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Synthesis of Selected Cationic Pnictanes [L$_n$PnX$_{3-n}$]$^{n+}$ (L = Imidazolium-2-yl; Pn = P, As; n = 1−3) and Replacement Reactions with Pseudohalogens

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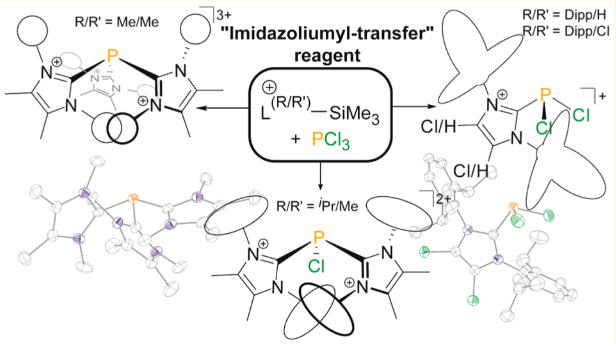
Supporting Information

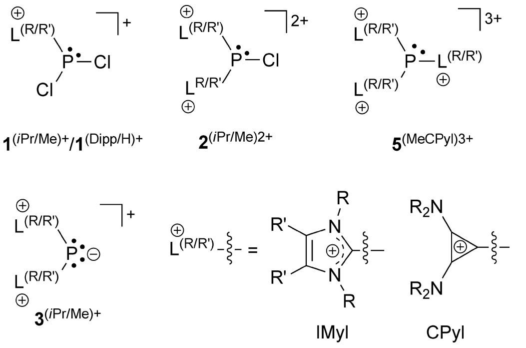


ABSTRACT: Herein we report on reactions of "imidazoliumyl-transfer" reagents [L$^{(R/R')}$SiMe$_3$][OTf] ($\mathbf{4}^{(R/R')}$[OTf]); L = imidazolium-2-yl, R/R′: Me/Me, ^{i}Pr/Me, Dipp/H, Dipp/Cl) with pnictogen trichlorides PnCl$_3$ (Pn = P, As, Sb) in various stoichiometries. In the case of the 1:1 reaction of [L$^{(R/R')}$SiMe$_3$][OTf] with PCl$_3$ the corresponding cationic imidazoliumyl-substituted dichlorophosphanes [L$^{(R/R')}$PCl$_2$]$^+$ ($\mathbf{1}_P{}^{(R/R')}$)$^+$ are obtained as triflate salts on a multigram scale. We found that the reactions using various stoichiometries of [L$^{(R/R')}$SiMe$_3$][OTf] and PnCl$_3$ are less selective in the case of the heavier congeners or by decreasing steric demand of the R-group attached to the N atoms of the heterocycle. An equilibrium between the monocation [L$^{(Me/Me)}$PCl$_2$]$^+$ ($\mathbf{1}_P{}^{(Me/Me)+}$), the dication [L$^{(Me/Me)}{}_2$PCl]$^{2+}$ ($\mathbf{2}_P{}^{(Me/Me)2+}$), and the trication [L$^{(Me/Me)}{}_3$P]$^{3+}$ ($\mathbf{5}_P{}^{(Me/Me)3+}$) is observed in solution. Reactions of the monocationic derivatives [L$^{(R/R')}$PnCl$_2$][OTf] (Pn = P, As) with Me$_3$SiX (X = CN, N$_3$) resulted in the exchange of the chloro groups for the respective pseudohalogen and yielded the dicyano [L$^{(R/R')}$Pn(CN)$_2$][OTf] ($\mathbf{6}_{Pn}{}^{(R/R')}$[OTf]) and diazido-substituted pnictanes [L$^{(R/R')}$Pn(N$_3$)$_2$][OTf] ($\mathbf{7}_{Pn}{}^{(R/R')}$[OTf]), respectively. All new compounds are thoroughly characterized by multinuclear NMR, IR, and Raman spectroscopy. For most cases the molecular structure was confirmed by X-ray crystal structure analysis.

■ INTRODUCTION

In the course of our investigation into stabilized cationic phosphorus compounds[1,2] we recently introduced a versatile protocol for the preparation of [L$^{(R/R')}$PCl$_2$]$^+$ ($\mathbf{1}^{(R/R')+}$; R/R′: ^{i}Pr/Me; Dipp/H)[3,4] and [L$^{(R/R')}{}_2$PCl]$^{2+}$ ($\mathbf{2}^{(iPr/Me)2+}$)[3] as triflate salts. These cations feature a trivalent P atom in the oxidation state +III in combination with supporting imidazoliumyl substituents (Chart 1; IMyl, e.g., L$^{(iPr/Me)}$ = 1,3-diisopropyl-4,5-dimethylimidazolium-2-yl; L$^{(Dipp/H)}$ = 1,3-bis(2,6-diisopropylphenyl)-imidazolium-2-yl). The most remarkable aspect of this synthesis is that the phosphorus atom remains in the oxidation state +III. It has been found that P^{III} derivatives often display a propensity toward the reductive formation of P^I species in the presence of a Lewis base. Therefore, they cannot be prepared directly via the reaction of PCl$_3$ and a N-heterocyclic carbene (NHC) in most cases. Thus, Macdonald and co-workers isolated the cationic imidazoliumyl-stabilized P^I compound [L$^{(iPr/Me)}{}_2$P]$^+$ ($\mathbf{3}^+$) from the reaction of the sterically less demanding 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene with PCl$_3$.[5] This reductive reaction pathway is circumvented by masking the Lewis base, that is, by reacting silylimidazolium salts such as [L$^{(R/R')}$SiMe$_3$][OTf] ($\mathbf{4}^{(R/R')}$[OTf], Scheme 1, **I**) as "imidazoliumyl-transfer" reagent with PCl$_3$. This approach allows an efficient synthesis of cations $\mathbf{1}^+$, $\mathbf{2}^{2+}$, and $\mathbf{5}^{3+}$ (Scheme 1, **II**, **III**, and **IV**). A reverse synthetic approach to triply L^R-stabilized cations $\mathbf{5}^{3+}$ uses P(SiMe$_3$)$_3$ and 1-chloro-2,3-bis(dialkylamino)-cyclopropenium salts (Chart 1; CPyl = cyclopropenyl, e.g., $\mathbf{5}^{(MeCPyl)3+}$).[6] This reaction also proceeds sequentially accompanied by the formation of Me$_3$SiCl to

Chart 1. Examples of Charged P^{III} Derivatives Supported by C-Centered Ligands (IMyl, CPyl)^a



^{a}Only one representative resonance structure for L$^{(R/R')+}$ is depicted.

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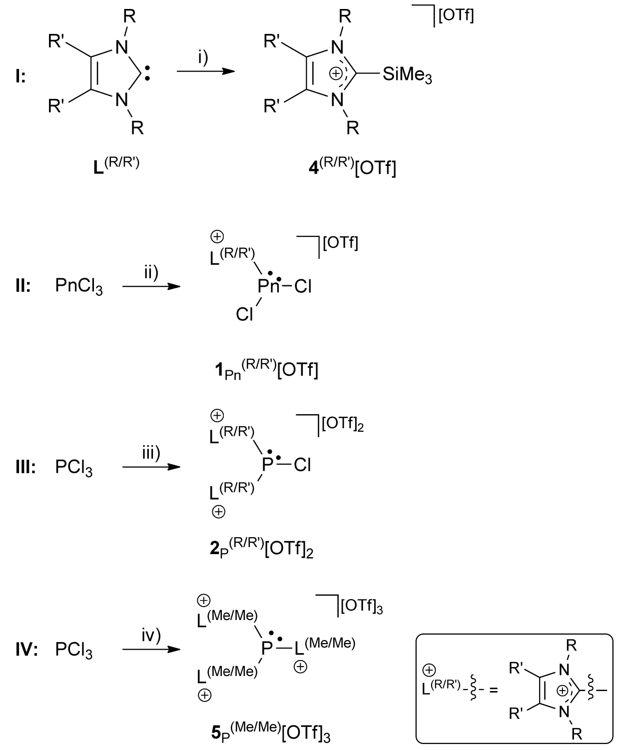
Scheme 1[a]



[a]Preparation of **I**: $\mathbf{4}^{(R/R')}$[OTf] (R/R′ = Me/Me,[14] ^{i}Pr/Me,[3] Dipp/H,[4] Dipp/Cl[15]): (i) +Me$_3$SiOTf, C_6H_5F, RT; **II**: $\mathbf{1}_{Pn}{}^{(R/R')}$[OTf]: (ii) +$\mathbf{4}^{(R/R')}$[OTf], −Me$_3$SiCl, (Pn = P: R/R′: Me/Me: excess PCl$_3$, neat, reflux,[15] Dipp/H,[4] Dipp/Cl: equimolar, C_6H_5F, Pn, As: R/R′: ^{i}Pr/Me: sonication, 50 °C,[3,15] Dipp/H: RT;[15] Pn = Sb: R/R′: ^{i}Pr/Me, sonication, 50 °C[7,14]); **III**: $\mathbf{2}_P{}^{(R/R')}$[OTf]$_2$ (R/R′: Me/Me,[14−16] ^{i}Pr/Me[3]): (iii) +2 $\mathbf{4}^{(R/R')}$[OTf], −2Me$_3$SiCl; **IV**: $\mathbf{5}_P{}^{(Me/Me)}$[OTf]$_3$: (iv) +3 $\mathbf{4}^{(Me/Me)}$[OTf], −3Me$_3$SiCl (solvent free, reflux)[15].

afford cyclopropeniumyl-stabilized phosphanes. Several other methods for the synthesis of mono-, di-, and tricationic phosphanes have been reported and have been recently reviewed by Alcarazo.[7] Nitrogen-centered Lewis bases, such as dimethylamino pyridine, quinuclidine, or various guanidines have been successfully reacted with phosphorus trichloride to afford the corresponding di- and tricationic phosphanes in usually very good to excellent yields.[8] Relatively persistent compounds bearing heavier group 15 element in the oxidation state +1 in combination with several ligands have been extensively reviewed by Mcdonald.[9]

In this contribution we report on the extension of our synthetic approach. We investigated selected silylimidazolium salts [L$^{(R/R')}$SiMe$_3$][OTf] ($\mathbf{4}^{(R/R')}$[OTf]) with substituents of differing steric demand (R = Me, ^{i}Pr, Dipp; R′ = H, Me, Cl) and electronic properties as “imidazoliumyl-transfer” reagents in the reaction with pnictogen trichlorides PnCl$_3$. Several cationic pnictanes are prepared as triflate salts [L$^{(R/R')}{}_n$Pn-Cl$_{3-n}$][OTf]$_n$ (L = imidazolium-2-yl; Pn = P, As, Sb;[10] n = 1−3; Scheme 1). Furthermore, some of the obtained monocations [L$^{(R/R')}$PnCl$_2$]$^+$ (Pn = P, As) are reacted with pseudohalogenides such as cyano and azido moieties from Me$_3$SiX (X = CN, N$_3$) to replace the chloro substituents.

■ RESULTS AND DISCUSSION

Synthesis of $\mathbf{4}^{(R/R')}$[OTf]. Salts of type $\mathbf{4}^{(R/R')}$[OTf] were obtained via dropwise addition of a slight excess of Me$_3$SiOTf (1.3 equiv) to a solution of the respective NHC L$^{(R/R')}$ (Me/Me,[11] ^{i}Pr/Me,[11] Dipp/H,[12] Dipp/Cl[13]) in C_6H_5F at ambient temperature.[3,4,17] Derivatives $\mathbf{4}^{(R/R')}$[OTf] (Me/Me,[15] ^{i}Pr/Me,[3] Dipp/H,[4] Dipp/Cl[15]) started to precipitate from the solution as colorless microcrystalline materials during or shortly after the addition. The reaction mixtures were stirred for 1 h after addition was complete. The precipitates were subsequently separated by filtration and washed with a small amount of C_6H_5F, and all volatiles were removed in vacuo to give analytically pure products in good to excellent yields (Scheme 1, **I**).[16] These adducts are moisture-sensitive and need to be handled under strictly inert atmosphere. However, rigorously dried solid materials stored in sealed ampules at room temperature did not show any sign of decomposition after one year.

Synthesis of $\mathbf{1}_{Pn}{}^{(R/R')}$[OTf]. PnCl$_3$ (Pn = P, As, Sb) was reacted with $\mathbf{4}^{(R/R')}$[OTf] (Me/Me, ^{i}Pr/Me, Dipp/H, Dipp/Cl) using the reaction conditions detailed in Scheme 1, **II**.[16] The formation of the expected cations $\mathbf{1}_P{}^{(R/R)+}$ was observed in all cases, and the respective products were isolated in good to excellent yields by fractional crystallization. The ^{31}P NMR spectroscopic data of all reported P compounds are summarized in Table 1. The resonances of the P atoms in the dichloro derivatives $\mathbf{1}_P{}^{(R/R)}$[OTf] are observed between δ = 107.2 and 114.9 ppm. Within the series the resonances are slightly shifted downfield with higher steric demand of L$^{R/R'}$. This may be rationalized by assuming an increasing p-character of the lone pair at phosphorus and thus a decreased shielding with greater bond angles at the phosphorus atom. However, all cations $\mathbf{1}_P{}^{(R/R)+}$ resonate significantly more upfield than related phosphanes of the type RPCl$_2$.[18]

Table 1. Selected ^{31}P{^{1}H} Nuclear Magnetic Resonance Spectroscopic Parameters of Various Cationic Phosphanes

δ in ppm[a]	Me/Me[b]	^{i}Pr/Me[c]	Dipp/H[d]	Dipp/Cl[b]
L$^{(R/R')}$PX$_2$				
X = Cl	107.2	109.1	113.5	114.9
X = N$_3$	98.2	98.4	103.9[b]	109.4
X= CN	−125.0	−120.2	−116.6[b]	−109.7
$^1J_{PC(CN)}$ in Hz	50.3	51.4	53.3	54.9
L$^{(R/R')}{}_2$PCl	6.9	19.9		
L$^{(R/R')}{}_3$P	−82.9			

[a]All data were obtained from CD$_3$CN solutions. [b]Reference 14. [c]Reference 3. [d]Reference 4.

The trend of the pronounced upfield shift can be primarily associated with the π-acceptor properties of the introduced imidazoliumyl substituent and only secondarily with the steric demand of the R-group attached to the N atoms of the heterocycle. By analogy with the phosphorus derivatives, $\mathbf{1}_{As}{}^{(iPr/Me)}$[OTf] and $\mathbf{1}_{As}{}^{(Dipp/H)}$[OTf] could be isolated in excellent yields (>90%) as colorless crystalline materials. For all reactions involving SbCl$_3$ complicated mixtures of several products were observed according to NMR spectroscopic investigations. Defined products could not be isolated in satisfactory yield from those reaction mixtures. However, it was possible to obtain small amounts of crystalline $\mathbf{1}_{Sb}{}^{(iPr/Me)}$[OTf] suitable for X-ray investigation by diffusion of n-hexane into the respective reaction mixture (see below for a comparative discussion of the obtained molecular structures).[19]

Equilibrium between $\mathbf{1}_P{}^{(Me/Me)}$[OTf], $\mathbf{2}_P{}^{(Me/Me)}$[OTf]$_2$, and $\mathbf{5}_P{}^{(Me/Me)}$[OTf]$_3$. Our previous investigations showed that the reaction of PCl_3 with 2 equiv of $\mathbf{4}^{(i\mathrm{Pr/Me})}$[OTf] yields the triflate salt of dication $\mathbf{2}_{\mathrm{P}}^{(i\mathrm{Pr/Me})2+}$.[3] We thus explored the syntheses of related dications with imidazoliumyl fragments of varying steric demand. Reacting PCl_3 with 2 equiv of $\mathbf{4}^{(\mathrm{Me/Me})}$[OTf] under various reaction conditions gave in all cases a mixture of three products as indicated by ^{31}P NMR spectroscopic investigations (Figure 1). The most downfield resonance (δ = 107.2 ppm) is attributed to the monocation $\mathbf{1}_{\mathrm{P}}^{(\mathrm{Me/Me})+}$ (vide supra). The resonance at δ = 6.9 ppm is assumed to indicate the presence of dication $\mathbf{2}_{\mathrm{P}}^{(\mathrm{Me/Me})2+}$ by analogy with $\mathbf{2}_{\mathrm{P}}^{(i\mathrm{Pr/Me})2+}$ (δ = 19.9 ppm).[3] The most upfield resonance (δ = −82.9 ppm) is attributed to trication $\mathbf{5}_{\mathrm{P}}^{(\mathrm{Me/Me})3+}$, which was separately sythesized (vide infra). In contrast to our previous findings regarding the synthesis of $\mathbf{2}_{\mathrm{P}}^{(i\mathrm{Pr/Me})}[\mathrm{OTf}]_2$, we were not able to isolate $\mathbf{2}_{\mathrm{P}}^{(\mathrm{Me/Me})}[\mathrm{OTf}]_2$ from any of the reaction mixtures. Thus, we assume that dication $\mathbf{2}_{\mathrm{P}}^{(\mathrm{Me/Me})2+}$ is in equilibrium with monocation $\mathbf{1}_{\mathrm{P}}^{(\mathrm{Me/Me})+}$ and trication $\mathbf{5}_{\mathrm{P}}^{(\mathrm{Me/Me})3+}$ via an intermolecular scrambling reaction, that is, an intermolecular exchange of imidazolium-2-yl and chloro substituents. The tendency of such a group transfer is known to rise with increasing electronegativity and decreasing steric demand of the substituents.[20] This may explain why a scrambling is not observed in the case of sterically more demanding ^{i}Pr substituents attached to the nitrogen atoms of the heterocycle in dication $\mathbf{2}_{\mathrm{P}}^{(i\mathrm{Pr/Me})2+}$, while it is of significance in the case of Me-substituents. To support this hypothesis, $\mathbf{1}_{\mathrm{P}}^{(\mathrm{Me/Me})}$[OTf] was reacted with $\mathbf{5}_{\mathrm{P}}^{(\mathrm{Me/Me})}[\mathrm{OTf}]_3$ (Scheme 2). ^{31}P NMR spectra of the resulting mixture after reaction times of 10 min to 16 h are depicted in Figure 2. Clearly, the intensity of the resonance at δ = 6.9 ppm increases at the expense of the intensity of those resonances attributed to mono- and trication $\mathbf{1}_{\mathrm{P}}^{(\mathrm{Me/Me})+}$ (δ = 107.2 ppm) and $\mathbf{5}_{\mathrm{P}}^{(\mathrm{Me/Me})3+}$ (δ = −82.9 ppm). In addition, the formation of PCl_3 (δ = 220.0 ppm) is observed. We thus conclude that dication $\mathbf{2}_{\mathrm{P}}^{(\mathrm{Me/Me})2+}$ is formed in the reaction of monocation $\mathbf{1}_{\mathrm{P}}^{(\mathrm{Me/Me})+}$ and trication $\mathbf{5}_{\mathrm{P}}^{(\mathrm{Me/Me})3+}$. From the reaction mixture of PCl_3 with 2 equiv of $\mathbf{4}^{(\mathrm{Me/Me})}$[OTf] layered with *n*-hexane and stored over a course of several months in the freezer (−30 °C), small amounts of colorless crystals of $\mathbf{2}_{\mathrm{P}}^{(\mathrm{Me/Me})}[\mathrm{OTf}]_2$ covered in oil were deposited. These crystals were suitable for X-ray structure determination (Figure 3) yet insufficient for full characterization.[21] The molecular structure of cation $\mathbf{2}_{\mathrm{P}}^{(\mathrm{Me/Me})2+}$ is similar to that of $\mathbf{2}_{\mathrm{P}}^{(i\mathrm{Pr/Me})2+}$ (Table 2). ^{31}P NMR spectroscopic

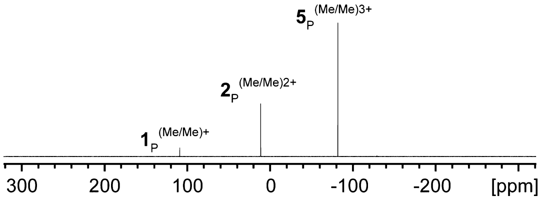
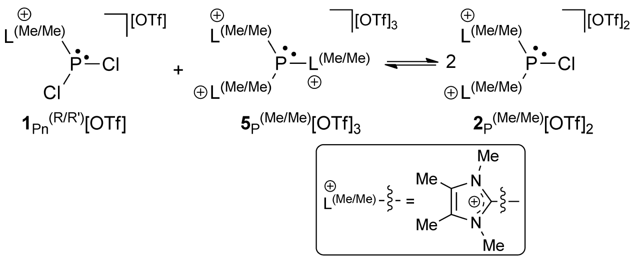


Figure 1. ^{31}P{^{1}H} NMR spectrum of the 2:1 reaction of $\mathbf{4}^{(\mathrm{Me/Me})}$[OTf] and PCl_3 in C_6F_5F illustrating the nonselective formation of cations $\mathbf{1}_{\mathrm{P}}^{(\mathrm{Me/Me})+}$, $\mathbf{2}_{\mathrm{P}}^{(\mathrm{Me/Me})2+}$, and $\mathbf{5}_{\mathrm{P}}^{(\mathrm{Me/Me})3+}$.

Scheme 2[a]



[a]Reaction of $\mathbf{1}_{\mathrm{P}}^{(\mathrm{Me/Me})}$[OTf] with $\mathbf{5}_{\mathrm{P}}^{(\mathrm{Me/Me})}[\mathrm{OTf}]_3$; (i) CD_3CN, microwave: 120 °C, for 10 min, 2 h, 5 h, 16 h (see Figure 2).

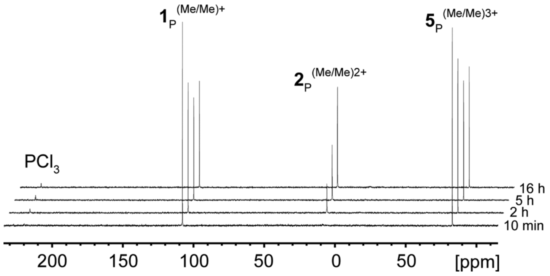


Figure 2. ^{31}P NMR spectra of the 1:1 reaction of $\mathbf{1}^{(\mathrm{Me/Me})}$[OTf] and $\mathbf{5}^{(\mathrm{Me/Me})}[\mathrm{OTf}]_3$ in CD_3CN illustrating the scrambling to cations $\mathbf{1}_{\mathrm{P}}^{(\mathrm{Me/Me})+}$, $\mathbf{2}_{\mathrm{P}}^{(\mathrm{Me/Me})2+}$, $\mathbf{5}_{\mathrm{P}}^{(\mathrm{Me/Me})3+}$, and PCl_3. After reaction times of more than 16 h the ratio of the resonances' intensities remained constant.

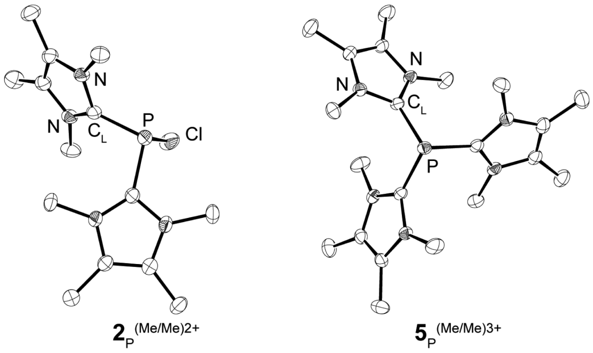


Figure 3. Molecular structures of cations $\mathbf{2}_{\mathrm{P}}^{(\mathrm{Me/Me})2+}$ and $\mathbf{5}_{\mathrm{P}}^{(\mathrm{Me/Me})3+}$ with thermal ellipsoids presented at a 50% probability level. The hydrogen atoms are omitted for clarity.

Table 2. Selected Geometrical Parameters of Crystallographically Characterized Compounds $\mathbf{2}_{\mathrm{P}}^{(\mathrm{R/R'})}[\mathrm{OTf}]_2$ and $\mathbf{5}_{\mathrm{P}}(\mathrm{Me/Me})[\mathrm{OTf}]_3$

R/R′	Me/Me[a]	^{i}Pr/Me[b]
	$[\mathrm{L}^{(\mathrm{R/R'})}{}_2\mathrm{PCl}]^{2+}$	
P−Cl in Å	2.0682(9)	2.0356(9)
P−C_L in Å	1.816(2)	1.850(2)
	1.829(2)	1.827(2)
N−C−N in deg	106.6(2)	107.6(2)
	106.9(2)	106.7(2)
∑ X−P−X in deg	301.26(9)	309.05(8)
	$[\mathrm{L}^{(\mathrm{R/R'})}{}_3\mathrm{P}]^{3+}$	
P−C_L in Å	1.813(2)	
	1.818(2)	
	1.825(2)	
N−C_L−N in deg	106.8(2)	
	107.2(2)	
	107.2(2)	
∑ X−P−X in deg	312.2(1)	

[a]Reference 15. [b]Reference 3.

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investigation of reaction mixtures containing PCl_3 and 2 equiv of the sterically more demanding silylimidazolium salts $\mathbf{4}^{(R/R)}$[OTf] (Dipp/H, Dipp/Cl) did not show the formation of the respective dications $\mathbf{2}_P^{(Dipp/H)2+}$ or $\mathbf{2}_P^{(Dipp/Cl)2+}$. As we recently reported on a related sterically encumbered bisimidzoliumyl substituted dication[22] we believe that such dications could generally be prepared. However, we conclude that they are not accessible via the reaction of very sterically demanding silylimidazolium salts $\mathbf{4}^{(R/R)}$[OTf] with PCl_3. Overall, the exchange reactions with silylimidazolium salts are very sensitive with respect to the steric requirements of the substituents on the nitrogen atoms of the heterocycle. The tendency of incorporating a second imidazoliumyl substituent decreases with increasing requirement of the substituents.

Synthesis of $\mathbf{5}_P^{(Me/Me')}$[OTf]$_3$. To prove that the resonance at $\delta = -82.9$ ppm originates from the presence of trication $\mathbf{5}_P^{(Me/Me)3+}$ we performed the 1:3 reaction of PCl_3 and $\mathbf{4}^{(Me/Me)}$[OTf] in several solvents but always obtained mixtures of products from which $\mathbf{5}_P^{(Me/Me)}$[OTf]$_3$ could not be isolated. However, heating a mixture of PCl_3 and 3 equiv of $\mathbf{4}^{(Me/Me)}$[OTf] without solvent at 140 °C for 3 h yielded a reddish colored viscous oil after the mixture cooled to room temperature. This oil was dissolved in acetonitrile, and the addition of diethyl ether led to the precipitation of analytically pure $\mathbf{5}_P^{(Me/Me)}$[OTf]$_3$ in excellent yield (>95%). Single crystals suitable for X-ray investigation were obtained by layering a concentrated solution of $\mathbf{5}^{(Me/Me)}$[OTf]$_3$ in MeCN with Et_2O at −32 °C.

The molecular structure of trication $\mathbf{5}_P^{(Me/Me)3+}$ is depicted in Figure 3. It reveals P−C bond lengths of 1.819 Å average (av), which are slightly shorter than in $\mathbf{2}_P^{(Me/Me)2+}$ (av 1.823 Å).[3] The wide N−C−N angles of the attached heterocyclic fragments (av 107.1° vs ~101° in NHCs)[23] indicate a pronounced delocalization of the positive charge over the imidazoliumyl fragments. The possibility of C_3 or C_{3v} symmetry of the cation is not attained due to steric interactions. The pyramidalization at the P atom (sum of X−P−X angle: 312.2°), similar to phosphanes, indicates the presence of a lone pair. Hence, we anticipated electronic properties of trication $\mathbf{5}_P^{(Me/Me)3+}$ similar to those of $\mathbf{5}_P^{(MeCPyl)3+}$[6], which should allow for complex formation with electron-rich transition metal fragments. However, reacting $\mathbf{5}_P^{(Me/Me)}$[OTf]$_3$ with K_2PdCl_4 and K_2PtCl_4 we were not able to isolate dicationic complexes $[\mathbf{5}_P^{(Me/Me)}MCl_3]^{2+}$ (M = Pd, Pt). Nevertheless, investigating the possible ligand properties of cation $\mathbf{5}_P^{(Me/Me)3+}$ is an objective of our ongoing research.

Single-Crystal X-ray Diffraction of $\mathbf{1}_P^{(Dipp/Cl)}$[OTf] and $\mathbf{1}_{Pn}^{(iPr/Me)}$[OTf] (Pn = As, Sb). The molecular structures of cations $\mathbf{1}_P^{(Dipp/Cl)+}$, $\mathbf{1}_{As}^{(iPr/Me)+}$, and $\mathbf{1}_{Sb}^{(iPr/Me)+}$ are depicted in Figure 4, and selected bonding parameters are listed in Table 3. The imidazoliumyl fragments within all cations display the typical bonding features as discussed earlier (vide supra). The two P−Cl bonds lengths in $\mathbf{1}_P^{(Dipp/Cl)+}$ (av 2.025 Å) are in the expected range, very similar to those in $\mathbf{1}_P^{(Dipp/H)+}$ (av 2.033 Å)[4] and are almost equal to one another. For the heavier congeners, two slightly different Pn−Cl bond distances are observed ($\mathbf{1}_{As}^{(iPr/Me)+}$ 2.1705(5) vs 2.2036(5) Å; $\mathbf{1}_{Sb}^{(iPr/Me)+}$ 2.3746(7) vs 2.4022(6) Å).[24] The decreased tendency of hybridization for the heavier pnictogen atoms is indicated by the sum of the X−Pn−X angles of the respective cations ($\mathbf{1}_P^{(Dipp/H)^+}$: 299.9(9)° ≈ $\mathbf{1}_P^{(Dipp/Cl)^+}$: 302.33(8)° > $\mathbf{1}^{As(^iPr/Me)^+}$: 292.00(4)° ≫ $\mathbf{1}_{Sb}^{(^iPr/Me)^+}$: 277.58(5)°).[25]

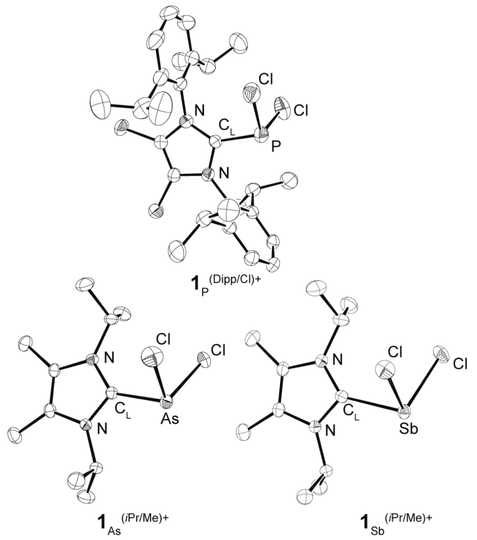


Figure 4. Molecular structures of cations $\mathbf{1}_P^{(Dipp/Cl)+}$, $\mathbf{1}_{As}^{(iPr/Me)+}$, and $\mathbf{1}_{Sb}^{(iPr/Me)+}$ with thermal ellipsoids presented at a 50% probability level. The hydrogen atoms are omitted for clarity.

Exchange Reaction of $\mathbf{1}_{Pn}^{(R/R')}$[OTf] with Me_3SiX (X = CN, N_3). The reactions of $\mathbf{1}_{Pn}^{(R/R')}$[OTf] with 2.1 equiv of Me_3SiCN (Pn = P: Me/Me, ^{i}Pr/Me,[3] Dipp/H, Dipp/Cl; Pn = As: ^{i}Pr/Me, Dipp/Cl; Scheme 3, **I**) or Me_3SiN_3 (Pn = P: Me/Me, ^{i}Pr/Me;[3] Dipp/Cl; Pn = As: ^{i}Pr/Me, Dipp/H; Scheme 3, **II**) yield clear, colorless (Me_3SiCN, MeCN as solvent) to yellow (Me_3SiN_3, C_6H_5F as solvent)[26,27] solutions of $\mathbf{6}_{Pn}^{(R/R')}$[OTf] or $\mathbf{7}_{Pn}^{(R/R')}$[OTf], respectively. Cyano derivatives $\mathbf{6}_{Pn}^{(R/R')}$[OTf] can be precipitated in good to excellent yields as colorless, analytically pure products by adding Et_2O to concentrated reaction mixtures. In the cases of derivatives $\mathbf{6}_P^{(R/R')}$[OTf] (Me/Me, ^{i}Pr/Me,[3] Dipp/H, Dipp/Cl) and $\mathbf{6}_{As}^{(iPr/Me)}$[OTf] crystals suitable for X-ray diffraction analysis were obtained from diffusion of Et_2O into concentrated MeCN solutions of the respective salt at low temperature (−32 °C; vide infra). Attempts to similarly isolate the azido-derivatives failed. Typically, the addition of *n*-hexane to the reaction mixtures resulted in the separation of all azido-derivatives as oils, which tend to readily decompose when stored at room temperature. The products are obtained as fairly pure, solid compounds after removing all volatiles in vacuo at low temperatures. Especially derivatives with a small steric demand of the R-group attached to the N atoms of the heterocycle ($\mathbf{7}_{Pn}^{(R/R')}$[OTf]; R/R′: Me/Me; ^{i}Pr/Me) are very sensitive and decompose slowly even when stored at low temperature.[28,29] Crystallization at −32 °C of the temperature-sensitive materials from CH_2Cl_2/*n*-hexane resulted in single crystals of $\mathbf{7}_P^{(iPr/Me)}$[OTf],[3] $\mathbf{7}_P^{(Dipp/Cl)}$[OTf], and $\mathbf{7}_{As}^{(Dipp/H)}$[OTf], which were suitable for X-ray structure determination (vide infra).

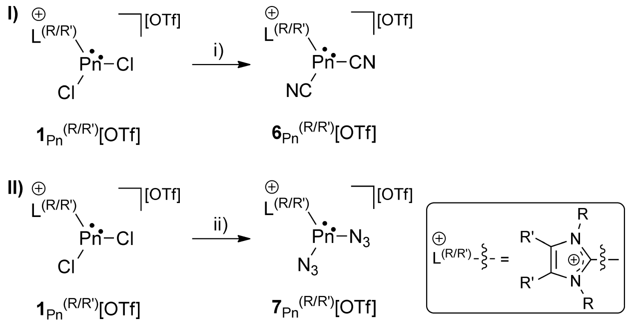
Vibrational Spectroscopy of $\mathbf{6}_{Pn}^{(R/R')}$[OTf] and $\mathbf{7}_{Pn}^{(R/R')}$[OTf]. Selected IR and Raman data of all isolated and stable crystalline dicyano/diazido-substituted salts are summarized in Table 4. The spectra display sharp bands in the expected region of $\nu \approx 2100{-}2200\ \mathrm{cm^{-1}}$, which are assigned either to the stretching frequencies ν_{CN}[30] of $\mathbf{6}_{Pn}^{(R/R')}$[OTf] or the asymmetric stretching frequencies $\nu_{as,N3}$ of $\mathbf{7}_{Pn}^{(R/R')}$[OTf]. An additional set of sharp bands is observed for derivatives $\mathbf{7}_{Pn}^{(R/R')}$[OTf] at $\nu \approx 1200{-}1300\ \mathrm{cm^{-1}}$ caused by the symmetric stretching vibrations $\nu_{sym,N3}$.[31] As already mentioned, compounds $\mathbf{7}_{Pn}^{(R/R')}$[OTf] readily decompose at room temper-

Table 3. Selected Geometrical Parameters of Crystallographically Characterized Cations $\mathbf{1}_{\mathbf{Pn}}{}^{(\mathbf{R/R'})+}$

R/R′	Dipp/H[a]	Dipp/Cl[b]	^{i}Pr/Me[b]	^{i}Pr/Me[b]
$L^{(R/R')}PnCl_2{}^+$	Pn = **P**	Pn = **P**	Pn = **As**	Pn = **Sb**
Pn–Cl in Å	2.025(2)	2.027(1)	2.1704(5)	2.3746(7)
	2.040(2)	2.022(1)	2.2036(5)	2.4022(6)
Pn–C_L in Å	1.845(4)	1.857(3)	1.974(2)	2.212(3)
N–C_L–N in deg	107.2(4)	107.8(2)	108.0(1)	106.8(2)
$\sum$ X–Pn–X in deg	299.9(9)	302.33(8)	292.00(4)	277.58(5)

[a] Reference 4. [b] Reference 15.

Scheme 3[a]



[a] Preparation of **I**: cyano-derivatives $\mathbf{6}_{\mathbf{Pn}}{}^{(R/R')}$[OTf] (Pn = P [R/R′: Me/Me (91%), ^{i}Pr/Me (65%),[3] Dipp/H (67%), Dipp/Cl (78%)]; Pn = As: [R/R′: ^{i}Pr/Me (66%), Dipp/H (98%)]): (i) +2 Me_3SiCN, MeCN, RT, −2 Me_3SiCl; **II**: azido-derivatives $\mathbf{7}_{\mathbf{Pn}}{}^{(R/R')}$[OTf] (Pn = P [R/R′: Me/Me (84%), ^{i}Pr/Me (43%),[3] Dipp/H (70%), Dipp/Cl (89%)]; Pn = As [R/R′: ^{i}Pr/Me (61%), Dipp/H (87%)]): (ii) +2 Me_3SiN_3, C_6H_5F, RT, −2 Me_3SiCl).

Table 4. Selected IR and Raman Data of Isolated Compounds $\mathbf{6}_{\mathbf{Pn}}{}^{(\mathbf{R/R'})}$[OTf] and $\mathbf{7}_{\mathbf{Pn}}{}^{(\mathbf{R/R'})}$[OTf]

ν in cm^{-1}	Me/Me	^{i}Pr/Me	Dipp/H	Dipp/Cl
$L^{(R/R')}P(CN)_2$		*a*		
IR (ν_{CN})	2193	2187	2188	2192
Raman (ν_{CN})	2193	2193	2190	2195
$L^{(R/R')}As(CN)_2$	*b*			*b*
IR (ν_{CN})		2187	2187	
Raman (ν_{CN})		2187	2192	
$L^{(R/R')}P(N_3)_2$	*c*	*a,d*		
IR ($\nu_{as,N3}$)		2169/*e*	2155/2129	2156/2135
($\nu_{sym,N3}$)		1272/*e*	1269/1255	1289/1269
Raman ($\nu_{as,N3}$)		2157/2148	2158/2136	2156/2141
($\nu_{sym,N3}$)		1287/*e*	1239/1226	1275/1239
$L^{(R/R')}As(N_3)_2$	*b*			*b*
IR ($\nu_{as,N3}$)		2112/*e*	2117/2093	
($\nu_{sym,N3}$)		1242/1222	1237/1220	
Raman ($\nu_{as,N3}$)		2106/2086	2117/2094	
($\nu_{sym,N3}$)		1235/1222	1237/*e*	

[a] Reference 3. [b] Compounds not obtained. [c] Compounds too labile to record IR and Raman data. [d] Raman data not recorded. [e] Resonances were not observed due to overlap of resonances.

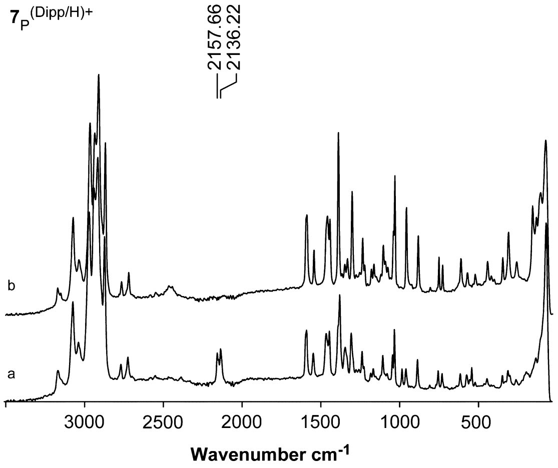
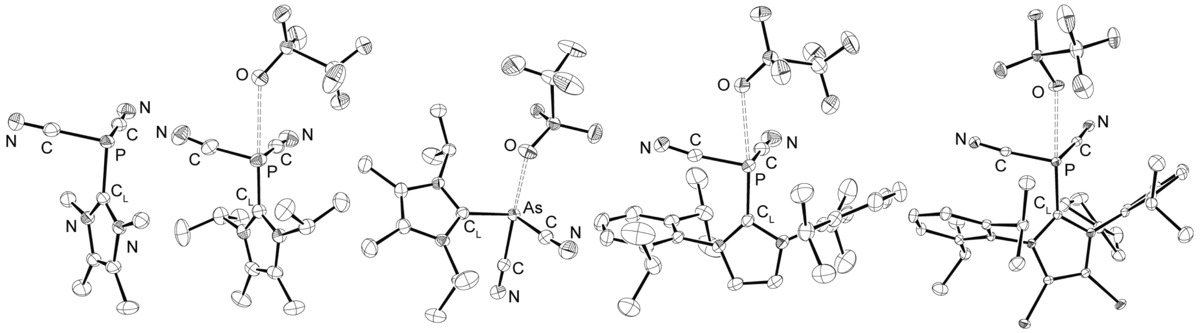


Figure 5. Raman spectra of solid $\mathbf{7}_{\mathbf{P}}{}^{(Dipp/H)}$[OTf], recorded after (a) storage for two years at −40 °C and (b) recorded after storage of a sample for 7 d at ambient temperature.

ature but seem to be reasonably stable in the case of the sterically more encumbered derivatives when stored at temperatures below −40 °C. The Raman spectra of compound $\mathbf{7}_{\mathbf{P}}{}^{(Dipp/H)}$[OTf] stored for two years at −40 °C is depicted in Figure 5a. The same sample that was stored for 7 days at room temperature showed complete decomposition of the compound as indicated by the disappearance of the characteristic azide bands at ~2150 cm^{-1} (Figure 5b). The azide decomposes to a complex mixture of products, which we are currently investigating.

Nuclear Magnetic Resonance Investigation into $\mathbf{6}_{\mathbf{Pn}}{}^{(\mathbf{R/R'})}$[OTf] and $\mathbf{7}_{\mathbf{Pn}}{}^{(\mathbf{R/R'})}$[OTf]. The $^{31}P\{^1H\}$ chemical shifts of the CD_3CN solutions of dicyano derivatives $\mathbf{6}_{\mathbf{P}}{}^{(R/R')}$[OTf] are given in Table 1. The observed values range from δ = −109.7 ($\mathbf{6}_{\mathbf{P}}{}^{(Dipp/Cl)+}$) to −125.0 ppm ($\mathbf{6}_{\mathbf{P}}{}^{(Me/Me)+}$), which is comparable to the chemical shift of $P(CN)_3$ (δ = −137.8 ppm).[32] Additionally, the chemical shifts of the dichloro derivatives $\mathbf{1}_{\mathbf{P}}{}^{(R/R')}$[OTf] (range from δ = 107.2 to 114.9 ppm, Table 1) are comparable to that of Cl_2PCN (δ = 93.8 ppm in CD_3CN).[33] Apparently, the imidazoliumyl and cyano substituents have similar general influences on ^{31}P NMR chemical shifts. The chemical shifts of the cyano derivatives $\mathbf{6}_{\mathbf{P}}{}^{(R/R')}$[OTf] decrease in the series Dipp/Cl > Dipp/H > ^{i}Pr/Me > Me/Me reflecting the more pronounced deshielding by the aryl- compared to the alkyl-substituted imidazole fragments. A related trend is observed for the absolute values of the $^1J(^{31}P-^{13}C)$ coupling constants. Within the mentioned series these decrease from 54.3 to 50.1 Hz, which is consistent with a higher group electronegativity of the aryl-substituted derivatives. The P-azide derivatives $\mathbf{7}_{\mathbf{P}}{}^{(R/R')}$[OTf] display the same trend of the group electronegativity; thus, a pronounced upfield shift is observed in the series Dipp/Cl > Dipp/H > ^{i}Pr/Me > Me/Me ranging from δ = 109.4 to 98.2 ppm, respectively (Table 1). Additional NMR investigations (^1H, ^{13}C, ^{19}F) into all isolated and stable compounds $\mathbf{6}_{\mathbf{Pn}}{}^{(R/R')}$[OTf] and $\mathbf{7}_{\mathbf{Pn}}{}^{(R/R')}$[OTf] display the expected characteristics of the respective derivatives.

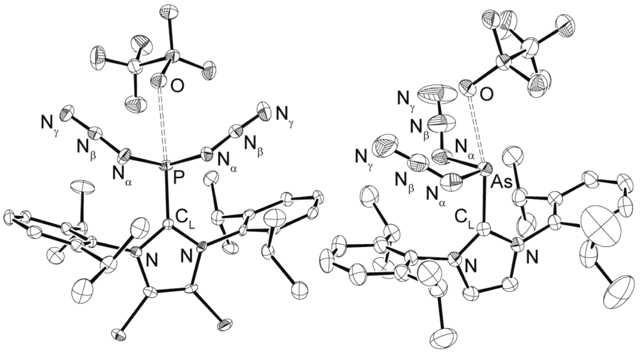
Single-Crystal X-ray Diffraction of $\mathbf{6}_{\mathbf{Pn}}{}^{(\mathbf{R/R'})}$[OTf] and $\mathbf{7}_{\mathbf{Pn}}{}^{(\mathbf{R/R'})}$[OTf]. Compounds $\mathbf{6}_{\mathbf{Pn}}{}^{(R/R')}$[OTf] (Pn = P: Me/Me, ^{i}Pr/Me,[3] Dipp/H, Dipp/Cl; Pn = As: ^{i}Pr/Me), $\mathbf{7}_{\mathbf{P}}{}^{(Dipp/Cl)}$-



$\mathbf{6}_P^{(Me/Me)+}$ $\mathbf{6}_P^{(iPr/Me)}$[OTf] $\mathbf{6}_{As}^{(iPr/Me)}$[OTf] $\mathbf{6}_P^{(Dipp/H)}$[OTf] $\mathbf{6}_P^{(Dipp/Cl)}$[OTf]

Figure 6. Molecular structures of cation $\mathbf{6}_P^{(Me/Me)+}$, compounds $\mathbf{6}_P^{(R/R')}$[OTf] (^{i}Pr/Me,[3] Dipp/H, Dipp/Cl) and $\mathbf{6}_{As}^{(iPr/Me)}$[OTf] with thermal ellipsoids presented at a 50% probability level. The hydrogen atoms are omitted for clarity.

[OTf], and $\mathbf{7}_{As}^{(Dipp/H)}$[OTf] crystallize in the monoclinic space groups $P2_1/c$ or $P2_1/n$ each with four molecules in the unit cell (Figures 6 and 7). The crystallographic data and refinement details for these compounds are summarized in the Experimental Section (Table 7). Selected bond lengths and angles are compiled in Tables 5 and 6. The bonding parameters within the molecular units of all cations are within the expected ranges.[27b,33,34] Similar to other P- and As-cyano derivatives[31,32] a significant deviation of the P−C−N angle from 180° is observed (Table 6). However, a remarkable trend is observed when the secondary interactions between the central Pn atom and the oxygen atoms of the triflate anions are considered. Counterintuitively within the frame of steric considerations, these secondary interactions increase in number and strength with increasing steric demand of the imidazoliumyl substituent. The P atom in $\mathbf{6}_P^{(Me/Me)}$[OTf] is essentially in a distorted Ψ-tetrahedral coordination environment. Only one very weak intermolecular interaction to the N atom of a neighboring cyano substituent (P···N = 3.343(3) Å, van der Waals distance: 3.4 Å) is observed, which we attribute to packing effects



$\mathbf{7}_P^{(Dipp/Cl)}$[OTf] $\mathbf{7}_{As}^{(Dipp/H)}$[OTf]

Figure 7. Molecular structures of $\mathbf{7}_P^{(Dipp/Cl)}$[OTf] and $\mathbf{7}_{As}^{(Dipp/H)}$[OTf] with thermal ellipsoids presented at a 50% probability level. The hydrogen atoms are omitted for clarity.

Table 6. Selected Geometrical Parameters of Crystallographically Characterized Cations $\mathbf{7}_{Pn}^{(R/R')+}$

R/R′	^{i}Pr/Me[a]	Dipp/H[b]	Dipp/Cl[b]
$L^{(R/R')}Pn(N_3)_2$	Pn = P	Pn = As	Pn = P
P−C_L in Å	1.837(3)	1.998(2)	1.870(7)
P−N_α in Å	1.725(2)	1.871(2)	1.720(7)
	1.753(3)	1.893(2)	1.725(7)
N_α−N_β in Å	1.244(3)	1.177(3)	1.240(9)
	1.216(4)	1.187(3)	1.24(1)
N_β−N_γ in Å	1.120(3)	1.144(3)	1.128(9)
	1.133(4)	1.141(3)	1.12(1)
Pn−$O_{triflate}$ in Å	2.864(3)	2.721(2)	2.666(7)
N_α−N_β−N_β in deg	172.0(3)	174.2(3)	172.6(9)
	174.6(4)	171.7(3)	171.2(9)
N−C_L−N in deg	107.8(2)	106.3(2)	105.7(6)
$\sum$ X−Pn−X in deg	289.8(1)	281.22(8)	288.9(3)

[a]Reference 3. [b]Reference 11.

Table 5. Selected Geometrical Parameters of Crystallographically Characterized Cations $\mathbf{6}_{Pn}^{(R/R')+}$

R/R′	Me/Me[a]	^{i}Pr/Me[b]	^{i}Pr/Me[a]	Dipp/H[a]	Dipp/Cl[a]
$L^{(R/R')}P(CN)_2$	Pn = P	Pn = P	Pn = As	Pn = P	Pn = P
Pn−C_L in Å	1.833(3)	1.823(2)	1.956(2)	1.851(2)	1.863(1)
Pn−C_{CN} in Å	1.803(3)	1.798(2)	1.935(2)	1.794(2)	1.799(2)
	1.800(4)	1.796(2)	1.939(2)	1.791(2)	1.793(2)
C≡N in Å	1.145(4)	1.140(3)	1.137(3)	1.131(3)	1.140(2)
	1.139(4)	1.130(3)	1.141(3)	1.137(5)	1.139(2)
Pn−$O_{triflate}$ in Å	>3.5	2.864(2)	2.751(3)	2.630(2)	2.541(1)
Pn−C−N in deg	176.4(3)	176.60(2)	170.8(2)	176.0(2)	173.5(1)
	174.3(3)	172.5(2)	177.8(2)	171.2(2)	174.8(1)
N−C_L−N in deg	108.3(2)	107.6(2)	108.2(2)	107.08(2)	107.5(1)
NC−Pn−CN in deg	93.5(1)	94.62(9)	91.48(9)	96.15(9)	94.39(7)
$\sum$ X−Pn−X in deg	290.9(1)	295.03(9)	285.23(8)	291.19(8)	290.57(6)

[a]Reference 15. [b]Reference 3.

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(compare intermolecular P···N interactions in $P(CN)_3$: 2.85, 2.98, and 2.97 Å).[35] In contrast, $\mathbf{6}_{P}^{(iPr/Me)}$[OTf] features a Ψ-trigonal bipyramidal coordination with the cyano substituents and the lone pair of electrons in the equatorial and the imidazoliumyl substituent in an axial position. The second axial position is occupied by the triflate anion with a P···O distance of 2.864(2) Å. Intermolecular P···N contacts are not observed. The same arrangement but with shorter P···O distances is found for $\mathbf{6}_{P}^{(Dipp/H)}$[OTf] (P···O = 2.630(2) Å) and $\mathbf{6}_{P}^{(Dipp/Cl)}$[OTf] (P···O = 2.541(1) Å). With decreasing P···O distances a slight increase of length of the $P{-}C_L$ bond is observed. We attribute this effect to the increasing group electronegativity in the series Me/Me < ^{i}Pr/Me < Dipp/H < Dipp/Cl leading to an increasing Lewis acidity and thus a stronger interaction with the triflate anion.

This is in line with the observed trend in the ^{31}P NMR spectroscopic shifts (vide supra), which also indicated a decreased shielding within the mentioned series. The related arsenic derivative $\mathbf{6}_{As}^{(iPr/Me)}$[OTf] also features a Ψ-trigonal bipyramidal coordination. But in contrast to the phosphorus analogue the imidazoliumyl substituent is found on the equatorial and one cyano substituent in the axial position. In comparison to the P-derivative, this may be due to the longer bond lengths involving arsenic. This leads to a reduced steric pressure and thus the possibility to accommodate the bulky triflate and imidazolium fragments in a 90° angle to one another. It may also be argued that the π-backbonding from the cyano substituent in an equatorial position to antibonding orbitals at the central Pn atom is not as intense in the case of arsenic compared to phosphorus. Thus, the tendency to accommodate the cyano substituent in the equatorial position is lowered, and the more bulky imidazolium fragment is observed in the more spacious equatorial position. Yet these arguments remain speculative. Compounds $\mathbf{7}_{P}^{(Dipp/Cl)}$[OTf] and $\mathbf{7}_{As}^{(Dipp/H)}$[OTf] show a similar Ψ-trigonal-bipyramidal arrangement as observed for the P-cyano derivatives, in which the equatorial positions are now occupied by two azide units. The structural parameters observed for the two azide units ($N_\alpha N_\beta N_\gamma$) in both compounds compare well to those observed in other phosphorus[36] or arsenic[31b,37] azide compounds. Again significant interionic interactions are observed between an oxygen atom of the triflate anion and the central Pn atom of the cation (P···O = 2.666(7) Å; As···O = 2.721(2) Å; Table 6). Intermolecular Pn···N interactions are not observed. The major difference between P-derivative $\mathbf{7}_{P}^{(Dipp/Cl)}$[OTf] and As-derivative $\mathbf{7}_{As}^{(Dipp/H)}$[OTf] lies in the relative orientation of the azide moieties. As illustrated in Figure 7 they adopt a V-shape arrangement in the P-derivative. The As-derivative reveals a rather askew arrangement with one of the azide groups inclined to the other. These types of orientations for azide groups have been discussed for other derivatives and are known to be energetically very similar to one another.[38] Thus, any packing effects in the solid state can easily distort their structures from the approximate C_{2v} or C_s symmetry. Obviously, the degree of freedom around the arsenic atom is much greater due to the increased van der Waals radius.

CONCLUSION

The reactions of $\mathbf{4}^{(R/R')}$[OTf] (R/R′: Me/Me; ^{i}Pr/Me, Dipp/H, Dipp/Cl) with $PnCl_3$ (Pn = P, As, Sb) strongly depend on the pnictogen atom and the steric demand of the R-group attached to the N-atoms of the heterocycle. Derivatives $\mathbf{1}_{P}^{(R/R')}$[OTf] (R/R′: Me/Me; ^{i}Pr/Me, Dipp/H, Dipp/Cl) and $\mathbf{1}_{As}^{(R/R')}$[OTf] (R/R′: ^{i}Pr/Me; Dipp/H) were isolated on a multigram scale and were fully characterized. Related Sb-derivatives could not be isolated as the reaction mixtures are significantly more complex compared to those involving phosphorus and arsenic compounds. However, we were able to identify and crystallographically characterize derivative $\mathbf{1}_{Sb}^{(iPr/Me)}$[OTf]. A decreased steric demand at the N-atoms of the heterocycle leads to an equilibrium between the monocation $\mathbf{1}_{P}^{(Me/Me)+}$, the dication $\mathbf{2}_{P}^{(Me/Me)2+}$, and trication $\mathbf{5}_{P}^{(Me/Me)3+}$ in solution. Of these compounds $\mathbf{1}_{P}^{(Me/Me)}$[OTf] and $\mathbf{5}_{P}^{(Me/Me)}[OTf]_3$ were isolated in excellent yields, and $\mathbf{2}_{P}^{(Me/Me)}[OTf]_2$ was structurally characterized. Selected exchange reactions of the chloro groups of derivatives $\mathbf{1}_{Pn}^{(R/R')}$[OTf] by cyano and azido moieties with Me_3SiX (X = CN, N_3) as source of the respective nucleophile yield the expected dicyano ($\mathbf{6}_{Pn}^{(R/R')}$[OTf]) and diazido derivatives ($\mathbf{7}_{Pn}^{(R/R')}$[OTf]), respectively. The obtained cyano and azido derivatives were thoroughly characterized by IR, Raman, and NMR spectroscopies, and their molecular arrangement was discussed with respect to the influence of the steric demand at the nitrogen atoms of the heterocycle.

EXPERIMENTAL SECTION

General Remarks. All manipulations were performed in a Glovebox MB Unilab (M. Braun; $p(O_2)/p^0 \leq 1$ ppm, $p(H_2O)/p^0 \leq 1$ ppm) or using Schlenk techniques under an atmosphere of purified argon. All chemicals were purchased from Sigma-Aldrich or ABCR. Dry, oxygen-free solvents (CH_2Cl_2, CD_2Cl_2, d_3-MeCN, C_6H_5F, $C_6H_4F_2$ (distilled from CaH_2), and *n*-hexane, toluene, tetrahydrofuran (thf, distilled from K)) were employed. All distilled solvents were stored either over molecular sieves (4 Å; CH_2Cl_2, CD_2Cl_2, MeCH, d_3-MeCN, C_6H_5F, $C_6H_4F_2$) or potassium mirror (Et_2O, thf, toluene, *n*-hexane). PCl_3, Me_3SiOTf, Me_3SiN_3, and Me_3SiCN were distilled prior to use. NHCs ($\mathbf{L}^{(Me/Me)}$, $\mathbf{L}^{(iPr/Me)}$, $\mathbf{L}^{(Dipp/H)}$, $\mathbf{L}^{(Dipp/Cl)}$) and imidazoliumyl-transfer reagents $\mathbf{4}^{(iPr/Me)}/\mathbf{4}^{(Dipp/H)}$[OTf] were prepared according to literature procedures.[3,4,8−10] All glassware was oven-dried at 160 °C prior to use. Solution NMR spectra were measured on a Bruker Avance (III) (^1H (400.03 MHz), ^{13}C (100.59 MHz), ^{31}P (161.94 MHz), ^{19}F (188.31 MHz), ^{29}Si (79.49 MHz)) at 300 K unless indicated otherwise. Assignments of individual resonances were done using two-dimensional techniques (HMBC, HSQC) where necessary. Chemical shifts (δ) were referenced to $\delta_{TMS} = 0.00$ ppm (^1H, ^{13}C) and $\delta_{H3PO4(85\%)} = 0.00$ ppm (^{31}P, externally) and are reported in parts per million. Melting points were recorded on an electrothermal melting point apparatus (Barnstead Electrothermal IA9100) in sealed capillaries under argon atmosphere and are uncorrected. Infrared (IR) and Raman spectra were recorded at ambient temperature using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd:YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parentheses. An ATR cell (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parentheses using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder. Elemental analyses were performed on an Elementar Cube elemental analyzer. Elemental analyses were not performed for the azide derivatives.

Caution! *Covalent azides are energetic materials and tend to explode under certain conditions. Appropriate safety precautions should be taken, especially when these compounds are prepared on a larger scale. As a precaution, laboratories and personnel should be properly grounded, and safety equipment such as Kevlar gloves, leather coats, face shields, and ear plugs should be used.*

Synthesis of $\mathbf{4}^{(Me/Me)}/\mathbf{4}^{(Dipp/Cl)}$[OTf]. A slight excess of Me_3SiOTf (1.3 equiv) was added dropwise to a solution of $\mathbf{L}^{(Me/Me)}/\mathbf{L}^{(Dipp/H)}$ in fluorobenzene. After 1 h, the suspension was filtrated, and the obtained residue was washed with fluorobenzene (3 × 20 mL). All volatiles from the residue were removed in vacuo, and $\mathbf{4}^{(\mathrm{Me/Me})}$/$\mathbf{4}^{(\mathrm{Dipp/Cl})}$[OTf] was obtained as analytical pure, colorless solid.

$4^{(\mathrm{Me/Me})}$[OTf]. $\mathrm{L}^{(\mathrm{Me/Me})}$: 18.7 g (150.4 mmol), Me_3SiOTf: 43.4 g (35.4 mL, 195.6 mmol, 1.3 equiv), fluorobenzene (60 mL); Yield: 33.3 g (64%, 96.2 mmol); mp 114−116 °C; Raman (90 mW, in cm^{-1}): ν = 3013(5), 2983(20), 2932(9), 2913(55), 1641(15), 1486(8), 1445(5), 1412(41), 1396(9), 1353(9), 1257(6), 1225(11), 1108(10), 1035(95), 756(34), 705(8), 644(6), 634(47), 595(35), 572(17), 348(35), 314(21), 233(5), 196(14), 99(5); IR (ATR, 300 K, in cm^{-1}): ν = 2961(w), 2285(vw), 1642(w), 1447(w), 1414(vw), 1383(w), 1258(vs), 1224(vw), 1150(m), 1033(s), 859(vs), 772(m), 755(vw), 705(w), 641(s), 572(m), 517(m); ^{1}H NMR (CD_3CN, 300 K, in ppm): δ = 0.55 (9H, s, SiCH_3), 2.21 (6H, s, CCH_3), 3.71 (6H, s, NCH_3); ^{13}C{^{1}H} NMR (CD_3CN, 300 K, in ppm): δ = 0.0 (s, $SiCH_3$), 9.1 (s, CCH_3), 35.3 (NCH_3), 122.3 (q, $^1J_{CF}$ = 320 Hz, CF_3), 130.5 (s, CCH_3), 148,5 (s, $CSiCH_3$); ^{29}Si{^{1}H} NMR (CD_3CN, 300 K, in ppm): δ = −4.0 (s); ^{19}F NMR (CD_3CN, 300 K, in ppm): δ = −79.3 (s, CF_3); elemental analysis: $C_{11}H_{21}F_3N_2O_3SSi$ (346.45): calcd: N 8.1, C 38.1, H 6.1, found: N 8.1, C 38.1, H 5.8%.

$4^{(\mathrm{Dipp/Cl})}$[OTf]. $\mathrm{L}^{(\mathrm{Dipp/Cl})}$: 2.10 g (4.6 mmol); Me_3SiOTf: (1.09 mL, 1.33 g, 6.0 mmol, 1.3 equiv), fluorobenzene (20 mL); Yield: 2.63 g (85%, 3.9 mmol); mp > 220 °C dec; Raman (70 mW, in cm^{-1}): ν = 3070(21), 2975(40), 2913(64), 2872(27), 1590(29), 1463(24), 1445(20), 1369(39), 1327(20), 1301(26), 1238(23), 1167(9), 1100(12), 1048(18), 1034(39), 990(16), 959(8), 886(21), 754(16), 736(11), 626(28), 605(14), 573(11), 453(14), 350(24), 316(27), 236(20), 170(24), 142(33), 84(95); IR (ATR, 300 K, in cm^{-1}): ν = 2972(w), 2360(w), 1578(m), 1464(w), 1440(w), 1390(vw), 1363(m), 1257(s), 1225(m), 1148(s), 1060(w), 1032(s), 989(m), 936(w), 848(s), 811(m), 787(w), 768(m), 754(vw), 636(vs), 572(m), 544(vw), 516(m), 437(w); ^{1}H NMR (CD_2Cl_2, 300 K, in ppm): δ = −0.11 (9H, s, SiCH_3), 1.28 (12H, d, $^3J_{HH}$ = 6.7 Hz, CHCH_3), 1.38 (12H, d, $^3J_{HH}$ = 6.7 Hz, CHCH_3), 2.41 (4H, *pseudo* sept, $^3J_{HH}$ = 6.7 Hz, $CHCH_3$), 7.51 (4H, d, $^3J_{HH}$ = 7.9 Hz, *m*−CH), 7.77 (2H, t, $^3J_{HH}$ = 7.9 Hz, *p*−CH); ^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, in ppm): δ = −0.5 (m, $^1J_{CSi}$ = 56.4 Hz), 23.6 (s, $CHCH_3$), 25.3 (s, $CHCH_3$), 29.8 (s, $CHCH_3$), 123.1 (q, $^1J_{CF}$ = 320.7 Hz, CF_3), 125.6 (s, CCl), 126.4 (s, *m*−C), 129.0 (s, *i*−C), 134.2 (s, *p*−C), 146.2 (s, *o*−C), 154.8 (s); ^{19}F NMR (CD_2Cl_2, 300 K, in ppm): δ = −78.8 (s, CF_3); ^{29}Si NMR (CD_2Cl_2, 300 K, in ppm): δ = 2.9 (s, $SiCH_3$, $^2J_{HSi}$ = 6.8 Hz, $SiCH_3$); elemental analysis: $C_{31}H_{45}F_3N_2O_3SSi$ (610.85): calcd: N 4.1, C 54.8, H 6.4, found: N 4.4, C 54.2, H 6.2%.

Synthesis of $1_P^{(\mathrm{Me/Me})}$[OTf]. $\mathbf{4}^{(\mathrm{Me/Me})}$[OTf] (2.50 g, 7.2 mmol) was suspended in PCl_3 (10 mL) as solvent and refluxed for 48 h (bath temperature: 120 °C). The formation of an orange suspension was observed after 30 min. After cooling to room temperature, the mixture separated into two phases. The supernatant solution was removed. From the remaining orange oil all volatiles were removed in vacuo to yield $\mathbf{1}_P^{(\mathrm{Me/Me})}$[OTf] as slight beige colored solid; Yield: 2.52 g (93%, 6.7 mmol); mp > 200 °C dec; Raman (250 mW, 300 K, in cm^{-1}): ν = 3002(30), 2965(82), 2932(95), 2792(9), 1633(45), 1451(54), 1410(63), 1399(41), 1389(41), 1337(71), 1264(30), 1222(19), 1104(43), 1048(11), 1029(82), 984(13), 769(15), 755(32), 599(48), 571(34), 504(95), 493(67), 416(11), 347(28), 311(32), 261(41), 182(41), 148(43), 103(88); IR (ATR, 300 K, in cm^{-1}): ν = 2965(vw), 1629(vw), 1491(vw), 1440(w), 1406(vw), 1381(vw), 1334(vw), 1252(vs), 1219(w), 1157(vw), 1144(w), 1099(vw), 1027(s), 857(w), 768(w), 634(vs); ^{1}H NMR (CD_3CN, 300 K, in ppm): δ = 2.31 (6H, s, CCH_3), 3.99 (6H, s, NCH_3); ^{13}C{^{1}H} NMR (CD_3CN, 300 K, in ppm): δ = 9.3 (s, CCH_3), 35.5 (d, $^3J_{CP}$ = 13 Hz, NCH_3), 122.2 (q, $^1J_{CF}$ = 323 Hz, CF_3), 134.1 (s, CCH_3), 139.0 (d, $^1J_{CP}$ = 106 Hz, $CPCl_2$); ^{19}F NMR (CD_3CN, 300 K, in ppm): δ = −79.3 (s, CF_3); ^{31}P{^{1}H} NMR (CD_3CN, 300 K, in ppm): δ = 107.8 (s); elemental analysis: $C_8H_{12}Cl_2F_3N_2O_3PS$ (375,12): calcd: N 7.4, C 25.6, H 3.2, found: N 6.6, C 26.6, H 3.4%.

Attempted Syntheses of $2_P^{(\mathrm{Me/Me})}$[OTf]$_2$. PCl_3 (0.08 mL, 0.13 g, 0.9 mmol) was combined with $\mathbf{4}^{(\mathrm{Me/Me})}$[OTf] (0.65 g, 1.9 mmol, 2 equiv) under several conditions (in fluorobenzene in the microwave: 80 °C, 2 h, 150 W; solvent free in the microwave: 80 °C, 2 h, 150 W; solvent free in an oil bath: 120 °C, 24 h) and led in all cases to a mixture of three compounds, identified in the ^{31}P NMR spectrum. All attempts to separate or isolate the compounds via fractional crystallization, extraction, or other techniques were unsuccessful. However, we obtained a few crystals out of the mother solution of the reaction mixtures, which were suitable for crystal structure analysis; Yield: negligible; ^{1}H NMR (CD_3CN, 300 K, in ppm): δ = 2.33 (s, CCH_3), 3.73 (s, NCH_3); ^{31}P{^{1}H} NMR (CD_3CN, 300 K, in ppm): δ = 11.5 (s).[39]

Scrambling Reaction of $1_P^{(\mathrm{Me/Me})}$[OTf] and $5_P^{(\mathrm{Me/Me})}$[OTf]$_3$ in CD_3CN. $\mathbf{1}^{(\mathrm{Me/Me})}$[OTf] (43 mg, 0.05 mmol, 1 equiv) was combined with $\mathbf{5}^{(\mathrm{Me/Me})}$[OTf]$_3$ (19 mg, 0.05 mmol, 1 equiv) in CD_3CN (1.5 mL) and heated in a CEM Discover microwave with pressure control at 120 °C. After 10 min, 2 h, 5 h, and 16 h ^{31}P{^{1}H} NMR spectra were measured. These are depicted in Figure 2.

Synthesis of $5_P^{(\mathrm{Me/Me})}$[OTf]$_3$. A mixture of PCl_3 (0.22 mL, 0.33 g, 2.4 mmol) and $\mathbf{4}^{(\mathrm{Me/Me})}$[OTf] (2.50 g, 7.2 mmol, 3 equiv) was refluxed (bath temperature: 140 °C) for 3 h. After cooling to room temperature the obtained red colored melt was dissolved in acetonitrile (20 mL). After the acetonitrile solution was treated with diethyl ether (60 mL), $\mathbf{5}_P^{(\mathrm{Me/Me})}$[OTf]$_3$ precipitated as pale brown colored solid; Yield: 1.95 g (95%, 2.3 mmol); mp 154−157 °C; Raman (250 mW, 300 K, in cm^{-1}): ν = 2978(5), 2938(30), 2185(11), 2172(6), 2158(11), 2147(12), 2138(5), 2061(12), 1622(20), 1448(14), 1405(55), 1382(27), 1332(41), 1270(3), 1225(6), 1092(27), 1037(39), 977(6), 756(15), 668(4), 597(11), 568(17), 519(3), 492(3), 467(6), 349(18), 314(9), 182(8), 81(95); IR (ATR, 300 K, in cm^{-1}): ν = 2972(vw), 1620(vw), 1486(vw), 1442(w), 1402(vw), 1377(vw), 1329(vw), 1253(vs), 1223(w), 1146(m), 1027(vs), 851(m), 773(w), 755(vw), 667(vw), 633(vs); ^{1}H NMR (CD_3CN, 300 K, in ppm): δ = 2.39 (s, CCH_3), 3.64 (s, NCH_3); ^{13}C{^{1}H} NMR (CD_3CN, 300 K, in ppm): δ = 9.0 (s, CCH_3), 34.9 (s, NCH_3), 122.2 (q, $^1J_{CF}$ = 320 Hz, CF_3), 125.8 (d, $^1J_{CP}$ = 20 Hz, CP), 136.0 (s, CCH_3); ^{19}F NMR (CD_3CN, 300 K, in ppm): δ = −79.3 (s, CF_3), ^{31}P{^{1}H} NMR (CD_3CN, 300 K, in ppm): δ = −82.9 (s); elemental analysis: $C_{24}H_{36}F_9N_6O_9PS_3$ (346.45): calcd: N 9.9, C 33.9, H 4.4, found: N 9.9, C 33.8, H 4.1%.

Synthesis of $1_{As}^{(\mathrm{iPr/Me})}$[OTf]. An excess of $AsCl_3$ (0.73 mL, 1.57 g, 8.7 mmol, 1.5 equiv) was added to a solution of $\mathbf{4}^{(\mathrm{iPr/Me})}$[OTf] (2.34 g, 5.8 mmol, 1.0 equiv) in fluorobenzene (20 mL). The reaction flask was placed into an ultrasonic bath at 50 °C for 12 h. The addition of *n*-hexane to the reaction mixture led to the precipitation of $\mathbf{1}_{As}^{(\mathrm{iPr/Me})}$[OTf], which was filtrated and washed with *n*-hexane (3 × 10 mL). After all volatiles were removed in vacuo, $\mathbf{1}_{As}^{(\mathrm{iPr/Me})}$[OTf] was obtained as pale yellow, analytically pure, and very moisture-sensitive material; Yield: 2.56 g (93%; 5.40 mmol); mp > 160 °C dec; Raman (250 mW, 300 K, in cm^{-1}): ν = 2994(23), 2956(9), 2938(41), 2883(7), 1613(50), 1478(8), 1460(12), 1448(12), 1422(24), 1402(24), 1387(11), 1368(26), 1306(6), 1278(75), 1241(14), 1219(10), 1155(11), 1140(8), 1024(87), 892(22), 778(11), 754(36), 573(9), 539(10), 462(7), 415(21), 390(99), 362(95), 347(41), 312(36), 290(7), 273(7), 196(51), 138(38), 120(21), 71(70); IR (ATR, 300 K, in cm^{-1}): ν = 2985(m), 2306(vw), 1613(w), 1447(vw), 1423(w), 1398(w), 1378(w), 1349(vw), 1287(w), 1234(vs), 1152(m), 1115(vw), 1085(w), 1024(m), 908(w), 777(w), 753(m), 693(w), 637(vs), 572(w), 540(vw), 515(m), 433(vw), 414(w); ^{1}H NMR (CD_3CN, 300 K, in ppm): δ = 1.62 (12H, d, $^3J_{HH}$ = 7.0 Hz, CHCH_3), 2.39 (6H, s, CCH_3), 5.33 (2H, *pseudo* sept, $^3J_{HH}$ = 7.0 Hz, $CHCH_3$); ^{13}C{^{1}H} NMR (CD_3CN, 300 K, in ppm): δ = 11.1 (s, CCH_3), 22.0 (s, $CHCH_3$), 54.8 (s, $CHCH_3$), 122.2 (q, $^1J_{CF}$ = 320.5 Hz, CF_3), 133.2 (s, CCH_3), 145.8 (s, $CAsCl_2$); ^{19}F NMR (CD_3CN, 300 K, in ppm): δ = −79.3 (s, CF_3); elemental analysis: $C_{12}H_{20}Cl_2F_3N_2O_3AsS$ (475.19): calcd: N 5.9, C 30.3, H 4.2, found: N 5.7, C 29.9, H 4.3%.

Synthesis of $1_{Sb}^{(\mathrm{iPr/Me})}$[OTf]. An excess of $SbCl_3$ (2.02 g, 8.9 mmol, 1.5 equiv) was added to a solution of $\mathbf{4}^{(\mathrm{iPr/Me})}$[OTf] (2.39 g, 6.0 mmol, 1.0 equiv) in fluorobenzene (20 mL). The reaction flask was placed into an ultrasonic bath at 70 °C for 48 h. Addition of *n*-hexane to the reaction mixture gave an oily substance. All attempts to purify the oil or to isolate $\mathbf{1}_{Sb}^{(\mathrm{iPr/Me})}$[OTf] from the oil were unsuccessful. Nevertheless, it was possible to obtain crystals, which were suitable for crystal structure analysis and NMR characterization, by diffusion of *n*-hexane into the respective reaction mixture at ambient temperature; Yield: negligible; ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 1.64 (12H, d, $^3J_{HH}$ = 6.9 Hz, CHC*H*$_3$), 2.39 (6H, s, CC*H*$_3$), 5.30 (2H, sept, $^3J_{HH}$ = 6.9 Hz, C*H*CH$_3$); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 10.1 (s, CCH$_3$), 21.0 (s, CHCH$_3$), 54.2 (s, CHCH$_3$), 120.7 (q, $^1J_{CF}$ = 320.1 Hz, CF$_3$), 130.5 (s, CCH$_3$), 159.6 (s, CSbCl$_2$); ^{19}F NMR (CD$_3$CN, 300 K, in ppm): δ = −78.9 (s, CF$_3$).

Synthesis of $\mathbf{1_P^{(Dipp/Cl)}/1_{As}^{(Dipp/H)}}$[OTf]. PnCl$_3$ (Pn = P, As) was added to a solution of **4**$^{(Dipp/Cl)}$/**4**$^{(Dipp/H)}$[OTf] in fluorobenzene (15 mL) and stirred for 20 h at ambient temperature. After the colorless solution was concentrated to one-third of its original volume, *n*-hexane (20 mL) was added to cause precipitation of the product. After filtration the obtained residue was washed with *n*-hexane (2 × 10 mL) and dried in vacuo.

$\mathbf{1_P^{(Dipp/Cl)}}$[OTf]. **4**$^{(Dipp/Cl)}$[OTf]: 3.37 g, (4.7 mmol); PCl$_3$ (0.56 mL, 0.88 g, 6.5 mmol); Yield: 3.20 g (90%, 4.2 mmol); mp > 200 °C dec; Raman (90 mW, in cm^{-1}): ν = 3069(25), 3033(11), 2976(36), 2943(40), 2915(45), 2873(24), 2775(7), 2728(9), 1589(25), 1553(36), 1471(25), 1445(29), 1408(14), 1369(79), 1327(27), 1286(55), 1271(29), 1238(31), 1168(17), 1101(19), 1046(19), 1032(49), 992(27), 959(11), 886(23), 808(9), 767(15), 752(21), 737(20), 670(11), 606(22), 572(15), 526(49), 511(35), 491(19), 448(21), 366(22), 347(31), 311(28), 299(27), 241(27), 158(55), 145(61), 124(42), 95(84), 76(95); IR (ATR, 300 K, in cm^{-1}): ν = 2971(w), 2932(vw), 1588(w), 1552(m), 1465(w), 1441(w), 1406(m), 1392(vw), 1367(m), 1324(vw), 1265(vs), 1221(m), 1180(w), 1143(s), 1113(vw), 1059(w), 1030(s), 991(vw), 933(w), 823(w), 808(m), 782(w), 766(m), 752(w), 636(s); ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 1.27 (12H, d, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 1.31 (12H, d, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 2.42 (4H, *pseudo* sept, $^3J_{HH}$ = 6.8 Hz, C*H*CH$_3$), 7.59 (4H, d, $^3J_{HH}$ = 7.9 Hz, *m*−CH), 7.81 (2H, t, $^3J_{HH}$ = 7.9 Hz, *p*−CH); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 23.9 (s, CHCH$_3$), 25.6 (s, CHCH$_3$), 30.4 (s, CHCH$_3$), 123.4 (q, $^1J_{CF}$ = 321.7 Hz, CF$_3$), 126.4 (s, CCl), 127.3 (s, *m*−C), 128.9 (d, $^3J_{CP}$ = 3.9 Hz, *i*−C), 135.2 (s, *p*−C), 144.2 (d, $^1J_{PC}$ = 132.7 Hz, CPCl$_2$), 147.3 (s, *o*−C); ^{19}F NMR (CD$_3$CN, 300 K, in ppm): δ = −79.3 (s, CF$_3$); ^{31}P{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 114.9 (s); elemental analysis: $C_{28}H_{34}Cl_4F_3N_2O_3PS$ (708.40): calcd: N 4.0, C 47.5, H 4.8, found: N 3.9, C 47.9, H 4.9%.

$\mathbf{1_{As}^{(Dipp/H)}}$[OTf]. **4**$_{As}^{(Dipp/H)}$[OTf] (2.00 g, 3.3 mmol); AsCl$_3$: (0.41 mL, 0.88 g, 4.9 mmol); Yield: 2.01 g (90%, 2.95 mmol); mp >188 °C dec; Raman (80 mW, in cm^{-1}): ν = 3162(7), 3076(24), 3036(4), 2971(20), 2939(73), 2915(4), 2872(26), 2768(6), 2722(8), 1589(36), 1550(32), 1468(19), 1445(37), 1407(4), 1367(49), 1329(34), 1297(32), 1238(24), 1223(4), 1164(10), 1133(3), 1106(17), 1081(4), 1047(16), 1028(65), 976(26), 961(7), 887(29), 809(3), 757(32), 732(12), 704(9), 634(3), 613(20), 575(5), 522(39), 461(17), 442(7), 403(96), 363(43), 348(23), 320(24), 279(35); IR (ATR, 300 K, in cm^{-1}): ν = 2966(vw), 1549(vw), 1465(w), 1423(vw), 1389(vw), 1366(vw), 1329(vw), 1281(m), 1233(m), 1223(vw), 1205(vw), 1158(s), 1118(vw), 1062(vw), 1025(s), 935(vw), 801(m), 755(m), 702(vw), 635(vs); ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 1.22 (12H, d, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 1.34 (12H, d, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 2.47 (4H, *pseudo* sept, $^3J_{HH}$ = 6.8 Hz, C*H*CH$_3$), 7.52 (4H, d, $^3J_{HH}$ = 7.9 Hz, *m*−CH), 7.73 (2H, t, $^3J_{HH}$ = 7.9 Hz, *p*−CH), 8.15 (2H, s, C═C); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 22.9 (s, CHCH$_3$), 26.0 (s, CHCH$_3$), 30.4 (s, CHCH$_3$), 122.2 (q, $^1J_{CF}$ = 320.0 Hz, CF$_3$), 126.2 (s, *m*−C), 130.4 (s, *i*−C), 130.8 (s, C═CH), 134.1 (s, *p*−C), 146.8 (s, *o*−CH), 149.2 (s, CAsCl$_2$); ^{19}F NMR (CD$_3$CN, 300 K, in ppm): δ = −79.2 (s, CF$_3$); elemental analysis: $C_{28}H_{36}AsCl_2F_3N_2O_3S$ (683.48): calcd: N 4.1, C 49.2, H 5.3, found: N 4.2, C 48.9, H 5.3%.

Synthesis of $\mathbf{6_P^{(Me/Me)}/6_P^{(Dipp/H)}/6_P^{(Dipp/Cl)}/6_{As}^{(iPr/Me)}/6_{As}^{(Dipp/H)}}$[OTf]. Me$_3$SiCN (2.1 equiv) was added to a solution of the respective **1**$_{Pn}^{(R/R\prime)}$[OTf] (Pn = P; As) in acetonitrile (5 mL). The pale yellow solution was stirred at ambient temperature for 12 h. Addition of diethyl ether (30 mL) gave a suspension, which was filtered. The obtained crystalline precipitate was washed with diethyl ether (3 × 10 mL) and dried in vacuo.

$\mathbf{6_P^{(Me/Me)}}$[OTf]. **1**$_P^{(Me/Me)}$[OTf] (1.00 g, 2.7 mmol); Me$_3$SiCN (0.56 g, 0.70 mL, 5.6 mmol, 2.1 equiv); Yield: 0.87 g (91%, 2.4 mmol): mp > 220 °C dec; Raman (95 mW, in cm^{-1}): ν = 2973(27), 2935(58), 2193(77), 1622(19), 1454(16), 1409(29), 1335(40), 1227(8), 1103(13), 1031(50), 757(17), 599(33), 575(14), 411(7), 350(21), 315(13), 227(7), 134(29), 77(95); IR (ATR, 300 K, in cm^{-1}): ν = 2193(vw), 1624(vw), 1491(w), 1444(vw), 1407(vw), 1380(vw), 1277(vw), 1224(vs), 1147(m), 1025(s), 983(w), 856(w), 773(w), 755(vw), 635(vs), 607(m), 573(m), 517(m), 451(m); ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 2.34 (6H, s, CC*H*$_3$), 3.99 (6H, s, NC*H*$_3$); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 9.8 (s, CCH$_3$), 36.5 (d, $^3J_{CP}$ = 7.7 Hz, NCH$_3$), 112.3 (d, $^1J_{PC}$ = 50.3 Hz, PCN), 122.2 (q, $^1J_{CF}$ = 321.1 Hz, CF$_3$), 128.2 (d, $^1J_{CP}$ = 24.0 Hz, N$_2$CP), 135.5 (s, CCH$_3$); ^{31}P{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = −125.0 (s); ^{19}F NMR (CD$_3$CN, 300 K, in ppm): δ = −79.3 (s).

$\mathbf{6_P^{(Dipp/H)}}$[OTf]. **1**$_P^{(Dipp/H)}$[OTf] (1.06 g, 1.7 mmol); Me$_3$SiCN (0.34 g, 0.43 mL, 3.5 mmol, 2.1 equiv); Yield: 0.71 g (67%, 1.14 mmol); mp > 200 °C dec; Raman (50 mW, 300 K, in cm^{-1}): ν = 3160(10), 3073(31), 3038(5), 2967(26), 2942(5), 2915(95), 2873(24), 2773(7), 2729(12), 2190(90), 1590(31), 1544(24), 1471(14), 1446(29), 1370(62), 1334(17), 1304(29), 1237(24), 1184(5), 1167(10), 1106(17), 1045(21), 1026(62), 984(24), 956(12), 886(29), 757(21), 731(10), 615(21), 575(10), 546(7), 520(5), 484(5), 465(10), 349(12), 313(12), 292(5), 199(7), 130(7), 76(10); IR (ATR, 300 K, in cm^{-1}): ν = 3158(vw), 2966(w), 2188(vw), 1542(vw), 1458(w), 1391(vw), 1369(vw), 1326(vw), 1289(w), 1237(s), 1217(w), 1183(vw), 1156(m), 1060(vw), 1024(vs), 936(vw), 806(m), 756(w), 713(vw), 636(vs); ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 1.22 (12H, d, $^3J_{HH}$ = 6.7 Hz, CHC*H*$_3$), 1.38 (12H, d, $^3J_{HH}$ = 6.7 Hz, CHC*H*$_3$), 2.36 (4H, *pseudo* sept, $^3J_{HH}$ = 6.7 Hz, C*H*CH$_3$), 7.57 (4H, d, $^3J_{HH}$ = 7.8 Hz, *m*−CH), 7.78 (2H, t, $^3J_{HH}$ = 7.8 Hz, *p*−CH), 8.39 (2H, s, C═C*H*); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 22.9 (s, CHCH$_3$), 26.1 (s, CHCH$_3$), 30.4 (s, CHCH$_3$), 108.5 (d, $^1J_{CP}$ = 53.3 Hz, CPCN), 122.2 (q, $^1J_{CF}$ = 320.0 Hz, CF$_3$), 126.6 (s, *m*−C), 130.2 (s, *i*−C), 132.9 (s, C=CH), 134.9 (s, *p*−C), 135.1 (s, CPCN), 146.8 (s, *o*−C); ^{19}F NMR (CD$_2$Cl$_2$, 300 K, in ppm): δ = −79.2 (s, CF$_3$); ^{31}P{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = −116.6 (s).

$\mathbf{6_P^{(Dipp/Cl)}}$[OTf]. **1**$_P^{(Dipp/Cl)}$[OTf] (1.00 g, 1.4 mmol); Me$_3$SiCN (0.29 g, 0.37 mL, 2.9 mmol, 2.1 equiv); Yield: 0.75 g (78%, 1.1 mmol); mp > 225 °C dec; Raman (70 mW, 300 K, in cm^{-1}): ν = 3075(26), 2974(27), 2913(63), 2873(15), 2195(81), 1590(17), 1569(24), 1445(19), 1382(95), 1331(17), 1304(40), 1240(31), 1219(10), 1166(13), 1105(19), 1049(20), 1025(72), 992(22), 889(22), 754(17), 710(19), 605(13), 462(22), 346(13), 312(43), 260(10); IR (ATR, 300 K, in cm^{-1}): ν = 2968(w), 2361(vw), 2192(vw), 1699(vw), 1568(w), 1541(vw), 1507(vw), 1458(w), 1412(vw), 1391(vw), 1371(vw), 1294(m), 1232(vs), 1216(w), 1185(vw), 1154(m), 1060(vw), 1023(s), 936(vw), 810(m), 783(vw), 766(w), 754(vw), 666(vw), 635(vs), 622(vw), 573(vw), 547(vw), 515(m), 462(w), 434(vw); ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 1.28 (12H, d, $^3J_{HH}$ = 6.7 Hz, CHC*H*$_3$), 1.36 (12H, d, $^3J_{HH}$ = 6.7 Hz, CHC*H*$_3$), 2.42 (4H, *pseudo* sept, $^3J_{HH}$ = 6.7 Hz, C*H*CH$_3$), 7.64 (4H, d, $^3J_{HH}$ = 7.9 Hz, *m*−CH), 7.86 (2H, t, $^3J_{HH}$ = 7.9 Hz, *p*−CH); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 24.2 (s, CHCH$_3$), 25.6 (s, CHCH$_3$), 30.4 (s, CHCH$_3$), 107.9 (d, $^1J_{PC}$ = 54.9 Hz, PCN), 122.1 (q, $^1J_{CF}$ = 320.4 Hz, CF$_3$), 127.4 (s, *i*−C), 127.7 (s, *m*−C), 130.5 (d, CCl), 135.7 (d, $^1J_{CP}$ = 43.8 Hz, CPCN), 136.0 (s, *p*−C), 147.5 (s, *o*−C); ^{19}F NMR (CD$_3$CN, 300 K, in ppm): δ = −79.3 (s, CF$_3$); ^{31}P{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = −109.7; elemental analysis: $C_{32}H_{37}Cl_2F_3N_5O_3PS$ (730.59): calcd: N 8.1, C 52.2, H 5.0, found: N 7.5, C 51.5, H 5.0%.

$\mathbf{6_{As}^{(\mathit{i}Pr/Me)}}$[OTf]. **1**$_{As}^{(iPr/Me)}$[OTf] (0.24 g, 0.5 mmol); Me$_3$SiCN (0.12 mL, 0.10 g, 1.0 mmol, 2.1 equiv); Yield: 0.15 g (66%, 0.33 mmol); mp > 180 °C dec; Raman (250 mW, 300 K, in cm^{-1}): ν = 2994(22), 2956(27), 2937(6), 2885(3), 2187(95), 1614(23), 1450(17), 1404(7), 1386(5), 1367(11), 1277(32), 1225(8), 1029(57), 888(17), 757(22), 574(13), 483(5), 463(20), 349(26), 315(13), 286(10), 164(7), 116(27), 66(70); IR (ATR, 300 K, [cm^{-1}]): ν = 2998(w), 2187(w), 1614(w), 1453(w), 1424(vw), 1403(w), 1383(w), 1343(vw), 1286(w), 1244(vs), 1155(m), 1029(vs), 984(w), 905(w), 777(w), 756(w), 637(vs), 574(w), 518(m), 468(w); ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 1.65 (12H, $^3J_{HH}$ = 6.9 Hz, d, CHC*H*$_3$), 2.41 (6H, s, CC*H*$_3$), 5.19 (2H, s(breit), C*H*CH$_3$); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 11.3 (s, CCH3), 21.3 (s, CHCH$_3$), 56.5 (s, CHCH$_3$), 114.7 (s, AsCN), 122.2 (q, $^1J_{CF}$ = 321.3 Hz, CF$_3$), 134.3 (s, CCH$_3$), 136.3 (s, CAsCN), ^{19}F NMR (CD$_3$CN, 300 K, in ppm): δ = −79.2 (s, CF$_3$); elemental analysis: $C_{14}H_{20}AsF_3N_4O_3S$ (456.04): calcd: N 12.3, C 36.9, H 4.4, found: N 12.5, C 36.6, H 4.0%.

$6_{As}^{(Dipp/H)}$[OTf]. $\mathbf{1}_{As}^{(Dipp/H)}$[OTf] (0.68 g, 1.00 mmol); Me$_3$SiCN (0.21 g, 0.26 mL, 2.1 mmol, 2.1 equiv); Yield: 0.66 g (quantitative, 0.99 mmol); mp 206−208 °C; Raman (30 mW, 300 K, in cm^{-1}): ν = 3158(9), 3076(28), 3040(5), 2969(38), 2940(8), 2914(50), 2871(38), 2770(11), 2724(10), 2187(43), 2178(10), 2061(33), 1591(30), 1549(19), 1468(14), 1446(28), 1391(38), 1374(14), 1352(5), 1333(10), 1303(28), 1237(14), 1166(9), 1106(16), 1046(10), 1026(5), 977(13), 961(20), 886(24), 757(9), 731(9), 614(14), 575(10), 613(15), 575(10), 493(6), 460(11), 349(5), 328(6), 312(10), 263(6), 71(95); IR(ATR, 300 K, in cm^{-1}): ν = 2965(vw), 2361(vw), 1541(w), 1508(vw), 1457(w), 1389(vw), 1367(vw), 1266(s), 1224(w), 1157(w), 1061(vw), 1032(m), 803(w), 756(w), 637(vs); ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 1.19 (12H, d, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 1.40 (12H, d, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 2.45 (4H, *pseudo* sept, $^3J_{HH}$ = 6.8 Hz, C*H*CH$_3$), 7.54 (4H, d, $^3J_{HH}$ = 7.9 Hz, *m*−CH), 7.74 (2H, t, $^3J_{HH}$ = 7.9 Hz, *p*−CH), 8.19 (2H, s, C═C*H*); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 22.9 (s, CHCH$_3$), 26.3 (s, CHCH$_3$), 30.3 (s, CHCH$_3$), 110.8 (s, CAsCN), 122.2 (q, $^1J_{CF}$ = 322.7 Hz, CF$_3$), 126.4 (s, *m*−C), 130.9 (s, *i*−C), 131.5 (s, C=CH), 134.6 (s, *p*−C), 143.2 (s, CAsCN), 147.0 (s, *o*−C); ^{19}F NMR (CD$_3$CN, 300 K, in ppm): δ = −79.2 (s, CF$_3$); elemental analysis: $C_{30}H_{36}AsF_3N_4O_3S$ (665.62): calcd: N 8.4, C 54.2, H 5.5, found: N 8.3, C 53.9, H 5.4%.

Synthesis of $7_P^{(Me/Me)}$/$7_P^{(Dipp/H)}$/$7_P^{(Dipp/Cl)}$/$7_{As}^{(iPr/Me)}$/$7_{As}^{(Dipp/H)}$[OTf]. Me$_3$SiN$_3$ was added dropwise to a suspension of the respective $\mathbf{1}_{Pn}^{(R/R')}$[OTf] (Pn = P, As) in fluorobenzene (10 mL) and stirred at ambient temperature for 24 h. After the addition of *n*-hexane (30 mL) the obtained oily phase was separated and washed with *n*-hexane (4 × 10 mL), yielding colorless solids after removing all volatiles in vacuo. Because of the labile nature of the azide derivatives, elemental analysis data were not obtained.

$7_P^{(Me/Me)}$[OTf]. $\mathbf{1}_P^{(Me/Me)}$[OTf] (0.38 g, 1.0 mmol); Me$_3$SiN$_3$ (0.28 mL, 0.24 g, 2.1 mmol); Yield: 0.33 g (84%, 0.8 mmol); ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 2.29 (6H, s, CCH$_3$), 3.89 (6H, s, NCH$_3$); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 8.0 (s, CCH$_3$), 33.9 (d, $^3J_{CP}$ = 10.8 Hz, NCH$_3$), 121.0 (q, $^1J_{CF}$ = 320.2 Hz, CF$_3$), 130.9 (s, CCH$_3$), 140.1 (d, $^1J_{CP}$ = 37.7 Hz, N$_2$CP); ^{19}F NMR (CD$_3$CN, 300 K, in ppm): δ = −79.3 (s, CF$_3$); ^{31}P{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 98.2 (s).[40]

$7_P^{(Dipp/H)}$[OTf]. $\mathbf{1}_P^{(Dipp/H)}$[OTf] (1.00 g, 1.6 mmol); Me$_3$SiN$_3$ (0.44 mL, 0.38 g, 3.3 mmol); Yield: 0.71 g (70%, 1.1 mmol); Raman (30 mW, 300 K, in cm^{-1}): ν = 3169(5), 3074(24), 3038(7), 2970(22), 2940(6), 2916(95), 2873(4), 2725(10), 2551(5), 2158(7), 2136(15), 1591(19), 1548(11), 1466(5), 1446(20), 1380(38), 1345(9), 1307(16), 1238(10), 1167(4), 1107(10), 1045(6), 1033(19), 985(5), 960(7), 887(10), 755(12), 731(4), 615(5), 575(7), 542(10), 445(5), 348(5), 313(7), 195(4), 70(66); IR (ATR, 300 K, in cm^{-1}): ν = 3169(vw), 2966(vw), 2932(vw), 2873(vw), 2155(w), 2129(m), 1596(vw), 1548(vw), 1464(w), 1449(2), 1389(vw), 1368(vw), 1330(vw), 1279(vw), 1259(m), 1223(vw), 1207(vw), 1156(s), 1119(vw), 1061(vw), 1030(vs), 936(vw), 808(m), 780(vw), 758(w), 726(vw), 711(vw), 697(vw), 636(vs); ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 1.23 (12H, d, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 1.35 (12H, d, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 2.39 (4H, *pseudo* sept, $^3J_{HH}$ = 6.8 Hz, C*H*CH$_3$), 7.54 (4H, d, $^3J_{HH}$ = 7.9 Hz, *m*−CH), 7.71 (2H, t, $^3J_{HH}$ = 7.9 Hz, *p*−CH), 8.07 (2H, s, C═C*H*); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 22.8 (s, CHCH$_3$), 25.5 (s, CHCH$_3$), 30.6 (s, CHCH$_3$), 122.2 (q, $^1J_{CF}$ = 320.9 Hz, CF$_3$), 126.1 (s, *p*−C), 130.1 (s, *i*−C), 130.9 (s, C=CH), 133.6 (s, *m*−C), 145.5 (d, $^1J_{PC}$ = 46.7 Hz, CPN$_3$), 146.2 (s, *o*−C); ^{19}F NMR (CD$_3$CN, 300 K, in ppm): δ = −79.3 (s, CF$_3$); ^{31}P{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 103.9 (s).

$7_P^{(Dipp/Cl)}$[OTf]. $\mathbf{1}_P^{(Dipp/Cl)}$[OTf] (0.35 g, 0.5 mmol); Me$_3$SiN$_3$ (0.19 mL, 0.17 g, 1.5 mmol); Yield: 0.32 g (89%, 0.4 mmol); Raman (30 mW, 300 K, in cm^{-1}: ν = 3082(15), 3066(17), 3034(10), 2995(28), 2971(50), 2941(45), 2910(57), 2871(35), 2721(8), 2156(35), 2141(27), 1598(22), 1586(25), 1573(23), 1471(30), 1446(31), 1416(5), 1380(97), 1332(37), 1305(42), 1275(10), 1239(28), 1221(11), 1184(7), 1169(9), 1105(20), 1048(20), 1029(55), 993(22), 959(7), 888(25), 752(17), 733(12), 660(7), 603(18), 569(13), 539(33), 445(10), 343(12), 338(18); IR(ATR, 300 K, in cm^{-1}): ν = 2970(vw), 2156(w), 2135(m), 1572(w), 1465(vw), 1444(vw), 1404(vw), 1369(vw), 1289(m), 1269(vw), 1245(vs), 1218(vw), 1182(vw), 1148(vs), 1107(vw), 1060(vw), 1028(s), 936(vw), 807(m), 780(vw), 766(w), 747(vw), 720(w), 636(vs); ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 1.29 (12H, d, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 1.35 (12H, d, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 2.43 (4H, *pseudo* sept, $^3J_{HH}$ = 6.8 Hz, C*H*CH$_3$), 7.63 (4H, d, $^3J_{HH}$ = 7.8 Hz, *m*−CH), 7.77 (2H, t, $^3J_{HH}$ = 7.8 Hz, *p*−CH); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 23.4 (s, CHCH$_3$), 25.2 (s, CHCH$_3$), 20.5 (s, CHCH$_3$), 121.5 (q, $^1J_{CF}$ = 320.9 Hz, CF$_3$), 134.7 (s, *p*−C), 127.7 (s, *i*−C), 127.1 (s, *m*−C), 137.4 (s, C=CCl), 145.8 (s, CPN$_3$), 147.0 (s, *o*−C); ^{19}F NMR (CD$_3$CN, 300 K, in ppm): δ = −79.2 (s, CF$_3$); ^{31}P{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 109.4 (s).

$7_{As}^{(iPr/Me)}$[OTf]. $\mathbf{1}_{As}^{(iPr/Me)}$[OTf] (0.25 g, 0.5 mmol); Me$_3$SiN$_3$ (0.20 mL, 0.17 g, 1.5 mmol, 3.0 equiv); Yield: 0.15 g (61%, 0.3 mmol); Raman (250 mW, 300 K, in cm^{-1}): ν = 3000(42), 2989(59), 2976(70), 2955(95), 2935(68), 2876(21), 2862(39), 2106(71), 2086(19), 2033(12), 1615(59), 1472(20), 1449(61), 1422(40), 1406(28), 1392(22), 1365(50), 1345(11), 1280(81), 1235(19), 1222(8), 1188(10), 1173(12), 1154(9), 1139(21), 1024(93), 890(31), 775(10), 757(41), 677(9), 574(21), 541(20), 457(78), 385(18), 353(82); IR (ATR, 300 K, in cm^{-1}): ν = 3319(w), 2978(m), 2457(w), 2112(s), 1615(w), 1557(vw), 1449(w), 1416(w), 1384(w), 1281(vw), 1242(vs), 1154(m), 1024(m), 906(w), 774(w), 755(w), 672(vw), 637(s), 572(w), 517(m), 455(m), 436(w); ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 1.64 (12H, $^3J_{HH}$ = 7.0 Hz, d, CHC*H*$_3$), 2.38 (6H, s, CC*H*$_3$), 5.26 (2H, s (broad), C*H*CH$_3$); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 10.0 (s, CCH$_3$), 20.8 (s, CHCH$_3$), 53.5 (s, CHCH$_3$), 120.9 (q, $^1J_{CF}$ = 322.9 Hz, CF$_3$), 131.8 (s, CCH$_3$), not observed (s, CAsN$_3$); ^{19}F NMR (CD$_3$CN, 300 K, in ppm): δ = −78.8 (s, CF$_3$).

$7_{As}^{(Dipp/H)}$[OTf]. $7_{As}^{(Dipp/H)}$[OTf]: 0.68 g (1.0 mmol; Me$_3$SiN$_3$ (0.27 mL, 0.24 g, 2.0 mmol, 2.0 equiv); Yield: 0.61 g (87%, 0.9 mmol); Raman (30 mW, 300 K, in cm^{-1}): ν = 3159(6), 3075(25), 3038(6), 2970(32), 2940(6), 2914(95), 2870(25), 2769(5), 2722(13), 2551(7), 2117(32), 2094(5), 1591(24), 1544(12), 1462(6), 1446(13), 1375(30), 1330(7), 1305(13), 1237(12), 1167(6), 1106(13), 1044(4), 1027(19), 980(11), 959(7), 886(11), 757(7), 731(6), 614(5), 576(7), 467(12), 372(5), 350(7), 315(6), 186(6), 71(81); IR (ATR, 300 K, in cm^{-1}): ν = 3157(vw), 2965(w), 2929(vw), 2871(vw), 2117(m), 2093(w), 1591(vw), 1544(vw), 1466(w), 1447(w), 1429(vw), 1389(vw), 1367(vw), 1328(vw), 1237(s), 1218(vw), 1160(m), 1117(vw), 1060(vw), 1025(s), 952(vw), 935(vw), 805(w), 786(vw), 756(m), 707(vw), 668(vw), 636(s); ^{1}H NMR (CD$_3$CN, 300 K, in ppm): δ = 1.22 (12H, d, $^3J_{HH}$ = 6.9 Hz, CHC*H*$_3$), 1.37 (12H, d, $^3J_{HH}$ = 6.9 Hz, CHC*H*$_3$), 2.45 (4H, *pseudo* sept., $^3J_{HH}$ = 6.9 Hz, C*H*CH$_3$), 7.54 (4H, d, $^3J_{HH}$ = 7.9 Hz, *m*−CH), 7.72 (2H, t, $^3J_{HH}$ = 7.9 Hz, *p*−CH), 7.98 (2H, s, C═C*H*); ^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm): δ = 22.9 (s, CHCH$_3$), 25.8 (s, CHCH$_3$), 30.5 (s, CHCH$_3$), 120.9 (q, $^1J_{CF}$ = 320.9 Hz, CF$_3$), 126.0 (s, *p*−C), 129.9 (s, *i*−C), 131.0 (s, C=CH), 133.7 (s, *m*−C), 146.7 (s, *o*−C), 151.5 (s, CAsN$_3$); ^{19}F NMR (CD$_3$CN, 300 K, in ppm): δ = −79.3 (s, CF$_3$).

Structure Solution and Refinement. The crystals were coated with Paratone-N oil, mounted using a glass fiber pin and frozen in the cold nitrogen stream on the goniometer. X-ray diffraction data for all compounds were collected on a Bruker AXS APEX CCD diffractometer equipped with a rotation anode or sealed tube X-ray source using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) or Cu Kα radiation (λ = 1.541 78 Å) at 153(2) K or 100(1) K with a scan width of 0.3° and variable exposure times typically between 5

Table 7. Crystallographic Data and Structure Refinements of the Reported Compounds

	$\mathbf{1}_{\mathrm{P}}^{(\mathrm{Dipp/Cl})}[\mathrm{OTf}]$	$\mathbf{1}_{\mathrm{As}}^{(i\mathrm{Pr/Me})}[\mathrm{OTf}]$	$\mathbf{1}_{\mathrm{Sb}}^{(i\mathrm{Pr/Me})}[\mathrm{OTf}]$	$\mathbf{2}_{\mathrm{P}}^{(\mathrm{Me/Me})}[\mathrm{OTf}]_2$	$\mathbf{4}^{(\mathrm{Me/Me})}[\mathrm{OTf}]$	$\mathbf{4}^{(\mathrm{Dipp/H})}[\mathrm{OTf}]$	$\mathbf{5}_{\mathrm{P}}^{(\mathrm{Me/Me})}[\mathrm{OTf}]_3$
formula	$C_{28}H_{34}Cl_4F_3N_2O_3PS$	$C_{12}H_{20}AsCl_2F_3N_2O_3S$	$C_{12}H_{20}Cl_2F_3N_2O_3SSb$	$C_{16}H_{24}ClF_6N_4O_6PS_2$	$C_{11}H_{21}F_3N_2O_3SSi$	$C_{31}H_{45}F_3N_2O_3SSi$	$C_{24}H_{36}F_9N_6O_9PS_3$
M_r in g mol^{-1}	708.40	475.18	522.01	612.93	346.45	610.84	850.74
crystal size in mm	0.50 × 0.30 × 0.07	0.12 × 0.11 × 0.04	0.17 × 0.15 × 0.08	0.14 × 0.03 × 0.01	0.20 × 0.02 × 0.02	0.683 × 0.338 × 0.198	0.22 × 0.02 × 0.02
color, habit	colorless plate	colorless plate	colorless plate	colorless stick	colorless stick	colorless block	colorless stick
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a in Å	12.1467(4)	9.0540(4)	10.1690(4)	14.6089(7)	7.4799(18)	9.7156(5)	8.1166(6)
b in Å	19.2370(5)	12.7877(5)	11.0255(4)	7.4064(4)	8.590(2)	22.3906(12)	35.056(3)
c in Å	14.2131(4)	16.2598(7)	17.2820(6)	23.5639(11)	12.967(3)	15.6593(9)	12.8427(1)
α in [deg]	90	90	90	90	92.509(4)	90	90
β in [deg]	97.840(2)	94.510(1)	90	101.021(1)	98.606(4)	103.048(3)	104.435(1)
γ in [deg]	90	90	90	90	94.336(4)	90	90
V in Å^3	3290.08(17)	1876.73(11)	1937.63(12)	2502.6(2)	820.1(3)	3318.5(3)	3538.9(5)
Z	4	4	4	4	2	4	4
T in K	153(1)	153(2)	153(2)	153(1)	153(1)	100(1)	153(1)
ρ_c in g cm^{-3}	1.430	1.682	1.789	1.627	1.403	1.223	1.597
$F(000)$	1464	960	1032	1256	364	1304	1752
λ in Å	1.541 84	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
μ in mm^{-1}	4.754	2.249	1.848	0.469	0.310	0.183	0.359
absorption correction	SADABS	SADABS	SADABS	SADABS	SADABS	SADABS	SADABS
reflections collected	18 850	18 806	19 271	24 660	8282	36 344	30 555
reflections unique	5921	4475	5218	5980	3909	8957	8437
R_{int}	0.0607	0.0248	0.0362	0.0316	0.0335	0.0510	0.0305
reflection obs. [$F > 2\sigma(F)$]	4851	4023	4953	4613	2902	6858	6624
residual density in e Å^{-3}	0.72,−0.42	0.409,−0.336	0.780,−0.398	0.810,−0.434	0.542,−0.524	0.45,−0.48	0.984,−0.928
parameters	397	223	223	333	197	381	481
GOF	1.050	1.040	1.021	1.016	1.007	1.064	1.033
R_1 [$I > 2\sigma(I)$]	0.0642	0.0245	0.0237	0.0434	0.0453	0.0440	0.0489
wR_2 (all data)	0.1965	0.0648	0.0545	0.1155	0.1200	0.1203	0.1407
CCDC	1055387	1055386	1055388	1055389	1055391	1055390	1055392

Table 8. Crystallographic Data and Structure Refinements of the Reported Compounds

	$\mathbf{6}_{\mathrm{P}}^{(\mathrm{Me/Me})}$[OTf]	$\mathbf{6}_{\mathrm{P}}^{(\mathrm{Dipp/H})}$[OTf] *$CH_2Cl_2$	$\mathbf{6}_{\mathrm{P}}^{(\mathrm{Dipp/Cl})}$[OTf] *$CH_3CN$	$\mathbf{6}_{\mathrm{As}}^{(\mathrm{iPr/Me})}$[OTf] *$CH_3CN$	$\mathbf{7}_{\mathrm{P}}^{(\mathrm{Dipp/Cl})}$[OTf]	$\mathbf{7}_{\mathrm{As}}^{(\mathrm{Dipp/H})}$[OTf]
formula	$C_{10}H_{12}F_3N_4O_3PS$	$C_{31}H_{38}Cl_2F_3N_4O_3PS$	$C_{32}H_{37}Cl_2F_3N_5O_3PS$	$C_{16}H_{23}AsF_3N_5O_3S$	$C_{28}H_{34}Cl_2F_3N_8O_3PS$	$C_{28}H_{36}AsF_3N_8O_3S$
M_r in g mol^{-1}	356.27	705.58	730.59	497.37	721.56	696.63
crystal size in mm	0.16 × 0.14 × 0.14	0.23 × 0.06 × 0.06	0.21 × 0.12 × 0.07	0.06 × 0.05 × 0.05	0.14 × 0.13 × 0.11	0.36 × 0.32 × 0.24
color, habit	colorless block	colorless stick	colorless block	colorless block	colorless block	colorless block
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a in Å	9.1518(2)	10.5148(7)	19.0009(6)	9.236(2)	11.7429(5)	11.3587(1)
b in Å	8.0666(1)	19.7085(12)	9.4953(3)	10.289(3)	18.0557(8)	18.8622(2)
c in Å	20.1474(3)	17.2472(11)	21.5807(7)	12.552(3)	16.0631(7)	16.0815(2)
α in [deg]	90	90	90	93.761(4)	90	90
β in [deg]	90.887(1)	97.743(1)	115.912(2)	106.742(3)	101.283(4)	101.563(1)
γ in [deg]	90	90	90	102.706(4)	90	90
V in Å^3	1487.18(4)	3541.6(4)	3502.1(2)	1103.7(5)	3340.0(3)	3375.54(6)
Z	4	4	4	2	4	4
T in K	153(2)	153(2)	100(1)	153(1)	100(1)	153(2)
ρ_c in g cm^{-3}	1.591	1.323	1.386	1.497	1.435	1.371
$F(000)$	728	1472	1520	508	1496	1440
λ in Å	1.541 84	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
μ in mm^{-1}	3.458	0.340	0.347	1.685	0.365	1.126
absorption correction	SADABS	SADABS	SADABS	SADABS	CrysAlisPro	SADABS
reflections collected	8131	35 744	43 723	11 331	66 447	36 850
reflections unique	2656	8443	11 271	5251	15 649	9061
R_{int}	0.0587	0.0206	0.0377	0.0210	0.1187	0.0341
reflection obs. [$F > 2\sigma(F)$]	2469	7281	8503	4607	14 094	7188
residual density in e Å^{-3}	0.657,−0.551	0.863,−0.883	0.73,−0.42	0.540,−0.253	1.53,−0.69	0.570,−0.484
parameters	203	445	454	269	424	405
GOF	1.064	1.020	1.029	1.047	1.119	1.059
R_1 [$I > 2\sigma(I)$]	0.0532	0.0497	0.0390	0.0368	0.1178	0.0369
wR_2 (all data)	0.1531	0.1343	0.1028	0.0767	0.3122	0.1033
CCDC	1055396	1055395	1055394	1055393	1055398	1055397

and 35 s. The frames were integrated using the Bruker SMART[41] soft-software package using the narrow frame algorithm. Data were corrected for absorption effects using the SADABS routine (empirical multiscan method).[42] For further crystal and data collection details see Tables 7 and 8. Structure solutions were found by using direct methods as implemented in the SHELXS package[43] and were refined with SHELXL[44] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atom positions were calculated, and each atom was allowed to ride on the carbon atom to which it was bonded, assuming C−H bond length of 0.95 Å. H atom temperature factors were fixed relative to the isotropic temperature factor of the C atom to which they are bonded. The locations of the largest peaks in the final difference Fourier map calculated as well as the magnitude of the residual electron densities in each case were of no chemical significance.

The crystal of $\mathbf{7}_{\mathrm{P}}^{(\mathrm{Dipp/Cl})}$[OTf] shows nonmerohedral twinning by a rotation of 180° about [001] in the ratio 64:36. Integrations and absorption corrections were performed using the CrysAlisPro[45] software. The structure was refined without restraints on HKL5 data but exhibits high R_{int}, R_1, and wR_2 values due to limited crystal quality.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Illustrated crystal and molecular structures, crystallographic data in CIF files. Available from the author. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00765.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

In memoriam of Prof. Dr. Dr. h. c. Heinrich Nöth.

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(28) Full characterization was especially problematic for derivative $7_{\mathrm{P}}{}^{(\mathrm{R,R'})}$[OTf] due its low stability. (R,R′ = Me/Me; *i*Pr/Me).

(29) All attempts to isolate the corresponding azide derivative $7_{\mathrm{As}}{}^{(\mathrm{R,R'})}$[OTf] (R,R′ = Me/Me; *i*Pr/Me) failed. Only complex reaction mixtures where obtained.

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