



Cite this: *Chem. Commun.*, 2022, 58, 310

Received 3rd November 2021,  
Accepted 29th November 2021

DOI: 10.1039/d1cc06205k

rsc.li/chemcomm

# Au(I)-mediated N<sub>2</sub>-elimination from triazaphospholes: a one-pot synthesis of novel N<sub>2</sub>P<sub>2</sub>-heterocycles†

Erlin Yue,<sup>‡</sup> Lea Dettling,<sup>‡</sup> Julian A. W. Sklorz,<sup>a</sup> Selina Kaiser,<sup>a</sup> Manuela Weber<sup>a</sup> and Christian Müller<sup>‡</sup>\*

**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(CH<sub>3</sub>)<sub>2</sub>, 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 λ<sup>3</sup>σ<sup>2</sup> 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.<sup>1</sup> 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.<sup>2</sup> Typically, a whole variety of alkyl- and aryl-substituted as well as donor-functionalized azides (*R*-N<sub>3</sub>) can be used for the preparation of triazaphospholes, but also TMS-N<sub>3</sub> or even H-N<sub>3</sub>.<sup>3</sup> 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.<sup>4</sup>

The first few reports on the coordination chemistry of triazaphospholes have only appeared in literature as recently as 2010.<sup>5</sup> 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).<sup>6</sup>

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.<sup>7</sup> *N*-Aryl/alkyl-substituted triazaphospholes are thermally robust and do not show any sign of reactivity upon irradiation with UV light (λ ≥ 280 nm).<sup>7a</sup> 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 [Rh<sub>2</sub>(OAc)<sub>4</sub>].<sup>8,9</sup> 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.<sup>10</sup> As anticipated, the 1,3-dipolar cycloaddition reaction of **1a/b** with <sup>t</sup>BuC≡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.

<sup>a</sup> Freie Universität Berlin, Institute of Chemistry and Biochemistry, Fabeckstr. 34/36, Berlin 14195, Germany. E-mail: c.mueller@fu-berlin.de, yueerlin@yau.edu.cn

<sup>b</sup> Shaanxi Key Laboratory of Chemical Reaction Engineering, Key Laboratory of New Energy & New Functional Materials, College of Chemistry and Chemical Engineering, Yan'an University, Yan'an, Shaanxi 716000, People's Republic of China

† Electronic supplementary information (ESI) available. CCDC 1983603, 1983601 and 1983602. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1cc06205k

‡ These authors have contributed equally.

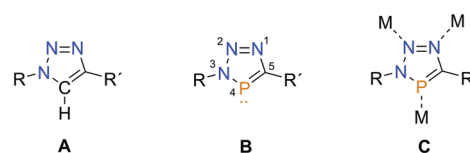
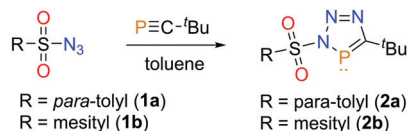


Chart 1 Triazaphosphole **A**, triazole **B** and possible coordination modes **C**.



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  $\text{DCM-d}_2$ . 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** ( $\delta(\text{ppm}) = 171.4$ ,  $\text{DCM-d}_2$ , see Fig. 2).<sup>1b,6b</sup>

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**.<sup>6b</sup>

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).<sup>11</sup>

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

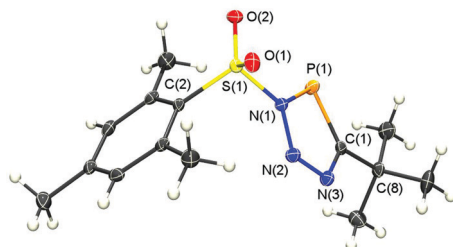
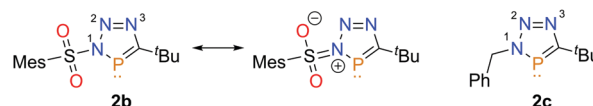


Fig. 1 Molecular structure of **2b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)–N(1): 1.7047(16), N(1)–N(2): 1.364(2), N(2)–N(3): 1.298(2), N(3)–C(1): 1.369(2), C(1)–P(1): 1.715(2), N(1)–S(1): 1.7108(16), S(1)–O(1): 1.4232(14), 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**<sup>6b</sup>

	P(1)–C(1)	P(1)–N(1)	N(1)–N(2)	N(2)–N(3)	N(3)–C(1)
<b>2b</b>	1.7047(16)	1.7047(16)	1.364(2)	1.298(2)	1.369(2)
<b>2c</b>	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  $\text{Au(I)}$ .<sup>12</sup>

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(III)-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  $\text{Au(I)Cl}$  fragments *via* both phosphorus donors. The molecular structure of **3b** is depicted in Fig. 4, along with selected bond lengths and angles (for the

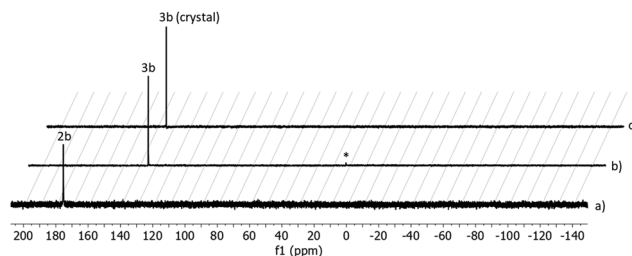
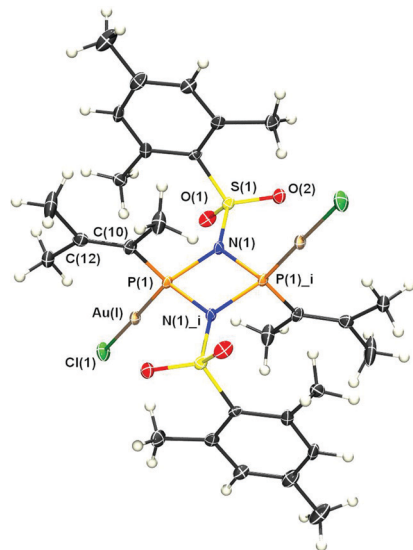


Fig. 3  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **2b** (a), the reaction mixture (b) and of the obtained crystals (c). (\*): unidentified species.



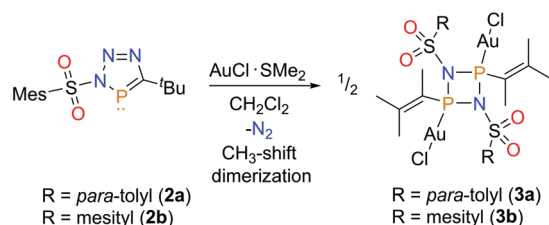


**Fig. 4** Molecular structure of **3b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)–N(1): 1.730(3), N(1)–P(1)<sub>i</sub>: 1.727(3), N(1)–S(1): 1.675(3), P(1)–Au(1): 2.2087(11), P(1)–C(10): 1.778(4), C(10)–C(12): 1.352(6), N(1)–P(1)–N(1)<sub>i</sub>: 79.87(18), P(1)–N(1)–P(1)<sub>i</sub>: 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(CH<sub>3</sub>)<sub>2</sub> under formation of a dinuclear *cyclo*-diphosphadiazane–Au(I) complex is summarized in Scheme 2.

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

**3b** crystallizes in the space group *P2<sub>1</sub>/c*. In **3b** (as well as in **3a**, Fig. S2, ESI†) a perfectly planar P<sub>2</sub>N<sub>2</sub>-ring with both the R-groups and the Au(I)Cl-fragments at the phosphorus atoms pointing in opposite directions (*trans* isomer) is present.



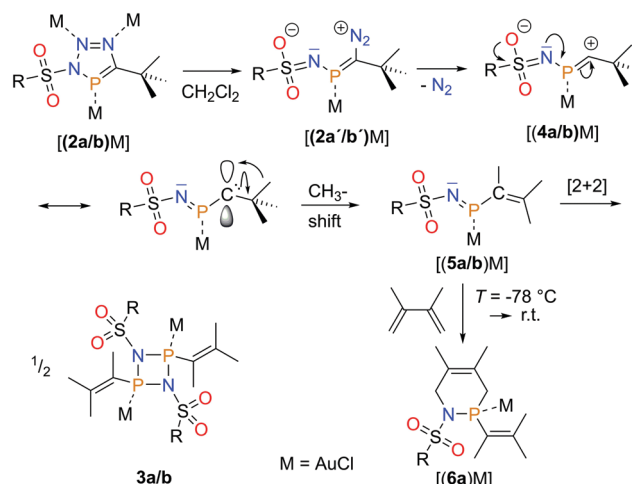
**Scheme 2** Synthesis of *cyclo*-1,3-diphospha-2,4-diazane–Au(I)-complexes **3a/b**.

As observed for other *cyclo*-1,3-diphosphadiazanes, the nitrogen atoms are almost planar (sum of bond angles 359.3°), while the λ<sup>3</sup>,σ<sup>3</sup>-phosphorus atoms are pyramidally coordinated and bind each *via* the lone pair to the Au(I) center.<sup>14a</sup> 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 –SO<sub>2</sub>R substituent, respectively.

The most striking feature of **3b** (and **3a**, Fig. S2, ESI†) is, however, that the ‘Bu-group of the original triazaphosphole was converted into an iso-pentenyl substituent. Obviously, a CH<sub>3</sub>-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 ‘Bu-substituted 1-sulfonyl-1,2,3-triazole into a tetrasubstituted iminoalkene.<sup>8</sup>

The rather selective conversion **2a/b** → **3a/b** requires the presence of stoichiometric amounts of AuCl·S(CH<sub>3</sub>)<sub>2</sub>. 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 PhCH<sub>2</sub>-substituted triazaphosphole **2c** does not undergo the transformation to the corresponding N<sub>2</sub>P<sub>2</sub>-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).<sup>16</sup> 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]-CH<sub>3</sub>-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).<sup>17</sup>

In order to identify the reactive iminophosphine [(5a/b)AuCl] as an intermediate in the proposed mechanism, *N*-tosyl-triazaphosphole **2a** and AuCl-SMe<sub>2</sub> 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 <sup>31</sup>P{<sup>1</sup>H} 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-SMe<sub>2</sub> in DCM. In this case the <sup>31</sup>P{<sup>1</sup>H} 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-SO<sub>2</sub>-Tol/N-SO<sub>2</sub>-Mes substituted P<sub>2</sub>N<sub>2</sub> 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.<sup>18</sup>

We could demonstrate for the first time that 3*H*-1,2,3,4-triazaphosphole derivatives, containing electron-withdrawing *N*-sulfonyl-groups at the N<sup>3</sup> 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(CH<sub>3</sub>)<sub>2</sub> and loss of N<sub>2</sub>. Single crystal X-ray diffraction studies show, that the *trans*-isomer of the substituted N<sub>2</sub>P<sub>2</sub> 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.

E. Y and C. M. are grateful for financial support provided by the Sino-German (CSC-DAAD) Postdoc Scholarship Program (57251553).

## Conflicts of interest

There are no conflicts to declare.

## Notes and references

- (a) Y. Y. C. Yeung Lam Ko and R. Carrié, *J. Chem. Soc., Chem. Commun.*, 1984, 1640; (b) Y. Y. C. Yeung Lam, Ko, R. Carrié, A. Muench and G. Becker, *J. Chem. Soc., Chem. Commun.*, 1984, 1634; (c) W. Rösch and M. Regitz, *Angew. Chem.*, 1984, **96**, 898; *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 900.
- L. Nyulászi, *Chem. Rev.*, 2001, **101**, 1229.
- See for example: (a) T. Allspach, M. Regitz, G. Becker and W. Becker, *Synthesis*, 1986, 31; (b) M. Regitz and P. Binger, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1484; (c) J. A. W. Sklorz and C. Müller, *Eur. J. Inorg. Chem.*, 2016, 595.
- J.-C. Guillemin, T. Janati and J.-M. Denis, *J. Org. Chem.*, 2001, **66**, 7864.
- (a) S. L. Choong, C. Jones and A. Stasch, *Dalton Trans.*, 2010, **39**, 5774; (b) S. L. Choong, A. Nafady, A. Stasch, A. M. Bond and C. Jones, *Dalton Trans.*, 2013, **42**, 7775.
- (a) J. A. W. Sklorz, S. Hoof, M. G. Sommer, F. Weißer, M. Weber, J. Wiecko, B. Sarkar and C. Müller, *Organometallics*, 2014, **33**, 511; (b) J. A. W. Sklorz, S. Hoof, N. Rades, N. De Rycke, L. Könczöl, D. Szieberth, M. Weber, J. Wiecko, L. Nyulászi, M. Hissler and C. Müller, *Chem. – Eur. J.*, 2015, **21**, 11096.
- (a) W. Rösch, T. Facklam and M. Regitz, *Tetrahedron*, 1987, **43**, 3247; (b) J. Kerth, U. Werz and G. Maas, *Tetrahedron*, 2000, **56**, 35; (c) M. Papke, L. Dettling, J. A. W. Sklorz, D. Szieberth, L. Nyulászi and C. Müller, *Angew. Chem.*, 2017, **129**, 16706; *Angew. Chem. Int. Ed.*, 2017, **56**, 16484.
- N. Selander, B. T. Worrell and V. V. Fokin, *Angew. Chem.*, 2012, **124**, 13231; *Angew. Chem. Int. Ed.*, 2012, **51**, 13054.
- For recent examples on rhodium(ii)-catalyzed reactions of *N*-sulfonyl-1,2,3-triazoles: (a) K. Pal, R. K. Shukla and C. M. Volle, *Org. Lett.*, 2017, **19**, 5764; (b) T. Miura, Q. Zhao and M. Murakami, *Angew. Chem., Int. Ed.*, 2017, **56**, 16645; (c) J. O. Strelnikova, N. V. Rostovskii, G. L. Starova, A. F. Khlebnikov and M. S. Novikov, *J. Org. Chem.*, 2018, **83**, 11232; (d) Y. Lv, A. A. Ogunlana, H. Li, D. Gao, C. Wang and X. Bao, *Catal. Sci. Technol.*, 2018, **8**, 3379; (e) C.-Z. Zhu, Y. Wei and M. Shi, *Org. Chem. Front.*, 2019, **6**, 2884; (f) J. Ge, X. Wu and X. Bao, *Chem. Commun.*, 2019, **55**, 6090; (g) N. Kahar, P. Jadhav, R. V. R. Reddy and S. Dawande, *Chem. Commun.*, 2020, **56**, 1207.
- J. Wang, J. Mei, E. Zhao, Z. Song, A. Qin, J. Z. Sun and B. Z. Tang, *Macromolecules*, 2012, **45**, 7692.
- F. A. Cotton and P. F. Stokely, *J. Am. Chem. Soc.*, 1970, **92**, 294.
- See for example: (a) N. Mézailles, L. Ricard, F. Mathey and P. Le Floch, *Eur. J. Inorg. Chem.*, 1999, 2233; (b) M. Rigo, L. Hettmanczyk, F. J. L. Heutz, S. Hohloch, M. Lutz, B. Sarkar and C. Müller, *Dalton Trans.*, 2017, **46**, 86.
- (a) A. Michaelis and G. Schroeter, *Ber. Dtsch. Chem. Ges.*, 1894, **27**, 490; (b) A. Schulz, A. Villinger and A. Westenkirchner, *Inorg. Chem.*, 2013, **52**, 11457; (c) J. Bresien, A. Hinz, A. Schulz, T. Suhrbier, M. Thomas and A. Villinger, *Chem. – Eur. J.*, 2017, **23**, 14738.
- See for example: (a) M. M. Siddiqui, J. T. Mague and M. S. Balakrishna, *Inorg. Chem.*, 2015, **54**, 6063; (b) M. S. Balakrishna, V. Sreenivasa Reddy and S. S. Krishnamurthy, *Coord. Chem. Rev.*, 1994, **129**, 1; (c) G. G. Briand, T. Chivers and M. Krahn, *Coord. Chem. Rev.*, 2002, **233–234**, 237; (d) M. S. Balakrishna, in *Copper(i) Chemistry of Phosphines, Functionalized Phosphines, and Phosphorus Heterocycles*, ed. M. S. Balakrishna, Elsevier, 2019, ch. 11, pp. 345–373; (e) A. J. Plajer, J. Zhu, P. Pröhm, F. J. Rizzuto, U. F. Keyser and D. S. Wright, *J. Am. Chem. Soc.*, 2020, **142**, 1029.
- For related species see: (a) A. Baceiredo, G. Bertrand, J.-P. Majoral and K. B. Dillon, *J. Chem. Soc., Chem. Commun.*, 1985, 562; (b) F. L. Bowden, A. T. Dronsfield, R. N. Haszeldine and D. R. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1973, 516.
- Low-temperature <sup>31</sup>P{<sup>1</sup>H} NMR measurements indicate a coordination of the Au(i)Cl fragment to the ambidentate triazaphosphole **2b**. See ESI†.
- See for example: (a) E. Niecke, W. Flick and S. Pohl, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 309; (b) E. Niecke, R. Rüger and W. W. Schoeller, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 10346; (c) N. Burford, T. S. Cameron, K. D. Conroy, B. Ellis, M. Lumsden, C. L. B. Macdonald, R. McDonald, A. D. Phillips, P. J. Ragogna, R. W. Schurko, D. Walsh and R. E. Wasylshen, *J. Am. Chem. Soc.*, 2002, **124**, 14012; (d) M. Lehmann, A. Schulz and A. Villinger, *Struct. Chem.*, 2011, **22**, 35; (e) M. Kuprat, M. Lehmann, A. Schulz and A. Villinger, *Inorg. Chem.*, 2011, **50**, 5784; (f) E. Niecke, M. Nieger and F. Reichert, *Angew. Chem.*, 1988, **100**, 1783.
- A. J. Plajer, K. Bold, F. J. Rizzuto, R. García-Rodríguez, T. K. Ronson and D. S. Wright, *Dalton Trans.*, 2017, **46**, 12775.

