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Faculty of Chemistry and Chemical Engineering

The case study of a polyfluorinated *m*-terphenyl substituent in main group organometallic chemistry.
Synthesis, characterization, and reactivity of 2,4,6-$(C_6F_5)_3C_6H_2$-substituted organosilicon and -pnicogen compounds

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PhD Thesis Abstract

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Contents

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Introduction

The substituents play a critical role with respect to physical and chemical properties of organometallic compounds and provide different means of controlling the reactivity of the metal centre. Different substituents/ligands have been and continue to be developed and employed in organometallic chemistry depending on the end goal of the research.

m-Terphenyls are sterically demanding building blocks that have been used extensively as substituents or ligands in the chemistry of a substantial number of metals.[1,2] The anatomy of *m*-terphenyls is simple: two aromatic moieties are connected in reciprocal *meta* position on a central aromatic ring. The two aryl groups, also referred to as flanking aromatic groups, are twisted with respect to the central ring and form a protective bowl shape cavity which can accommodate the metal (Figure 1).

Electronic and steric properties of a *m*-terphenyl can be modified by formally introducing various functional groups on the flanking or central aromatic ring. The flanking aromatic groups are commonly decorated with alkyl groups, such as methyl, *iso*-propyl, or *tert*-butyl (Figure 1) which increase considerably steric hindrance (kinetic stabilization). In addition, the lateral aromatic groups become electron-rich and are more suitable to establish $M\cdots\pi$ interactions (a form of thermodynamic stabilization). *m*-Terphenyl substituents containing aryl groups such as 2,4,6-$Me_3C_6H_2$ (Mes), Me_5C_6, 2,6-(i-Pr)$_2C_6H_3$ or 2,4,6-(i-Pr)$_3C_6H_2$ have been frequently employed for the stabilization of low-valent organometallic compounds featuring multiple bonds between heavy main group atoms.[3-5] The introduction of bulky substituents in position 3 and 5 of the central aromatic ring can also block the rotation of the flanking aryl groups and consequently prevent possible undesired cyclometallation reactions between the reactive metal centre and the flanking aromatic rings.[6]

One of the first employed method of preparation for *m*-terphenyls was the one-pot protocol developed by Hart *et al.* in mid 80s.[7] In this protocol, 2,6-dibromoiodobenzene was reacted with different aromatic organomagnesium reagents to obtain 2,6-diarylphenylmagnesium halides which were quenched with an electrophile, usually water or iodine, in order to isolate and characterize the products. Iodoterphenyls were obtained by this protocol with fairly good yields.[7] The method was improved later with the introduction of the more affordable 1,3-$Cl_2C_6H_3$ as starting material. In the amended protocol, 1,3-$Cl_2C_6H_3Li$ instead of 2,6-$Cl_2C_6H_3I$ was reacted with two or more equivalents of organolithium or -magnesium reagents to obtain, after quenching with iodine, *m*-terphenyl derivatives with very good yields.[8] This method, still used today for multi-gram synthesis of *m*-terphenyl precursors, was preferred by the group of Power who, in upcoming years, would transform it into routine and contribute significantly to the development *m*-terphenyls and *m*-terphenyl-based organometallic chemistry.[9-15]

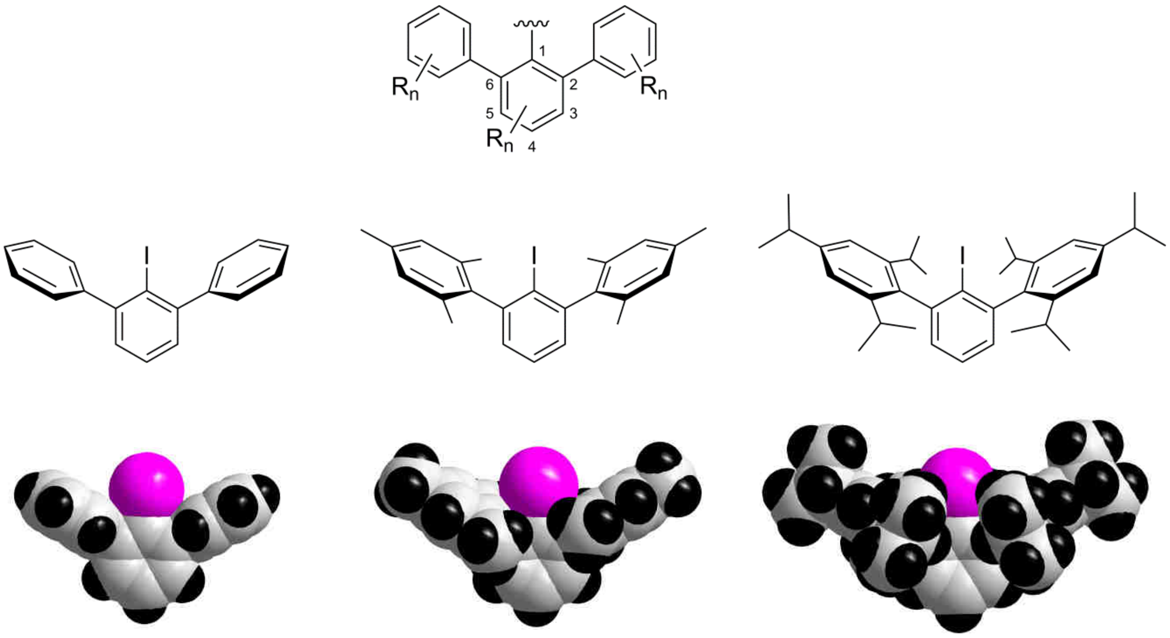


Figure 1. Generalized *m*-terphenyl substituent (top), common *m*-terphenyl iodides and the space-filling depiction of their molecular structures determined by single-crystal X-ray diffraction.[9,16,17]

With the development of versatile and highly efficient catalysts for aromatic carbon-carbon bond formation, a series of alternative methods for the synthesis of *m*-terphenyl precursors became available. An advantage of some of these cross-coupling methodologies is that they allow the preparation of *m*-terphenyls with functional groups that are incompatible with the reaction conditions of the Hart method (strongly basic organolithium or -magnesium compounds and high temperatures); Suzuki and Negishi protocols, for example, are considered more tolerant in this respect. In a recent review different synthetic approaches to preparing terphenyl derivatives, including *ortho* and *para*-terphenyls have been discussed.[18]

A 2014 survey in the Cambridge Structural Database revealed that a significant number of compounds bearing *m*-terphenyl substituents have been characterized by single-crystal X-ray diffraction. This was true for most main group elements (except noble gases, radioactive elements, and K, Rb, Cs, Sr, Ba), a substantial number of transition metals, and some lanthanides.[19]

The first crystal structure of an organometallic compound bearing a *m*-terphenyl substituent was reported by Power *et al.* in 1991 for $[(2,4,6\text{-}Ph_3C_6H_2)GaP(\textit{cyclo}\text{-}C_6H_{11})]_3$

featuring a cyclic Ga_3P_3 ring.[20] Developments in the *m*-terphenyl supported main group and transition metal organometallic chemistry field continued since and culminated with the isolation of the first stable compound featuring a fivefold metal-metal bond (Figure 2).[21]

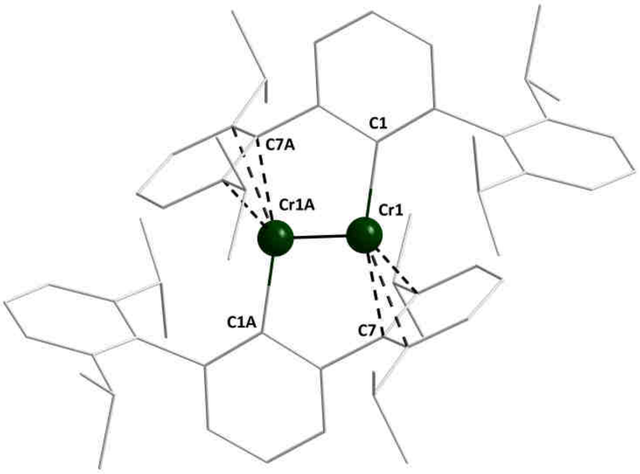


Figure 2. Depiction of the molecular structure of [2,6-{2',6'-(*i*-Pr)$_2$C$_6$H$_3$}$_2$C$_6$H$_3$Cr]$_2$. Hydrogen atoms were omitted for clarity.[21]

In the introductory part of the thesis, a discussion highlighting the remarkable structures of some transition metal compounds supported by *m*-terphenyl substituents was presented.[22-26] Many other results in this area have been reviewed recently.[27,28]

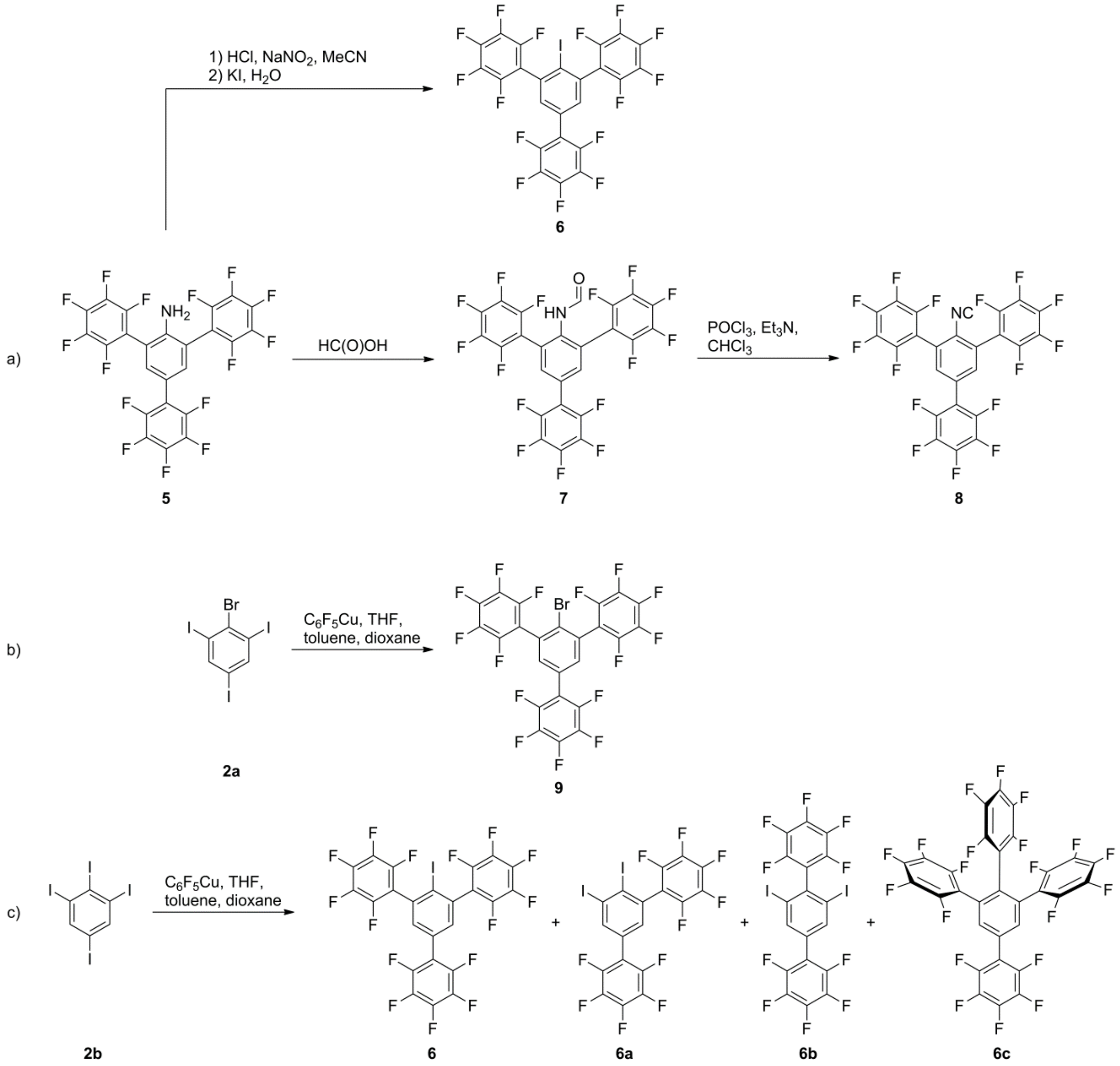
Important advances have been made also in the area of main group organometallic chemistry.[1,2,11] The introductory section of the thesis gives also a concise presentation of the impact this class of substituents had in main group organometallic chemistry. The discussion is not exhaustive and is constrained mainly to examples of organosilicon and organopnicogen compounds bearing at least one *m*-terphenyl moiety.[4,29-35]

Results

In this study, a series of main group (silicon and group 15 elements) organometallic compounds containing a polyfluorinated *m*-terphenyl substituent, 2,4,6-$(C_6F_5)_3C_6H_2$, was synthesized and characterized by spectroscopic methods (NMR, IR where applicable), mass spectrometry and single-crystal X-ray diffraction when possible.

The primary goal of this work was to survey the behavior and properties of the electron-poor polyfluorinated 2,4,6-$(C_6F_5)_3C_6H_2$ substituent and to contribute to the chemistry of main group elements (with emphasis on the pnicogens). Investigations of the reactivity of some of these compounds were undertaken. Attempts were made to isolate previously unknown or under-studied species.

The thesis starts with a brief discussion of the work done regarding the synthesis of several functionalized polyfluorinated arenes (Scheme 1).[36]



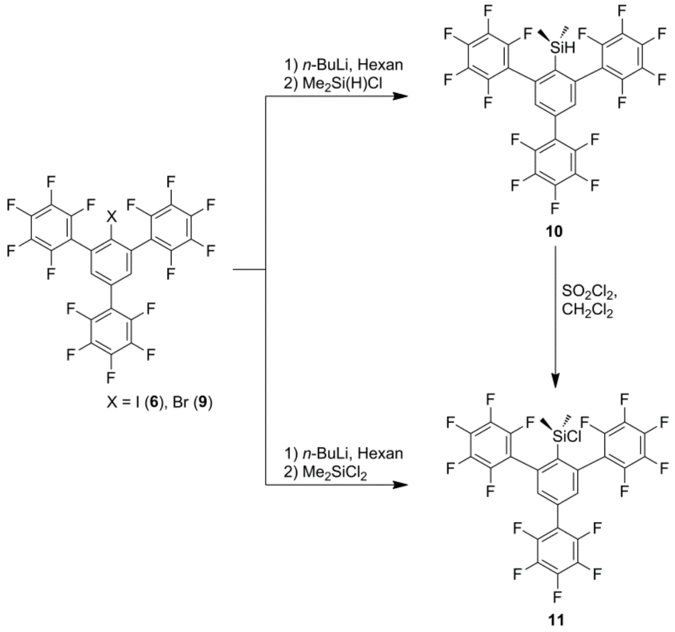
Scheme 1. Synthesis of organic compounds **6–9**.[36]

The precursor 2,4,6-$(C_6F_5)_3C_6H_2Br$ (**9**) [Scheme 1, (b)] was obtained in the Ullmann-type cross-coupling reaction between 2,4,6-$I_3C_6H_2Br$ (**2a**) and C_6F_5Cu. The aniline derivative, 2,4,6-$(C_6F_5)_3C_6H_2NH_2$ (**5**), was used to synthesize the isocyanide derivative 2,4,6-$(C_6F_5)_3C_6H_2NC$ [Scheme 1, (a)]. The iodide 2,4,6-$(C_6F_5)_3C_6H_2I$ (**6**) was obtained by two different routes: using 2,4,6-$(C_6F_5)_3C_6H_2NH_2$ as starting material in a Sandmeyer reaction or starting from 2,4,6-$(C_6F_5)_3C_6H_2Br$ which was subjected to lithiation followed by quenching the organolithium intermediate with iodine. The direct synthesis of **6** was also attempted in the reaction of 1,2,3,5-$I_4C_6H_2$ (**2b**) and C_6F_5Cu [Scheme 1, (c)].

The coupling test was carried out despite the fact that the starting material had four iodine atoms of approximately equal reactivity. The reasoning was that if the coupling reaction takes place initially with a great preference for positions 1 or 3 (statistically more favored than position 2), then position 2 would react with greater difficulty (or not at all) since there would be steric hindrance provided by the initially coupled C_6F_5 group. However, the rationale failed and a mixture of coupling products (including the tetra-substituted arene **6c**) was obtained with no selectivity for the formation of **6**. The structures of compounds **6b** and **6c** were determined by single-crystal X-ray diffraction while the formation of **6** and **6a** was inferred from ^{1}H and ^{19}F NMR spectra.

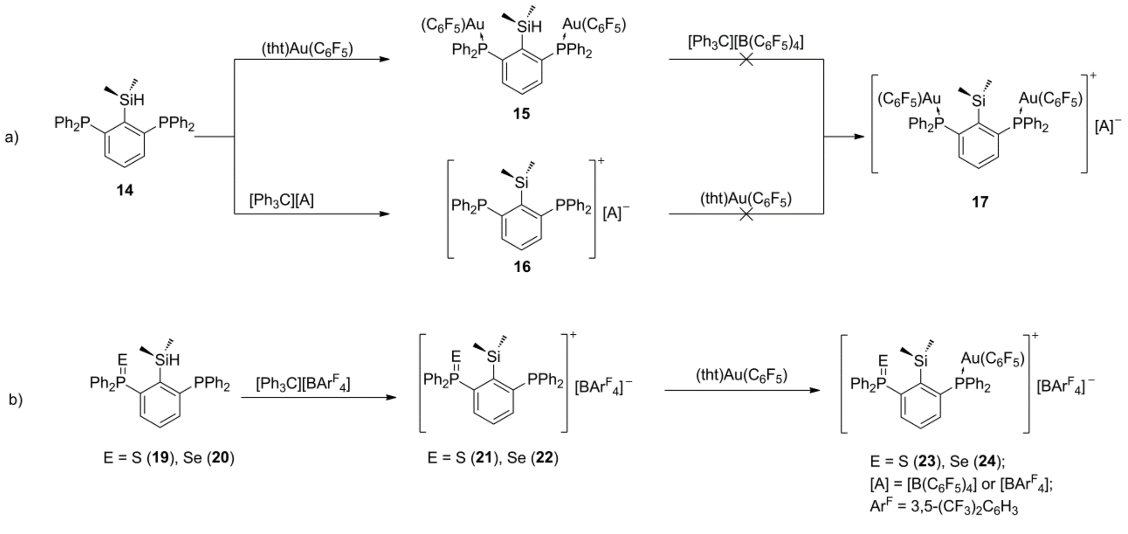
Metallation reactions were studied using both 2,4,6-$(C_6F_5)_3C_6H_2Br$ (**9**) and 2,4,6-$(C_6F_5)_3C_6H_2I$ (**6**) as starting materials. The first organosilicon derivative synthesized was 2,4,6-$(C_6F_5)_3C_6H_2Si(H)Me_2$ (**10**).[36] Initial lithiation conditions were sufficient to allow the synthesis of **10** in good yields. Thus reaction of **6** with *n*-BuLi in hexane at −80 °C (for 2 h) followed by the addition of $Me_2Si(H)Cl$ gave **10** with 74% (Scheme 2). The same reaction performed using **9** as starting material gave only a small amount of product while most of the precursor was recovered unreacted despite the fact that the lithiation reaction was extended to 5 h. When the lithium bromine exchange reaction was carried at room temperature (1.5 h), the reactivity of **9** increased significantly, and product **10** was isolated with 60% yield. Reaction of 2,4,6-$(C_6F_5)_3C_6H_2Li$ with Me_2SiCl_2 gave 2,4,6-$(C_6F_5)_3C_6H_2Si(Cl)Me_2$ (**11**) as the main product. The purification of moisture sensitive compound **11** was cumbersome. Reaction of **10** with SO_2Cl_2 gave **11** almost quantitatively with no need for further purification steps.[36]

Several attempts were made to isolate the silylium species [2,4,6-$(C_6F_5)_3C_6H_2SiMe_2$][$B(C_6F_5)_4$] to no avail. Surprisingly the reaction of **10** with [Ph_3C][$B(C_6F_5)_4$] in C_6D_6 at room or high temperature did not afford the silylium species [2,4,6-$(C_6F_5)_3C_6H_2SiMe_2$][$B(C_6F_5)_4$] (**12**). In all attempts the starting material was recovered. Reactions of **11** with K[$B(C_6F_5)_4$] or Ag[$B(C_6F_5)_4$] were not successful either, but the reaction of **11** with Ag[PF_6] in C_6D_6 gave 2,4,6-$(C_6F_5)_3C_6H_2Si(F)Me_2$ (**13**) as the main product.[36] This result indicated that the formation of **12** did took place, even if as a short lived species, but the 2,4,6-$(C_6F_5)_3C_6H_2$ substituent was not able to provide enough kinetic stabilization. Not surprisingly, the highly Lewis acidic **12** abstracted a fluoride ion from the PF_6 anion, which led to the formation of **13**.



Scheme 2. Synthesis of **10** and **11**.[36]

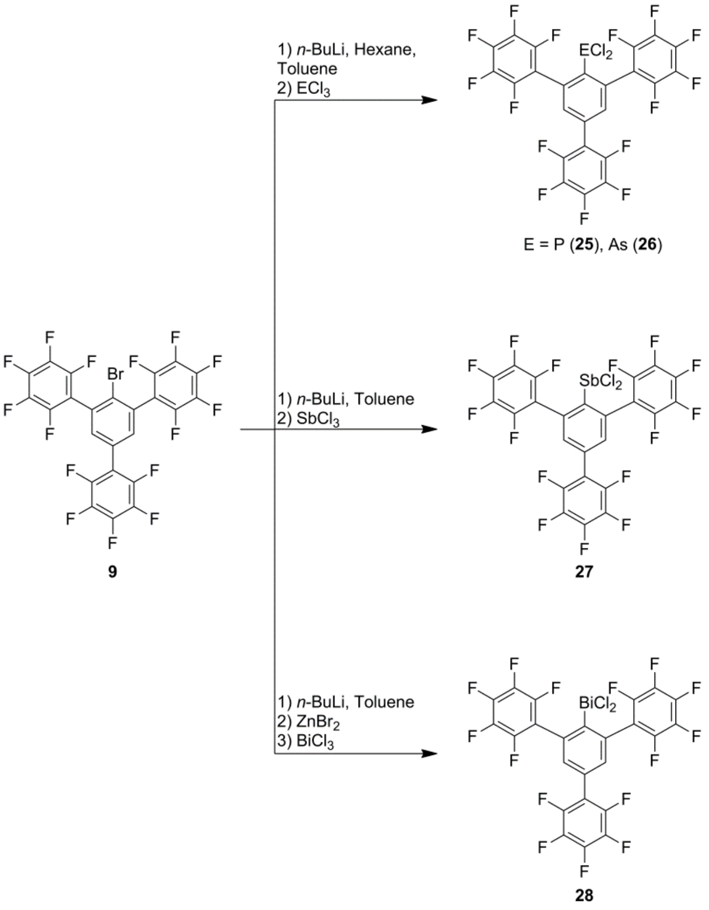
Targeting still silylium ions and inspired in part by a previous study regarding silylium species featuring Fe···Si interactions,[37] a side-project was addressed next. This project had as the main goal the isolation of cationic silyl species displaying stabilizing Si···Au interactions (Scheme 3).



Scheme 3. Synthetic strategies employed for the synthesis of **17**, **23** and **24**.[38]

Two alternative strategies were tested in order to synthesize the target silylium species $[2,6\text{-}\{Ph_2P(AuC_6F_5)\}_2C_6H_3SiMe_2][B(C_6F_5)_4]$ (**17**) and both failed as a direct result of the product's high reactivity. The *P,C,P*-ligand system was then altered so that one donating group (S or Se), would coordinate from close proximity the positively charged silicon atom while the other flanking position would still be available to support a gold containing moiety for further Si···Au stabilizing interactions. This strategy greatly pacified the Lewis acidity of the silylium species, and thus allowed the isolation of the target compounds [2-$Ph_2P(AuC_6F_5)$-6-$Ph_2P(E)$-$C_6H_3SiMe_2$][$BAr^F{}_4$], E = S (**23**), Se (**24**).[38]

Monoorganopnicogen(III) halides, 2,4,6-$(C_6F_5)_3C_6H_2EX_2$ (E = P, As, Sb, Bi; X = F, Cl) were synthesized and fully characterized. The lithiation reaction conditions were modified and improved in order to isolate the organopnicogen chlorides with good purity. Reaction of **9** with one equivalent of *n*-BuLi in a mixture of hexane and toluene (3:1 v/v) at 0 °C proceeded smoothly within 2 to 4 h to give the organolithium derivative 2,4,6-$(C_6F_5)_3C_6H_2Li$. In the next step, 2,4,6-$(C_6F_5)_3C_6H_2Li$ was reacted with PCl_3 or $AsCl_3$ at temperatures below −35 °C in order to obtain 2,4,6-$(C_6F_5)_3C_6H_2PCl_2$ (**25**) and 2,4,6-$(C_6F_5)_3C_6H_2AsCl_2$ (**26**), respectively (Scheme 4).



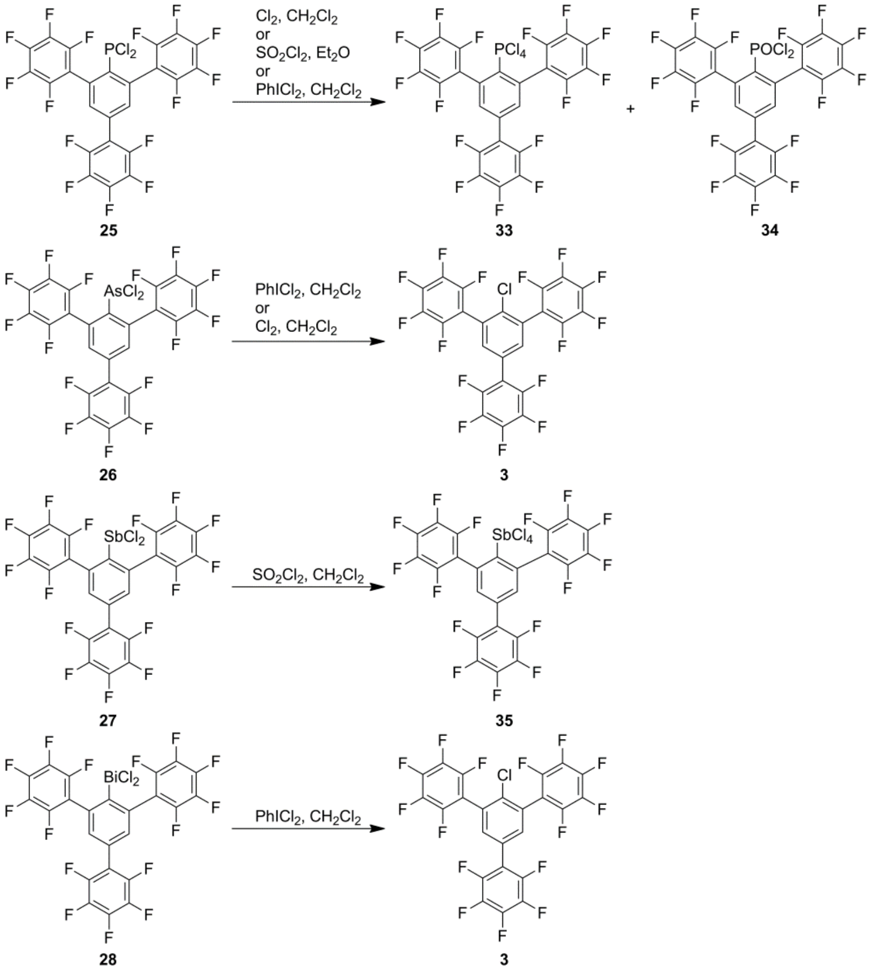
Scheme 4. Synthesis of **25–28**.

The fast addition of a solution of $SbCl_3$ dissolved in the minimum volume of toluene over the pre-cooled (−60 °C) suspension of 2,4,6-$(C_6F_5)_3C_6H_2Li$ gave, after removal of LiCl and all other volatiles, 2,4,6-$(C_6F_5)_3C_6H_2SbCl_2$ (**27**) as the main product. In order to obtain 2,4,6-$(C_6F_5)_3C_6H_2BiCl_2$ (**28**) and disfavor the formation of [2,4,6-$(C_6F_5)_3C_6H_2]_2BiCl$, the organolithium intermediate was treated with an excess of $ZnBr_2$.

The very slow addition of the organozinc intermediates over a solution of $BiCl_3$ in toluene (at room temperature) afforded **28** as main product.

Compounds **25–28** were isolated as white or off-white solids that can be stored in air at least for weeks without noticeable decomposition. In solution **25–28** react with traces of water and oxygen. When a solution of **25** was exposed to air and moisture, the initial formation of, most likely, $2,4,6\text{-}(C_6F_5)_3C_6H_2P(O)HCl$ (**29**) was observed to take place. Derivative **29** reacted further when exposed to air and moisture to give an insoluble (in C_6D_6, $CDCl_3$, CH_2Cl_2) white product identified as $2,4,6\text{-}(C_6F_5)_3C_6H_2P(O)H(OH)$ (**29a**). Compounds **27** and **28** decomposed slowly with formation of $1,3,5\text{-}(C_6F_5)_3C_6H_3$ and inorganic by-products upon exposure of their solutions to atmospheric conditions.

Compounds **25** and **26** reacted with ZnF_2 to afford the corresponding fluorides $2,4,6\text{-}(C_6F_5)_3C_6H_2PF_2$ (**30**) and $2,4,6\text{-}(C_6F_5)_3C_6H_2AsF_2$ (**31**). The isolation and purification of **31** was unsuccessful.

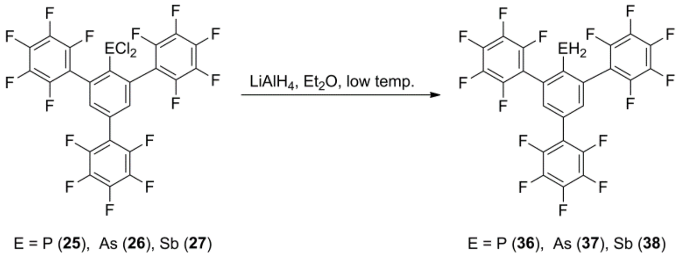


Scheme 5. Synthesis of **33–35**.

Well-defined, pentacoordinated monoorganopnicogen(V) tetrahalides with known molecular structures determined by single-crystal X-ray diffraction are very rare. This motivated the synthesis and structural characterization of organopnicogen(V) tetrachlorides of type 2,4,6-$(C_6F_5)_3C_6H_2ECl_4$ (E = P–Bi).

Reaction of 2,4,6-$(C_6F_5)_3C_6H_2PCl_2$ with SO_2Cl_2, $PhICl_2$ or chlorine gas (Scheme 5), gave in all cases two products: the tetrachloride 2,4,6-$(C_6F_5)_3C_6H_2PCl_4$ (**33**) as the main product and a variable amount of 2,4,6-$(C_6F_5)_3C_6H_2P(O)Cl_2$ (**34**). Due to its sensitivity toward hydrolysis, **33** could not be obtained free of **34**. The latter reacted slowly with water to give eventually 2,4,6-$(C_6F_5)_3C_6H_2P(O)(OH)_2$ (**34a**). The attempts to oxidize **26** and **28** in reactions with Cl_2 or $PhICl_2$ failed to afford the corresponding monoorganopnicogen tetrachlorides. The only product isolated from the aforementioned trials was 2,4,6-$(C_6F_5)_3C_6H_2Cl$.[36] The oxidation reaction of 2,4,6-$(C_6F_5)_3C_6H_2SbCl_2$ with SO_2Cl_2 afforded 2,4,6-$(C_6F_5)_3C_6H_2SbCl_4$ (**35**) as the main product.

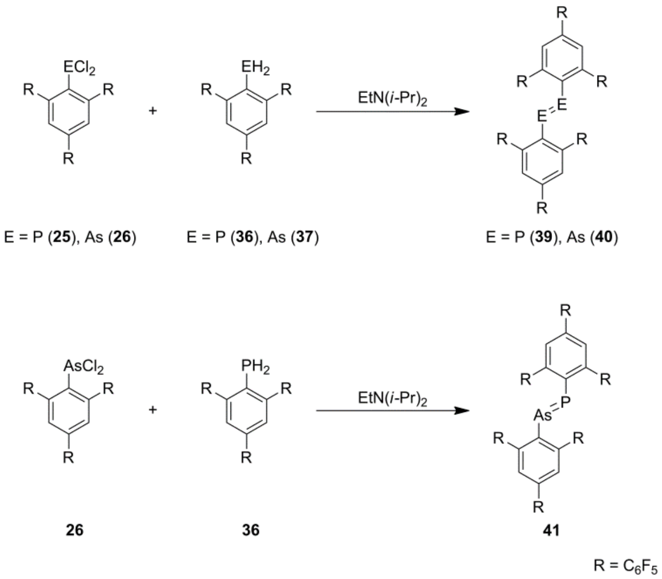
Reactions of 2,4,6-$(C_6F_5)_3C_6H_2ECl_2$ [E = P (**25**), As (**26**), Sb (**27**)] with $LiAlH_4$ in Et_2O afforded the corresponding hydrides 2,4,6-$(C_6F_5)_3C_6H_2EH_2$ [P (**36**), As (**37**), Sb (**38**)] in good yields (Scheme 7).



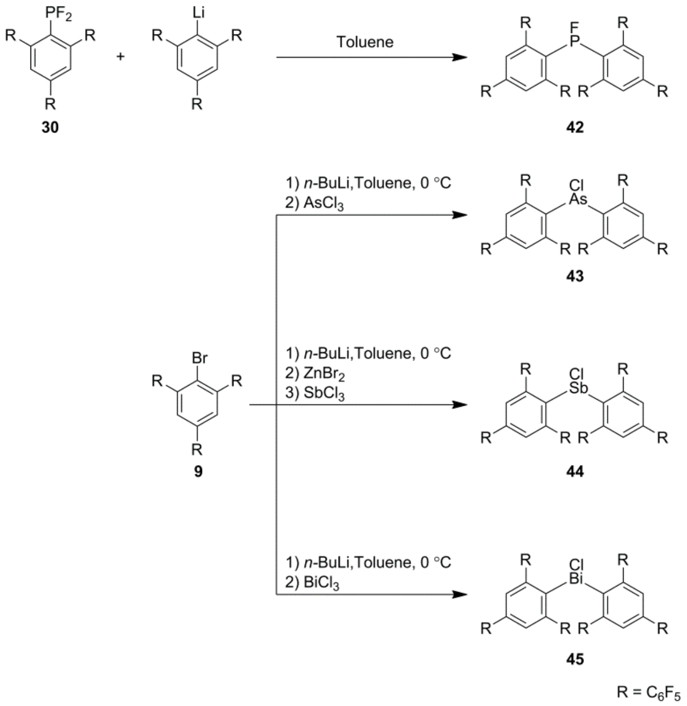
Scheme 6. Synthesis of **36–38**.

Unfortunately all efforts undertaken in order to obtain crystals of these hydrides suitable for single-crystal X-ray diffraction studies were unsuccessful. Their identity was however univocally established by NMR spectroscopy. The resonance signals corresponding to the two hydrogen atoms bonded to pnicogens were in all cases observable by ^1H NMR spectroscopy.

With the monoorganopnicogen(III) chlorides and, except for bismuth, all monoorganopnicogen hydrides at hand, the synthesis of dipnictenes was attempted next. All attempts to prepare dipnictenes by following previously reported methods have failed to give the desired products. The use of Hunig's base [(*i*-Pr)$_2$NEt] as HCl sequestration reagent was however rewarding and allowed [2,4,6-$(C_6F_5)_3C_6H_2E]_2$ [E = P (**39**), As (**40**)] and 2,4,6-$(C_6F_5)_3C_6H_2As{=}PC_6H_2(C_6F_5)_3$-2,4,6 (**41**) to be obtained upon reacting monoorganopnicogen(III) chlorides with monosubstituted pnicogen hydrides (Scheme 7). Efforts to isolate these dipnictenes were impeded by their limited stability.



Scheme 7. Synthesis of **39–41**.



Scheme 8. Synthesis of **42–45**.

The complete homologues series of diorganopnicogen(III) halides was prepared and all compounds were completely characterized. The synthetic methods used to obtain diorganopnicogen(III) halides $[2,4,6\text{-}(C_6F_5)_3C_6H_2]_2EX$ [E = P (**42**), As (**43**), Sb (**44**), Bi (**45**), X = F or Cl] are presented in Scheme 8**Error! Reference source not found.**. To ensure the preparation of $[2,4,6\text{-}(C_6F_5)_3C_6H_2]_2PF$ is successful, $2,4,6\text{-}(C_6F_5)_3C_6H_2PF_2$ was used as starting material. For the synthesis of the heavier analogues compounds this precaution was not necessary. In fact, because of the larger atomic radius of bismuth and a slightly decreased steric encumbrance of the 2,4,6-$(C_6F_5)_3C_6H_2$ substituent, the triorganobismuthine $[2,4,6\text{-}(C_6F_5)_3C_6H_2]_2Bi[2\text{-}(Me_2NCH_2)C_6H_4]$ (**46**) could also be obtained easily. Thus reaction of 2,4,6-$(C_6F_5)_3C_6H_2Li$ with 2-$(Me_2NCH_2)C_6H_4BiBr_2$ in toluene at 0 °C afforded compound **46** with 70% yield.[39] All these compounds were isolated as fairly robust nonvolatile solids characterized by high (above 200 °C) melting points. All compounds were stable to atmospheric conditions in solid state. Two of the compounds were seemingly inert to hydrolysis in solution and withstood separation by column chromatography. Attempts to obtain single-crystals of **44** eventually resulted in complete decomposition of the product with formation of 2,4,6-$(C_6F_5)_3C_6H_3$ and insoluble inorganic byproducts. The heavier congener, **45**, had a similar fate. Unfortunately all attempts to generate the corresponding pnictenium cations were not successful due to a poor reactivity of the $[2,4,6\text{-}(C_6F_5)_3C_6H_2]_2ECl$ [E = P (**42**), Bi (**45**)] derivatives towards halide abstraction reagents.

Other results, referring to bulky phenol derivatives with *m*-terphenyl backbone have been also briefly accounted.[40]

Conclusions

Overall, the 2,4,6-$(C_6F_5)_3C_6H_2$ substituent behaves to some extent similarly to a mid-size classic *m*-terphenyl group with respect to steric properties. It is true that the polyfluorinated *m*-terphenyl is more prone to engage in undesired side reactions and in this respect it may be difficult for it to support an extraordinarily reactive functional group. Some compounds that were studied herein displayed rather unusually high reactivity. For example, the 2,4,6-$(C_6F_5)_3C_6H_2Li$ seemed to be slowly decomposing at room temperature and 2,4,6-$(C_6F_5)_3C_6H_2AsCl_4$ decomposed very easily to 2,4,6-$(C_6F_5)_3C_6H_2Cl$. The substituent cannot be held responsible for not providing sufficient kinetic stabilization for both cases. If for the former compound one can imagine LiF elimination as a possible cause of the compound's instability, for the latter, one could reasonably blame electronic effects. A similar observation could be made for the rather surprising sensitivity of $[2,4,6\text{-}(C_6F_5)_3C_6H_2]_2ECl$ (E = Sb, Bi) toward hydrolysis. The nature and extent these electronic effects influenced the reactivity of some of the studied compounds cannot be, at the moment, quantified as this matter requires more (future) investigations. Hopes are this thesis will provide a good starting point if such an endeavor is to be taken.

The projected physical properties the 2,4,6-$(C_6F_5)_3C_6H_2$ substituent would impose in the compounds studied in this thesis was confirmed in most cases. Predicted properties such as high solubility in a broad spectrum of organic solvents and improved volatility (with respect to sublimation points) observed for most of the studied compounds also applied to the side-products and other impurities as well. More often than not this was a setback as it reduced the efficiency of most purification methods available. In some cases the unavailability of any efficient purification methods prohibited the isolation of the pure target product. In other cases the only way to avoid significant (yield) losses was to design the reaction in a way it would produce the least amount of side-products.

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