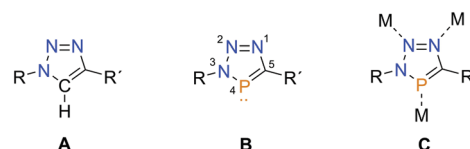
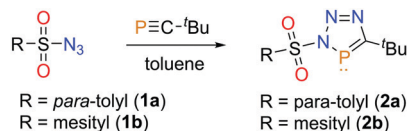


Chart 1 Triazaphosphole **A**, triazole **B** and possible coordination modes **C**.



Scheme 1 Synthesis of triazaphospholes **2a/b**.

The hitherto unknown *N*-arylsulfonyl-triazaphospholes show single resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR at $\delta(\text{ppm}) = 177.2$ (**2a**) and $\delta(\text{ppm}) = 175.2$ (**2b**) in DCM-d_2 . Although the *N*-arylsulfonyl group is supposed to be an electron withdrawing substituent, the resonances of **2a/b** in the $^{31}\text{P}\{^1\text{H}\}$ spectra are only slightly shifted more downfield compared to the literature known benzyl-substituted triazaphosphole **2c** ($\delta(\text{ppm}) = 171.4$, DCM-d_2 , see Fig. 2).^{1b,6b}

Single crystals of **2b** suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the compound at low temperature. The molecular structure is shown in Fig. 1 along with selected bond lengths and angles. Compound **2b** crystallizes in the monoclinic space group $P2_1/c$. While the NMR spectroscopic data of **2a/b** are very similar to triazaphosphole **2c**, the crystallographic characterization of **2b** reveals a clear influence of the *N*-arylsulfonyl group on the bond distances within the P-heterocycle (Fig. 2 and Table 1). As a matter of fact, the N(1)–N(2) distance in **2b** is longer than in the known compound **2c**, while the N(2)–N(3) distance is shorter. Moreover, both the C(1)–N(3) and P(1)–N(1) bond lengths in **2b** are longer, while the C(1)–P(1) bond lengths is shorter compared to the situation in **2c**.^{6b}

As also observed for *N*-sulfonamides, the N(1)–S(1) bond is with 1.7108(16) significantly shorter than the predicted value for pure S–N single bonds, indicating the presence of a resonance structure with a partial S=N double bond (Fig. 2).¹¹

Accordingly, the structural parameters are in line with a significant disruption of the aromaticity in **2b** along with more localized bonds (Fig. 2).

Apparently, the electronic structures of the hitherto unknown *N*-sulfonyl-substituted phosphorus heterocycles **2a/b** differ considerably from classical aryl- and alkyl-functionalized triazaphospholes. This should consequently also lead to a pronounced different chemical reactivity of **2a/b** in comparison

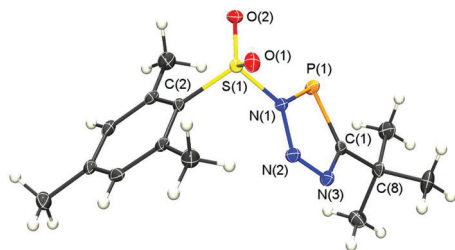
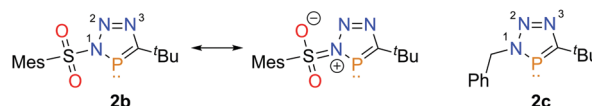


Fig. 1 Molecular structure of **2b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)–N(1): 1.7047(16), N(1)–N(2): 1.364(2), N(2)–N(3): 1.298(2), N(3)–C(1): 1.369(2), C(1)–P(1): 1.715(2), N(1)–S(1): 1.7108(16), S(1)–O(1): 1.4232(14), S(1)–O(2): 1.4280(14), N(1)–P(1)–C(1): 85.35(9).

Fig. 2 Resonance structures of **2b** and comparison of **2b** with **2c**.Table 1 Comparison of selected bond lengths in **2b** and **2c**^{6b}

	P(1)–C(1)	P(1)–N(1)	N(1)–N(2)	N(2)–N(3)	N(3)–C(1)
2b	1.7047(16)	1.7047(16)	1.364(2)	1.298(2)	1.369(2)
2c	1.7128(17)	1.6834(19)	1.340(2)	1.314(2)	1.351(3)

to **2c**. As we were primarily interested in the coordination chemistry of aromatic $\lambda^3\sigma^2$ -phosphorus compounds, also with respect to applications, we first considered the reaction of **2a/b** with $\text{AuCl}\cdot\text{S}(\text{CH}_3)_2$. It is well documented that phosphorus in low-coordination readily forms complexes with $\text{Au}(i)$.¹²

Interestingly, a spontaneous and vigorous gas-evolution is observed when dichloromethane is added to a 1 : 1 mixture of either **2a** or **2b** and $\text{AuCl}\cdot\text{S}(\text{CH}_3)_2$ at room temperature. The gas was identified as dinitrogen by means of GC-TCD. For triazaphosphole **2b** (R = mesityl), the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the slightly yellow reaction mixture shows only two resonances at $\delta(\text{ppm}) = 133.9$ and $\delta(\text{ppm}) = 11.6$ in a ratio of approximately 4 : 1. Stirring the reaction solution for 2 h at $T = 60^\circ\text{C}$ immediately after addition of the solvent leads, however, to a ratio of 20 : 1 (Fig. 3b). The isolation of the pure, air and moisture sensitive product **3b** in 36% yield was achieved by washing the reaction mixture with toluene. For **2a** (R = *p*-tolyl) the reaction seems to be less selective (see Fig. S10, ESI†).

Crystals of **3a** and **3b**, suitable for X-ray diffraction, could be obtained from both reaction mixtures. Dissolving the crystalline material of **3b** in dichloromethane gave indeed the identical resonance of the major product observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture (Fig. 3c). Much to our surprise, the crystallographic characterization of **3a** and **3b** reveals the formation of a *cyclo*-1,3-diphospha(m)-2,4-diazane, rather than the presence of a simple triazaphosphole-Au(i) complex. Moreover, the *cyclo*-diphosphadiazane serves as a ligand, which binds to a total of two $\text{Au}(i)\text{Cl}$ fragments *via* both phosphorus donors. The molecular structure of **3b** is depicted in Fig. 4, along with selected bond lengths and angles (for the

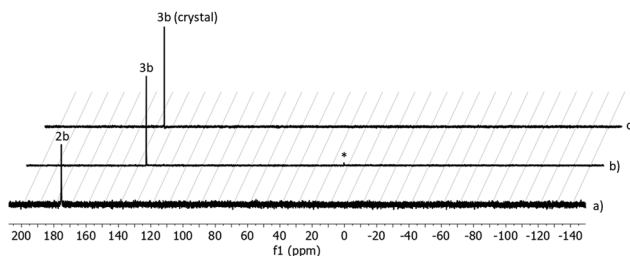


Fig. 3 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2b** (a), the reaction mixture (b) and of the obtained crystals (c). (*): unidentified species.



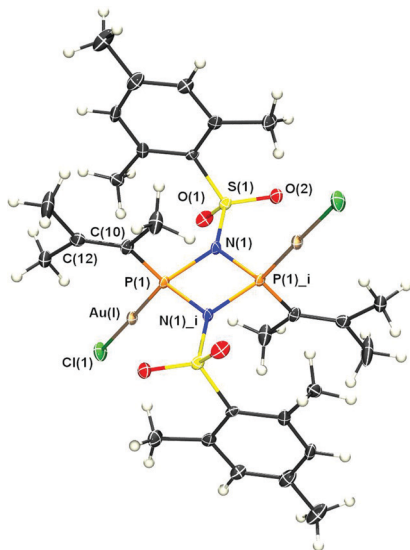
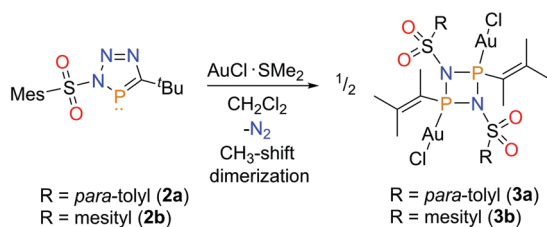


Fig. 4 Molecular structure of **3b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)–N(1): 1.730(3), N(1)–P(1)_i: 1.727(3), N(1)–S(1): 1.675(3), P(1)–Au(1): 2.2087(11), P(1)–C(10): 1.778(4), C(10)–C(12): 1.352(6), N(1)–P(1)–N(1)_i: 79.87(18), P(1)–N(1)–P(1)_i: 100.13(18).

single crystal X-ray structure of **3a** see Fig. S2, ESI†). Based on the structural characterization of **3a/b**, the novel and, in the case of **2b**, highly selective “one-pot” reaction with stoichiometric amounts of AuCl·S(CH₃)₂ under formation of a dinuclear *cyclo*-diphosphadiazane–Au(I) complex is summarized in Scheme 2.

As a matter of fact, such N₂P₂ heterocycles are most commonly obtained as 1,3-dichloro-*cyclo*-1,3-diphospha(m)-2,4-diazanes of the type [ClP(μ-NR)₂PCl] by reacting primary amines with PCl₃.¹³ Subsequent reaction with appropriate nucleophiles leads to *cyclo*-diphosphadiazanes of the type [R'P(μ-NR)₂PR'] (R' = alkyl, aryl; OR, NR''₂, NHR''), which can then be converted to the corresponding coordination compounds by reaction with an appropriate metal precursor.¹⁴ Importantly, there are no reports on cyclodiphospha(m)zanes featuring the exact substitution pattern of **3a/b**, potentially due to synthetic difficulties.¹⁵ Therefore, our here described approach offers access to novel P₂N₂ heterocycles, which were so far not accessible.

3b crystallizes in the space group *P2*₁/*c*. In **3b** (as well as in **3a**, Fig. S2, ESI†) a perfectly planar P₂N₂-ring with both the R-groups and the Au(I)Cl-fragments at the phosphorus atoms pointing in opposite directions (*trans* isomer) is present.



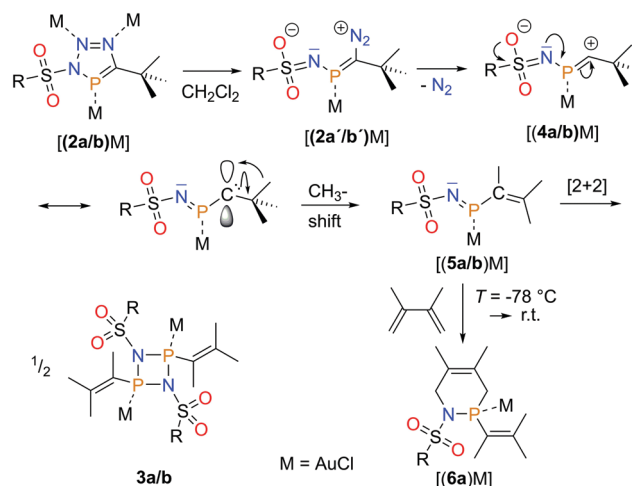
Scheme 2 Synthesis of *cyclo*-1,3-diphospha-2,4-diazane–Au(I)-complexes **3a/b**.

As observed for other *cyclo*-1,3-diphosphadiazanes, the nitrogen atoms are almost planar (sum of bond angles 359.3°), while the λ³,σ³-phosphorus atoms are pyramidally coordinated and bind each *via* the lone pair to the Au(I) center.^{14a} The P–N bond lengths of 1.730(3) Å and 1.727(3) Å are slightly shorter than observed in other *cyclo*-diphosphadiazanes, which might be due to a reduced electrostatic repulsion between the P- and N-lone pairs, which are involved in an interaction with the metal center and the –SO₂R substituent, respectively.

The most striking feature of **3b** (and **3a**, Fig. S2, ESI†) is, however, that the ^tBu-group of the original triazaphosphole was converted into an iso-pentenyl substituent. Obviously, a CH₃-shift took place during the conversion **2a/b** → **3a/b**, which implies the formation of a carbene intermediate. This has also been observed by Fokin and co-worker during the Rh-catalyzed denitrogenative transformation of a ^tBu-substituted 1-sulfonyl-1,2,3-triazole into a tetrasubstituted iminoalkene.⁸

The rather selective conversion **2a/b** → **3a/b** requires the presence of stoichiometric amounts of AuCl·S(CH₃)₂. We could not observe the formation of any *cyclo*-diphosphadiazane upon heating **2a/b** in the absence of Au(I). Moreover, the presence of the electron withdrawing *N*-sulfonyl-group at N(3) is crucial for the dinitrogenative generation of **3a/b**, as the PhCH₂-substituted triazaphosphole **2c** does not undergo the transformation to the corresponding N₂P₂-heterocycle.

Based on NMR-spectroscopic data, we propose the following mechanism for the conversion of the *N*-sulfonyl-triazaphosphole into the corresponding Au(I)-complex: the Au(I)Cl-fragment first coordinates to the donor-atoms of the phosphorus heterocycle in a dynamic exchange process (Scheme 3).¹⁶ Due to the electron-withdrawing nature of the *N*-sulfonyl-group, the aromaticity of the triazaphosphole is strongly disrupted and ring-opening to [(2a'/b')AuCl] is facilitated. Loss of dinitrogen gives the zwitterionic species [(4a/b)AuCl], for which a neutral resonance structure exist. According to the HSAB concept, we anticipate that the Au(I)-fragment coordinates exclusively to the remaining soft phosphorus atom in [(4a/b)AuCl]. The neutral species is an



Scheme 3 Proposed mechanism for the formation of **3a/b**.



iminophosphine-carbene, which undergoes a [1,2]-CH₃-shift to the more stable iminophosphine [(5a/b)AuCl]. Iminophosphinines are known to form dimers and even trimers from the parent monomer depending on the substituents on both the phosphorus and nitrogen atom. Dimerization of [(5a/b)AuCl], especially in presence of electron-withdrawing sulfonyl groups then leads to the observed main product 3a/b (Scheme 3).¹⁷

In order to identify the reactive iminophosphine [(5a/b)AuCl] as an intermediate in the proposed mechanism, *N*-tosyl-triazaphosphole 2a and AuCl-SMe₂ were cooled to *T* = -196 °C and a solution of dimethylbutadiene as a trapping reagent in dichloromethane was condensed into the reaction vessel. The solution was first stored at *T* = -78 °C and then slowly warmed to room temperature over 6–8 hours. Subsequent ³¹P{¹H} NMR spectroscopy at room temperature showed only one major phosphorus resonance at δ(ppm) = 104.0. Analysis of the product by means of ESI-MS indeed provided evidence for the expected trapping product [(6a)AuCl] (Scheme 3). Further confirmation for cyclodiphosphazane formation *via* dimerization of two iminophosphines is provided by a cross-reaction of a 1 : 1 mixture of 2a and 2b with AuCl-SMe₂ in DCM. In this case the ³¹P{¹H} NMR of the reaction mixture showed the formation of 3a and 3b as well as a third species at δ(ppm) = 130.7, which we tentatively assigned to a mixed N-SO₂-Tol/N-SO₂-Mes substituted P₂N₂ ring. A similar cross reactivity in phosphazane chemistry has recently been described by Wright *et al.* as the authors also found evidence for the transient formation of monomeric phosphazane intermediates.¹⁸

We could demonstrate for the first time that 3*H*-1,2,3,4-triazaphosphole derivatives, containing electron-withdrawing *N*-sulfonyl-groups at the N³ atom, are synthetically accessible. These phosphorus heterocycles show a remarkable different reactivity compared to their classical alkyl- or aryl-substituted counterparts. Interestingly, the hitherto unknown *N*-sulfonyl-1,2,3,4-triazaphospholes undergo a highly selective and unprecedented transformation to *cyclo*-1,3-diphospha(m)-2,4-diazane-Au(i) complexes in the presence of stoichiometric amounts of AuCl-S(CH₃)₂ and loss of N₂. Single crystal X-ray diffraction studies show, that the *trans*-isomer of the substituted N₂P₂ heterocycle has been generated, while NMR-spectroscopic and mass-spectrometric investigations give insight into the mechanism of its formation. Our results pave the way to explore the chemistry of *N*-sulfonyl-substituted triazaphospholes in detail and provide a first step in transferring the fascinating chemistry, reported for the phosphorus-lacking *N*-sulfonyl-1,2,3-triazoles, to their isolobal phosphorus congeners.

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Conflicts of interest

There are no conflicts to declare.

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