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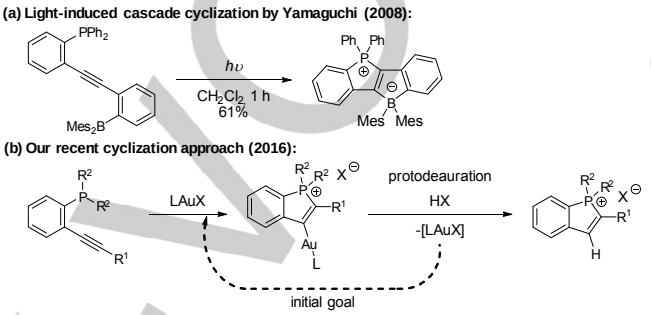
Direct Access to π-Extended Phosphindolium Salts by Simple Proton-Induced Cyclization of (*o*-Alkynylphenyl)phosphanes

Sebastian Arndt,[a] Max M. Hansmann,[a] Frank Rominger,[a] Matthias Rudolph[a] and A. Stephen K. Hashmi*[a,b]

Abstract: A detailed synthetic and mechanistic study for the synthesis of phosphindolium salts from easy accessible (*o*-alkynylphenyl)phosphanes is reported. Mechanistic investigation indicates a fast protonation at phosphorus as evidenced by the isolation of the phosphonium intermediate, followed by a protophosphonylation reaction across the alkyne moiety. DFT calculations support our mechanistic proposal and indicate a reaction highly exergonic compared to our recently reported phosphinoauration. Photophysical measurements recorded fluorescence quantum yields up to 97% in solution for the phosphindolium core and fluorescence was observed in the solid state.

In the past decade, phosphorus-containing π-extended systems such as non-fused phospholes[1,2] and benzophospholes[3-6] have attracted extensive interest as materials for organic electronics, reasoned by their unique photophysical and electronical properties. Phospholes have been widely explored in the recent years and research has led to phosphole-cored dendrimers, phosphole-based polymers, fused phosphole-derivatives and other phosphole congeners.[1-7] As part of our research, we are specifically interested in phosphindolium salts. The limited reports on this substrate class[6,8–10] can be rationalized by the common synthetic strategies towards phosphindole systems. Most of the strategies towards the phosphindole core are either based on the prior formation of a phosphindole bearing a trivalent phosphorous atom,[3,4,8,9,11,12] or on the direct formation of a phosphindole oxide.[13] Due to the reduced stability of the trivalent phosphindole core these species are most often directly oxidized to their more stable benzo[*b*]phosphole oxide derivatives before isolation. Transformation to the salts is challenging[6,8–10] which might be attributed to the partial conjugation of the phosphorus electron pair.[8] Based on the low efficiency of post functionalized approaches towards the phosphindolium salts, alternatives in which the compounds are directly formed in one synthetic step are highly attractive. So far, direct syntheses were only described by Pietrusiewicz[14] and Yamaguchi.[15,16] Yamaguchi *et al.* successfully demonstrated the formation of the borate-bridged 2-benzophosphindolium structure that was triggered by a borane in an intramolecular fashion (Scheme 1a). In Pietrusiewicz's work only one derivative was synthesized in low yields and a large excess of the dihalide precursor was necessary.

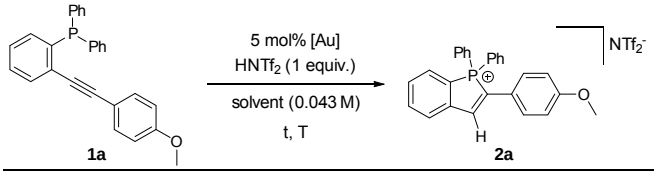


Scheme 1. Synthetic approaches to phosphindolium derivatives.

Recently, we reported the intramolecular phosphino-auration of alkynes starting from [IPr-Au]NTf_2 and *ortho*-phosphane tolanes.[17] After a prior coordination of the phosphane to the cationic gold fragment, cyclization afforded [(phosphindolium)-Au-IPr]$^+NTf_2^-$ as product. A protodeauration experiment revealed that substitution of the [IPr-Au]$^+$ by a proton was possible. By using strong acids in combination with weakly coordinating counterions, we envisioned a catalytic process affording the protonated phosphindolium salt (Scheme 1b). Our investigation finally led to a highly efficient gold-free process, which is presented here.

Initial experiments were conducted by using catalytic amounts of IPrAuNTf_2 (5 mol%) in the presence of 1 equivalent of $HNTf_2$. Indeed, full conversion (no side reactions) was observed by ^{31}P NMR (Table 1, entry 1). In order to accelerate the reaction, the considerably larger IPr* ligand[18] was applied (entry 2). In contrast to our prior findings concerning the stoichiometric reaction,[17] the catalytic reaction rate turned out to be independent of the catalyst used. Based on this result, we performed the reaction in the absence of any gold catalyst and **2a** was isolated in 93% (entry 3).[19]

Table 1. Cyclization in the presence of catalytic amounts of gold.



1a **2a**

Entry	Solvent	[Au]	Acid	T/°C	t	Yield
1	CH_2Cl_2	IPrAuNTf_2	$HNTf_2$	60	2 d	99%
2	CH_2Cl_2	IPr*AuNTf_2	$HNTf_2$	60	2 d	93%
3	**CH_2Cl_2**	**none**	**$HNTf_2$**	**60**	**2 d**	**93%**

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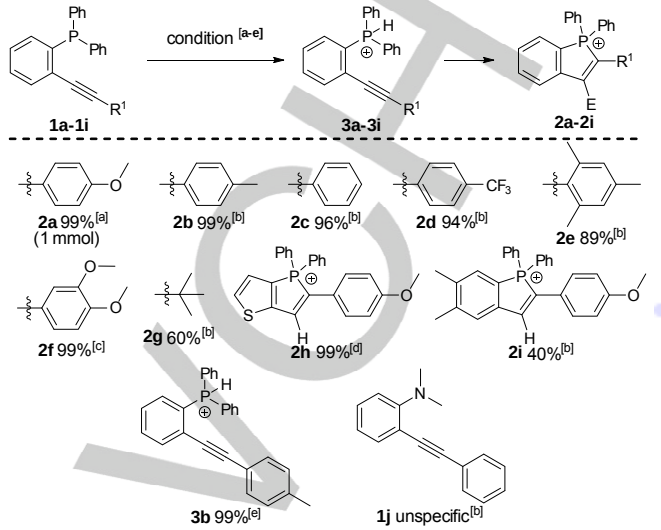
We next evaluated the general applicability of this methodology. Various phenylacetylene precursors **1a-1i** were reacted in the presence of $HNTf_2$ as acid (Scheme 2). **1b** bearing the less electron-rich methyl substituent showed no conversion to the final product under the same conditions. Instead protonation of the phosphane was observed [^{31}P NMR 3.32 ppm; ^{1}H NMR 8.86 ppm (d, J = 520.3 Hz)] and could be verified by an X-ray analysis of **3b** (Fig. 1). Fortunately, upon heating to 150 °C in bromobenzene, **3b** could be further cyclized to the final product **2b** (99%). Under the elevated temperatures, all of the applied tolane derivatives **1c**-**1f** could be transferred to the corresponding phosphindolium triflimides **2c**-**2f** in excellent yields no matter if electron-neutral (**2c**), electron-deficient (**2d**), electron-donating (**2f**) or sterically bulky arene moieties were attached (**2e**). Even a *tert*-butyl-substituted alkyne afforded the cyclization product **2g** in moderate yield. Then different aromatic backbones were investigated. Besides a dimethyl-substituted benzene backbone that delivered **2i** in moderate yield, even a thiophene backbone gave rise to the phospholothiophenium scaffold (**2h**) in excellent yield. Interestingly, we also investigated the substitution of phosphorus by nitrogen (substrate **1j**). In agreement with reports by Bertrand *et al.*, only protonation of the aniline was observed not leading to the desired cyclization product.[20] It should be highlighted that in order to affect the cyclization with the aniline derivatives a cationic gold catalyst is necessary, in stark contrast to our findings with the here described phosphorus system.

As a next step, we investigated the scope of acidic promoters. For some strong acids such as HOTf or HBF_4 undesired degradation pathways were observed (Table 2, entries 1, 2). For this reason, acids with lower acidity were selected. Indeed, clean reactions were observed by using hydrochloric acid (entry 3), trifluoroacetic acid (HTFA, entry 4) and monochloracetic acid (HMCA, entry 5). In the case of HCl, polymerization was observed which was prevented at low temperatures. *In situ* NMR experiments showed that with **1a** a cyclization reaction can be even performed at -10 to 0 °C. Phenol as well as methanol showed an unspecific reaction (entry 7, 8). Surprisingly, a different product (**4**) was found, if water was present in the reaction media. An aqueous solution of acetic acid (entry 6) afforded the phosphane oxide product **4** that is most probably formed *via* a hydroxyphosphorane intermediate in good accordance to reports of Winter *et al.*[22] Reactions conducted with a $HNTf_2$/water mixture (entry 9) confirmed this reactivity, highlighting the importance of anhydrous conditions. Nevertheless, the isolated phosphindolium product **2a** showed no decomposition or rearrangement into **4** over one month in wet chloroform.

Besides the use of a proton as electrophile we were curious if boranes can also affect the cyclization step, similar to the reactivity observed by frustrated Lewis pairs.[15,16,23] When $B(C_6F_5)_3$ was reacted with **1a**, **b** and **1d** the corresponding desired products were cleanly formed in less than 30 min at rt and the structure clearly established by X-ray diffraction (Scheme 3, Fig. 2).

We investigated the optical and photophysical properties of the 2-phenyl phosphindolium structure in solution (all compounds are highly soluble in CH_2Cl_2, 0.74 - 1.5 mol/l). For all tested analogues (**2a**, **2b**, **2e**, **2h**, **5a**, **5b**), the UV-vis absorption spectra showed an intense absorption band in the UV and violet region (Fig. 3).[2] Depending on the number of methoxy groups bound to the 2-phenyl substituent, a red-shift of absorption was observed for **2a**, **2e**, **5a** relative to those structures without methoxy groups (**2b**, **5b**; Table 3).



Scheme 2. Substrate scope. Conditions: [a] CH_2Cl_2 (0.20 M), 1.00 eq. $HNTf_2$, 60 °C, 2 d (sealed vial); [b] C_6H_5Br (0.04 M), 1.00 eq. $HNTf_2$, 150 °C, 1 d – the yiled of **2i** is reduced due to losses during the recrystallization; [c] C_6H_5Br (0.04 M), 1.00 eq. $HNTf_2$, 90 °C, 1 d; [d] C_6H_5Br (0.04 M), excess HCl (in dioxane), 150 °C, 1 d; [e] CH_2Cl_2 (0.04 M), 1.00 eq. $HNTf_2$, -20 °C, 5 min. Counter-anions are omitted (NTf_2^- or Cl^-).

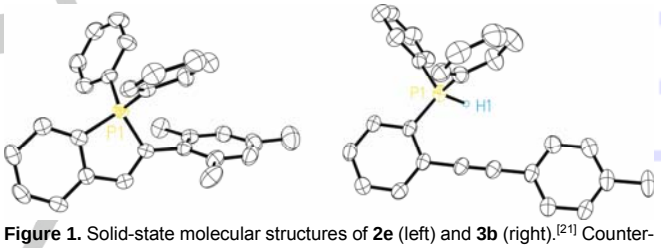
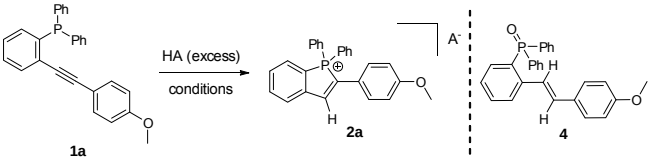


Figure 1. Solid-state molecular structures of **2e** (left) and **3b** (right).[21] Counter-anions and co-crystallized solvent molecules are omitted. Selected bond distances [Å] for **2e**: P1-C11 1.781(4), P1-C41 1.783(4), P1-C31 1.788(4), P1-C2 1.819(4), C2-C3 1.333(6), C3-C12 1.474(6), C3-H3 0.9500, C11-C12 1.409(6). For **3**: P1-C31 1.781(4), P1-C12 1.787(3), P1-C41 1.788(4), P1-H1 1.29(4), C10-C20 1.205(5), C10-C11 1.433(5), C11-C12 1.412(5), C20-C21 1.432(5).

Table 2. Acid scope.



Entry	Solvent	acid	T/°C	t	Yield
1	C_6H_5Br	HOTf	150	1 d	87%[a]
2	C_6H_5Br	HBF_4	150	1 d	75%[a]
3	**CH_2Cl_2**	**HCl**	**-78…rt**	**1 d**	**100%**
4	C_6H_5Br	HTFA	150	3 h	100%
5	C_6H_5Br	HMCA	150	2.5	97%
6	C_6H_5Br	AcOH	150	1 d	100% (**4**)
7	C_6H_5Br	PhOH	140	1 d	Unspecific

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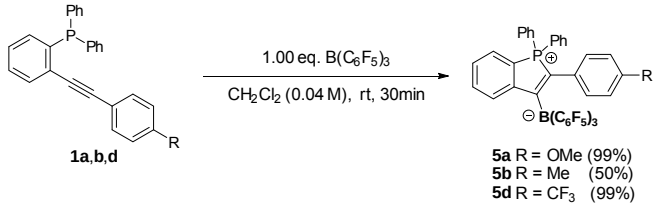
8	C_6H_5Br	MeOH	80	7 h	Unspecific
9	C_6H_5Br	$H_2O/HNTf_2$ (10 mol%)	100	1 d	99% (**4**)

Notes: [a] small impurities detected.



Scheme 3. Tris(pentafluorophenyl)borane-induced rearrangements. The yield of **5b** is reduced due to losses during the recrystallization.

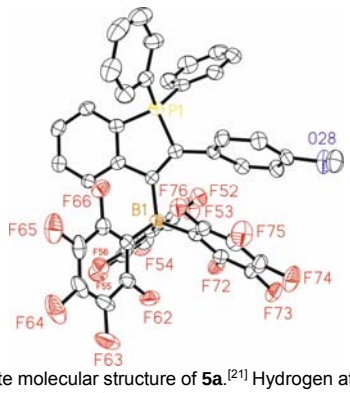


Figure 2. Solid-state molecular structure of **5a**.[21] Hydrogen atoms are omitted. Selected bond distances in [Å]: P1-C11 1.764(3), P1-C2 1.796(3), B1-C3 1.644(4), C2-C3 1.368(4), C3-C12 1.505(4), C11-C12 1.405(4).

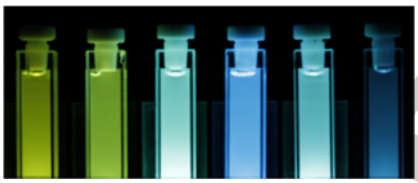


Figure 3. Fluorescence in solution of **2h, 2e, 2a, 2b, 5a** and **5b** (from left to right).

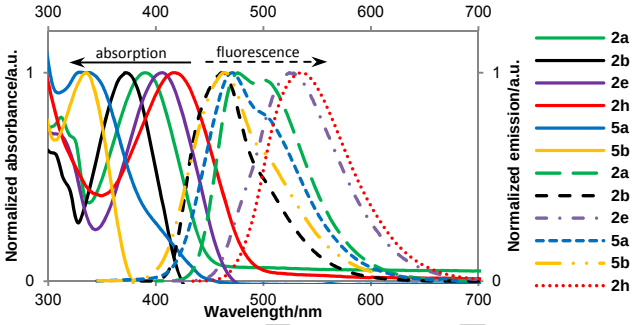


Figure 4. UV/Vis absorption spectra (solid lines) and emission spectra (dotted lines) in CH_2Cl_2.

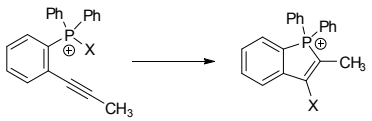
Table 3. Optical and photophysical data in CH_2Cl_2.

Compound	λ_{abs}/nm (log ε)	λ_{em}[a]/nm (Φ_F[b])	Stokes shift/nm
2a	390 (4.13)	476 (88.1%)	116279
2b	374 (3.82)	463 (83.7%)	112360
2e	406 (4.45)	524 (82.5%)	84746
2h	417 (3.92)	535 (69.8%)	84746
5a	334 (4.39)	471 (76.4%)	72933
5b	336 (4.65)	464 (96.9%)	78125

Notes: [a] excited at λ_{abs}; [b] fluorescence quantum yields in solution.

A blue-shift for λ_{abs} was observed for **5a** and **5b** with the borate as substituent in 3-position of the phosphindolium core, while the phospholium core structure **2h** showed a red-shifted λ_{abs}. Fluorescence spectra of **2a**, **2b**, **2e**, **2h**, **5a** and **5b** showed a strong emission in the visible region (Fig. 3). In general, a large Stokes shift was determined [86 nm (**2a**), 89 nm (**2b**), 118 nm (**2e**, **h**), 137 nm (**5a**) and 128 nm (**5b**)]. According to the spectra measured (Fig. 3), the 2-substituent had a greater influence on the emission than the 3-substituent. The phosphindolium salts showed Φ_F in the range from 70% (**2h**) to 97% (**5b**) [88% (**2a**), 84% (**2b**), 83% (**2e**), 76% (**5a**), 83% in average]. The values are comparable to those reported for phosphindole oxide structures.[12]

DFT calculations were performed in order to investigate the mechanism for the protophosphonylation reaction. First the thermodynamics of the cyclization transformation was calculated at the M06-2X-D3-SMD(C_6H_5Br)/cc-pVDZ level of theory as a function of the electrophile employed (AuCl, BMe_3, H^+) (Scheme 4). Interestingly, due to the strong affinity of gold and boron to phosphorus the calculations predict only a slightly electronic stabilization of the cyclization product over the starting material [AuCl: ΔE = -0.9 kcal/mol; BMe_3: ΔE = -4.3 kcal/mol]. In these two cases it seems important that steric bulk weakens the P-Au/P-B interaction, thereby favoring the cyclization as demonstrated above with the sterically demanding borane $B(C_6F_5)_3$. Importantly, in contrast to Au and B the cyclization with H^+ is electronically strongly favored [H^+: ΔE = -36.0 kcal/mol]. It seems likely that reversible protonation allows the cyclization to proceed.

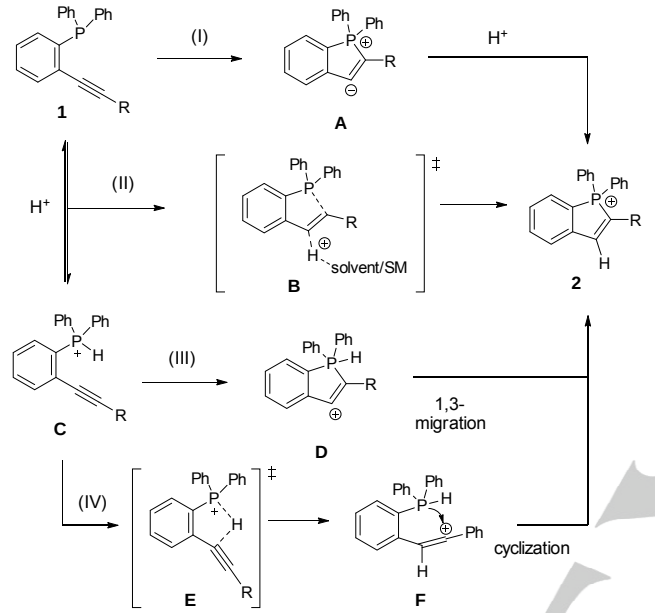


Scheme 4. DFT calculated electronic energy differences (ΔE) for the cyclization reaction with different electrophiles at the M06-2X-D3-SMD(C_6H_5Br)/cc-pVDZ level of theory.

Mechanistically, we analyzed four different reaction pathways (Scheme 5): Pathway I involves the direct cyclization of the *ortho*-alkynylphosphane to form zwitterionic compound **A**, according to the hydrolysis mechanism proposed by Winter *et al.*,[8] followed by protonation to give the desired cyclization product. DFT optimization of compound **A** (R = Ph) at the M06-2X-D3-SMD(C_6H_5Br)/cc-pVDZ level of theory predict ΔG = +23.7 kcal/mol [for R = Me; B3LYP-D3BJ/cc-pVDZ ΔG = +29.2 kcal/mol[17]] to form **A**. This high value is not in agreement with the experimental results which disfavors mechanism I. More reasonably, there is an equilibrium between **1** and the P-protonated phosphonium **C** which we could identify by X-ray diffraction (see above). In analogy to our recently described gold mediated cyclization, H^+ (as the free acid, protonated solvent or compound **C**) could engage in the electrophilic activation of the alkyne moiety followed by a concerted nucleophilic attack of

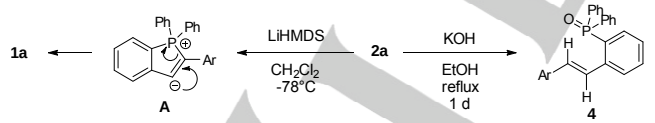
10.1002/chem.201700889

phosphorus (path II). Alternatively, we envisioned either a cyclization of the alkyne onto the cationic phosphorus center, followed by a 1,3-shift (path III), or first a (*intra*-molecular) protonation of the alkyne (**E**) to form vinyl cation **F** followed by cyclization (path IV). Pathway III involving a 1,3-hydride migration seems unlikely as we could not locate compound **D** as a stable minimum on the potential surface. Mechanism II involving a concerted protonation/cyclization event or mechanism IV involving a stepwise protonation/cyclization seem most likely and are in agreement with the observed rate acceleration with electron donating groups on the aryl group.



Scheme 5. Mechanistic pathways for the protophosphonylation reaction.

Interestingly, we could detect different reaction pathways by subjecting the cyclization product **2** to two different bases (Scheme 6). While **2** is cleaved with KOH to phosphane oxide product **4**, a strong base such as LiHMDS under inert conditions affords starting material **1**. It seems likely that in the first case OH^- attacks at phosphorus followed by opening and protonation, while in the second case with the more bulky and more nucleophilic base the vinyl proton can be deprotonated leading to zwitterionic-intermediate **A** which undergoes a rapid ring opening to **1**.



Scheme 6. Ring-opening reactions of phosphindolium **2** mediated by KOH and LiHMDS.

In conclusion, in this study an acid-promoted, intramolecular *trans*-protophosphonylation was discovered, giving rise to highly stable and structurally valuable phosphindolium salts. This atom-economic transformation was found to proceed under mild reaction conditions cleanly affording the corresponding cyclization products in up to quantitative yield. The simple and direct access to the phosphindolium salts combined with their valuable properties, such as fluorescence, stability and good solubility, offers an attractive alternative strategy to common methodologies that are based on the post-functionalization of trigonal phosphindole systems.

Experimental Section

General Procedure for the Synthesis of Phosphindolium Salts: Under an atmosphere of argon the corresponding 2-phosphane tolane, and the given amount of acid were dissolved in 0.6 mL solvent, the mixture was transferred to a Young-NMR tube and heated to the described temperature. The reactions were monitored using ^{31}P and ^{1}H NMR spectroscopy. Upon complete conversion, the crude product was washed using diethyl ether or precipitated in solvent/pentane.

Keywords: phosphorus compounds • Brønsted-acid • π-extended systems • rearrangement • phospholes

[1] a) C. Fave, T.-Y. Cho, M. Hissler, C.-W. Chen, T.-Y. Luh, C.-C. Wu, R. Reau, *J. Am. Chem. Soc.* **2003**, *125*, 9254–9255; b) M. Hissler, P. W. Dyer, R. Réau, *Coord. Chem. Rev* **2003**, *244*, 1–44; c) F. Mathey, *Angew Chem., Int. Ed.* **2003**, *42*, 1578–1604; d) J. Crassous, R. Reau, *Dalton Trans.* **2008**, 6865–6876; e) O. Fadhel, M. Gras, N. Lemaitre, V. Deborde M. Hissler, B. Geffroy, R. Réau, *Adv. Mater.* **2009**, *21*, 1261–1265; f) D. Joly, D. Tondelier, V. Deborde, W. Delaunay, A. Thomas, K. Bhanuprakash, B. Geffroy, M. Hissler, R. Réau, *Adv. Funct. Mater.* **2012**, *22*, 567–576; g) H. Chen, W. Delaunay, J. Li, Z. Wang, P.-A. Bouit, D. Tondelier, B. Geffroy, F. Mathey, Z. Duan, R. Reau et al., *Org. Lett.* **2013**, *15*, 330–333; h) T. Baumgartner, R. Reau, *Chem. Rev.* **2006**, *106*, 4681–4727; i) H.-C. Su, O. Fadhel, C.-J. Yang, T.-Y. Cho, C. Fave, M. Hissler, C.-C. Wu, R. Reau, *J. Am. Chem. Soc.* **2006**, *128*, 983–995.

[2] D. Joly, D. Tondelier, V. Deborde, B. Geffroy, M. Hissler, R. Réau, *New J. Chem.* **2010**, *34*, 1603–1611.

[3] A. Fukazawa, Y. Ichihashi, Y. Kosaka, S. Yamaguchi, *Chem. Asian J.* **2009**, *4*, 1729–1740.

[4] Y. Matano, H. Imahori, *Org. Biomol. Chem.* **2009**, *7*, 1258–1271.

[5] a) Y. Ren, T. Baumgartner, *Dalton Trans.* **2012**, *41*, 7792–7800; b) T. Baumgartner, *Acc. Chem. Res.* **2014**, *47*, 1613–1622; c) M. Stolar, T. Baumgartner, *Chem. Asian J.* **2014**, *9*, 1212–1225; d) P. Hibner-Kulicka, J. A. Joule, J. Skalik, P. Bałczewski, *RSC Adv* **2017**, *7*, 9194–9236.

[6] E. Yamaguchi, C. Wang, A. Fukazawa, M. Taki, Y. Sato, T. Sasaki, M. Ueda, N. Sasaki, T. Higashiyama, S. Yamaguchi, *Angew. Chem., Int. Ed.* **2015**, *54*, 4539–4543.

[7] a) G. Märkl, *Z. Naturforschung B*, *1962*, 84–85; b) O. Berger, J.-L. Montchamp, *Beilstein J. Org. Chem.* **2014**, *10*, 732–740.

[8] T. Butters, W. Winter, *Chem. Ber.* **1984**, *117*, 990–1002.

[9] W. Winter, *Tetrahedron Lett.* **1975**, *16*, 3913–3914.

[10] W. Winter, J. Strähle, *Chem. Ber.* **1977**, *110*, 1477–1483.

[11] a) Y. Unoh, Y. Yokoyama, T. Satoh, K. Hirano, M. Miura, *Org. Lett.* **2016**; b) B. Wu, R. Chopra, N. Yoshikai, *Org. Lett.* **2015**, *17*, 5666–5669; c) B. Wu, M. Santra, N. Yoshikai, *Angew. Chem.* **2014**, *126*, 7673–7676; d) K. Baba, M. Tobisu, N. Chatani, *Angew. Chem., Int. Ed.* **2013**, *52*, 11892–11895; e) H. Tsuji, K. Sato, L. Ilies, Y. Itoh, Y. Sato, E. Nakamura, *Org. Lett.* **2008**, *10*, 2263–2265; f) G. Märkl, G. Y. Jin, K.-P. Berr, *Tetrahedron Lett.* **1993**, *34*, 3103–3106; g) D. G. Holah, A. N. Hughes, D. Kleemola, *J. Heterocyclic Chem.* **1977**, *14*, 705–707; h) W. Egan, R. Tang, G. Zon, K. Mislow, *J. Am. Chem. Soc.* **1971**, *93*, 6205–6216; i) T. H. Chan, L. T. L. Wong, *Can. J. Chem.* **1971**, *49*, 530–531; j) M. D. Rausch, L. P. Klemann, *J. Am. Chem. Soc.* **1967**, *89*, 5732–5733; k) G. Wittig, A. Maercker, *Chem. Ber.* **1964**, *97*, 747–768.

[12] Y. Matano, Y. Motegi, S. Kawatsu, Y. Kimura, *J. Org. Chem.* **2015**, *80*, 5944–5950.

[13] a) Y. Unoh, K. Hirano, T. Satoh, M. Miura, *Angew. Chem., Int. Ed.* **2013**, *52*, 12975–12979; b) Y.-R. Chen, W.-L. Duan, *J. Am. Chem. Soc.* **2013**, *135*, 16754–16757; c) Y. Hayashi, Y. Matano, K. Suda, Y. Kimura, Y. Nakao, H. Imahori, *Chem. Eur. J.* **2012**, *18*, 15972–15983; d) T. Sanji, K. Shiraishi, T. Kashiwabara, M. Tanaka, *Org. Lett.* **2008**, *10*, 2689–2692.

[14] K. M. Pietrusiewicz, M. Kuźnikowski, *Phosphorous, Sulfur, Silicon Relat. Elem.* **2006**, *77*, 57–60.

[15] A. Fukazawa, H. Yamada, S. Yamaguchi, *Angew. Chem., Int. Ed.* **2008**, *47*, 5582–5585.

10.1002/chem.201700889

[16] A. Fukazawa, E. Yamaguchi, E. Ito, H. Yamada, J. Wang, S. Irle, S. Yamaguchi, *Organometallics* **2011**, *30*, 3870–3879.

[17] S. Arndt, M. M. Hansmann, P. Motloch, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Chem. Eur. J.* **2016**, DOI:10.1002/chem.201605914.

[18] G. Berthon-Gelloz, M. A. Siegler, A. L. Spek, B. Tinant, J. N. H. Reek, I. E. Marko, *Dalton Trans.* **2010**, *39*, 1444–1446.

[19] Only one example for a related intramolecular process exists: E. Vedejs, P. L. Steck, *Angew. Chem., Int. Ed.* **1999**, *38*, 2788–2791.

[20] a) C. A. Gaggioli, G. Ciancaleoni, L. Biasiolo, G. Bistoni, D. Zuccaccia, L. Belpassi, P. Belanzoni, F. Tarantelli, *Chem. Comm.* **2015**, *51*, 5990–5993; b) X. Zeng, R. Kinjo, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2010**, *122*, 954–957.

[21] CCDC-1530186 (**3b**), CCDC-1530187 (**2e**), CCDC-1530188 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[22] T. Butters, I. Haller-Pauls, W. Winter, *Chem. Ber.* **1982**, *115*, 578–592.

[23] a) M. A. Dureen, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 8396–8397; b) C. Jiang, O. Blacque, H. Berke, *Organometallics* **2010**, *29*, 125–133.

10.1002/chem.201700889

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The acid-mediated cyclization of 2-phosphane tolanes to phosphindolium salts is described. The process allows for a general metal-free and extraordinary simple protocol towards the target structures. The rearrangement proceeds in complete atom economy without the need for further purification.

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Page No. – Page No.

Direct Access to π-Extended Phosphindolium Salts by Simple Proton-Induced Cyclization of (*o*-Alkynylphenyl)phosphanes