ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

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_2-elimination from triazaphospholes: a one-pot synthesis of novel N_2P_2-heterocycles†

Erlin Yue, ‡[ab] Lea Dettling, ‡[a] Julian A. W. Sklorz,[a] Selina Kaiser,[a] Manuela Weber[a] and Christian Müller *[a]

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$_3$)$_2$, *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 $\lambda^3\sigma^2$ phosphorus heterocycles can be prepared in a modular [3+2] cycloaddition reaction, starting from organic azides and phosphaalkynes, 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*-N$_3$) can be used for the preparation of triazaphospholes, but also TMS-N$_3$ or even H–N$_3$.[3] On the other hand, the substituent *R*′ can only be varied to some extend due to the limited availability of the corresponding phosphaalkynes, although less sterically demanding phosphaalkynes 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 ($\lambda \geq 280$ 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 [Rh$_2$(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 ^{t}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.

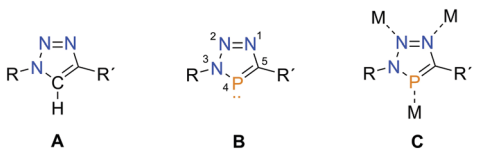
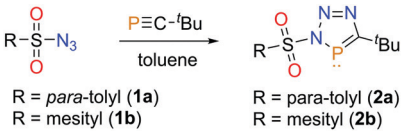


Chart 1 Triazaphosphole **A**, triazole **B** and possible coordination modes **C**.

[a] *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*
[b] *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.



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

The hitherto unknown *N*-arylsulfonyl-triazaphospholes show single resonances in the $^{31}P\{^1H\}$ NMR at δ(ppm) = 177.2 (**2a**) and δ(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 $^{31}P\{^1H\}$ spectra are only slightly shifted more downfield compared to the literature known benzyl-substituted triazaphosphole **2c** (δ(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

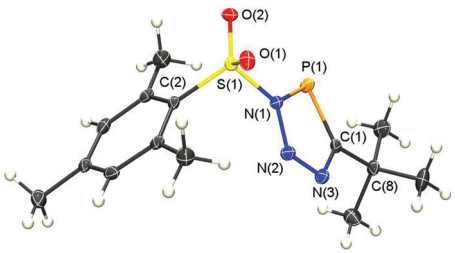


Fig. 1 Molecular structure of **2b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)–N(1): 1.7047(16), N(1)–N(2): 1.364(2), N(2)–N(3): 1.298(2), N(3)–C(1): 1.369(2), C(1)–P(1): 1.715(2), N(1)–S(1): 1.7108(16), S(1)–O(1): 1.4232(14),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

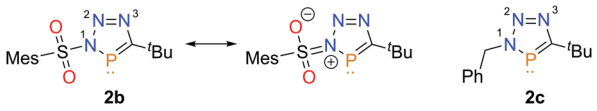


Fig. 2 Resonance structures of **2b** and comparison of **2b** with **2c**.

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 AuCl·S(CH_3)$_2$. It is well documented that phosphorus in low-coordination readily forms complexes with 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 AuCl·S(CH_3)$_2$ at room temperature. The gas was identified as dinitrogen by means of GC-TCD. For triazaphosphole **2b** (R = mesityl), the $^{31}P\{^1H\}$ NMR spectrum of the slightly yellow reaction mixture shows only two resonances at δ(ppm) = 133.9 and δ(ppm) = 11.6 in a ratio of approximately 4 : 1. Stirring the reaction solution for 2 h at T = 60 °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 $^{31}P\{^1H\}$ 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 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

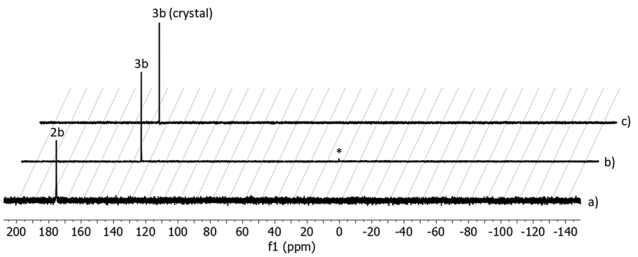


Fig. 3 $^{31}P\{^1H\}$ NMR spectra of **2b** (a), the reaction mixture (b) and of the obtained crystals (c). (*): unidentified species.

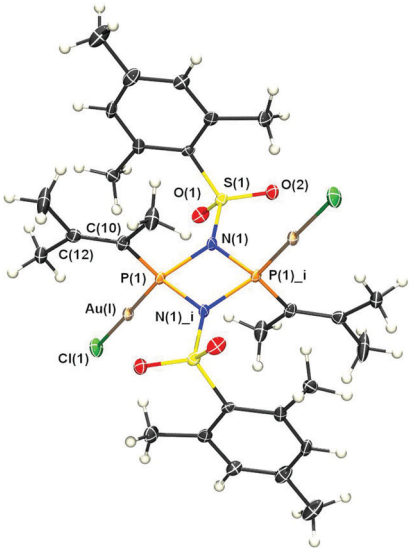
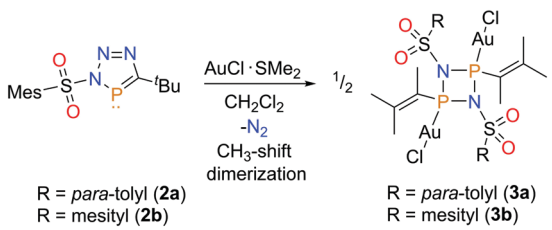


Fig. 4 Molecular structure of **3b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angels (°): P(1)–N(1): 1.730(3), N(1)–P(1)_i: 1.727(3), N(1)–S(1): 1.675(3), P(1)–Au(1): 2.2087(11), P(1)–C(10): 1.778(4), C(10)–C(12): 1.352(6). N(1)–P(1)–N(1)_i: 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(CH_3)$_2$ under formation of a dinuclear *cyclo*-diphosphadiazane–Au(I) complex is summarized in Scheme 2.

As a matter of fact, such N_2P_2 heterocylces are most commonly obtained as 1,3-dichloro-*cyclo*-1,3-diphospha(III)-2,4-diazanes of the type [ClP(μ-NR)$_2$PCl] by reacting primary amines with PCl_3.[13] Subsequent reaction with appropriate nucleophiles leads to *cyclo*-diphosphadiazanes of the type [R′P(μ-NR)$_2$PR′] (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(III)zanes featuring the exact susbstitution pattern of **3a/b**, potentially due to synthetic difficulties.[15] Therefore, our here described approach offers access to novel P_2N_2 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 P_2N_2-ring with both the R-groups and the Au(I)Cl-fragments at the phosphorus atoms pointing in opposite directions (*trans* isomer) is present.



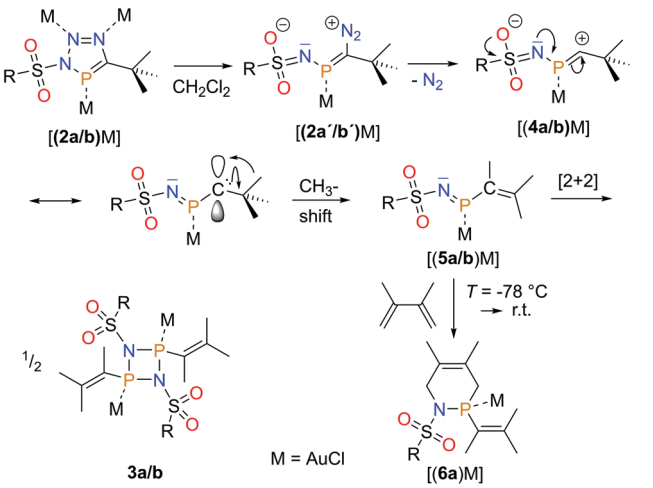
Scheme 2 Synthesis of *cyclo*-1,3-diphospha-2,4-diazane-Au(I)-complexes **3a/b**.

As observed for other *cyclo*-1,3-diphosphadiazanes, the nitrogen atoms are almost planar (sum of bond angles 359.3°), while the λ^3,σ^3-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*-diphosphadizanes, 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_2R substituent, respectively.

The most striking feature of **3b** (and **3a**, Fig. S2, ESI†) is, however, that the ^{t}Bu-group of the original triazaphosphole was converted into an iso-pentenyl substituent. Obviously, a CH_3-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 ^{t}Bu-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(CH_3)$_2$. 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 $PhCH_2$-substituted triazaphosphole **2c** does not undergo the transformation to the corresponding N_2P_2-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]-CH_3-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·SMe_2 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 $^{31}P\{^1H\}$ 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·SMe_2 in DCM. In this case the $^{31}P\{^1H\}$ 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-SO_2-Tol/N-SO_2-Mes substituted P_2N_2 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 N^3 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(III)-2,4-diazane-Au(I) complexes in the presence of stoichiometric amounts of AuCl·$S(CH_3)_2$ and loss of N_2. Single crystal X-ray diffraction studies show, that the *trans*-isomer of the substituted N_2P_2 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

1 (*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.
2 L. Nyulászi, *Chem. Rev.*, 2001, **101**, 1229.
3 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.
4 J.-C. Guillemin, T. Janati and J.-M. Denis, *J. Org. Chem.*, 2001, **66**, 7864.
5 (*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.
6 (*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.
7 (*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.
8 N. Selander, B. T. Worrell and V. V. Fokin, *Angew. Chem.*, 2012, **124**, 13231; *Angew. Chem. Int. Ed.*, 2012, **51**, 13054.
9 For recent examples on rhodium(II)-catalyzed reactions of *N*-sulfonyl-1,2,3-triazoles: (*a*) K. Pal, R. K. Shukla and C. M. R. Volla, *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.
10 J. Wang, J. Mei, E. Zhao, Z. Song, A. Qin, J. Z. Sun and B. Z. Tang, *Macromolecules*, 2012, **45**, 7692.
11 F. A. Cotton and P. F. Stokely, *J. Am. Chem. Soc.*, 1970, **92**, 294.
12 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.
13 (*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.
14 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.
15 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.
16 Low-temperature $^{31}P\{^1H\}$ NMR measurements indicate a coordination of the Au(I)Cl fragment to the ambidentate triazaphosphole 2b. See ESI†.
17 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. Wasylishen, *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.
18 A. J. Plajer, K. Bold, F. J. Rizzuto, R. García-Rodríguez, T. K. Ronson and D. S. Wright, *Dalton Trans.*, 2017, **46**, 12775.