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Reduction reactions of alkyne and butadiyne derived fluorinated cyclophosphazenes

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ABSTRACT

Alkyl derivatives of fluorinated cyclophosphazenes having phenyl or ferrocenyl units separated by two and four CH_2 units from the cyclophosphazene ring are prepared by hydrogenation of the alkyne/butadiyne unit of the corresponding alkyne/dialkyne derived cyclic fluorophosphazenes. Hydrogenation of the ethynyl units in compounds $[PhC{\equiv}C(F)PN](PNF_2)_2$, $[FcC{\equiv}C(F)PN](PNF_2)_2$ and $[(FcC{\equiv}C)_2PN](PNF_2)_2$ using Pd/C as catalyst resulted in compounds $Ph(CH_2)_2P_3N_3F_5$ (**1**), $Fc(CH_2)_2P_3N_3F_5$ (**2**) and $[(FcCH_2CH_2)_2PN](PNF_2)_2$ (**3**) (Fc = ferrocenyl), respectively. Similar, hydrogenation reaction of the butadiynyl units in compounds $[PhC{\equiv}C{-}C{\equiv}C(F)PN](PNF_2)_2$, $[FcC{\equiv}C{-}C{\equiv}C(F)PN](PNF_2)_2$ and $[(FcC{\equiv}C{-}C{\equiv}C)_2PN](PNF_2)_2$ using Pd/C as catalyst resulted in compounds $Ph(CH_2)_4P_3N_3F_5$ (**4**), $Fc(CH_2)_4P_3N_3F_5$ (**5**) and $[\{Fc(CH_2)_4\}_2PN](PNF_2)_2$ (**6**), respectively. Hydrogenation of the butadiynyl and ethynyl units in the unsymmetrically substituted cyclophosphazene $[(FcC{\equiv}C)(FcC{\equiv}C{-}C{\equiv}C)PN](F_2PN)_2$ resulted in the alkyl derived cyclophosphazene $[\{Fc(CH_2)_4\}\{Fc(CH_2)_2\}PN](F_2PN)_2$ (**7**). Partial hydrogenation of $[FcC{\equiv}C(F)PN](PNF_2)_2$ using Lindlar catalyst resulted in the alkene derived cyclophosphazene $[FcCH{=}CH(F)PN](PNF_2)_2$ (**8**) which was further reduced using Pd/C catalyst to give the alkyl derivative $Fc(CH_2)_2P_3N_3F_5$ (**2**). An attempted hydrogenation of chlorinated phosphazene, $[FcC{\equiv}C(Cl)PN](PNCl_2)_2$ using Pd/C as catalyst resulted in compound $[(FcCH_2CH_2)(OCH_3)PN](PNCl_2)_2$ (**9**) having methoxy substitution on the alkyl substituted phosphorus atom. All new compounds were characterized by IR, NMR [^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$] and HRMS studies. Compounds $[FcC{\equiv}C(F)PN](PNF_2)_2$ and **2** have also been structurally characterized.

1. Introduction

Reactivity of fluorinated cyclophosphazenes, an important class of inorganic heterocycles, varies considerably when compared to the relatively more well-known chlorinated cyclophosphazenes [1]. Although chlorophosphazenes are the preferred precursors for preparing derivatives having P–O or P–N bonds, fluorophosphazenes fare better in selectivity and yields in reactions involving organolithium, Grignard or organocopper reagents [2–8]. The main reasons for this difference in reactivity is the relative higher bond enthalpy of the P–F bonds, stability of higher coordination numbers upon fluorination of phosphorus sites and absence of competing side reactions in reactions involving organometallic reagents. In general, alkynyl, alkenyl and alkyl derivatives of cyclophosphazenes are some of the most difficult derivatives of fluorophosphazeneness to prepare. The pioneering work by Allen and co-workers has shown that the alkynyl derivatives of fluorinated cyclophosphazenes are accessible by the reaction of fluorophosphazenes with organolithium reagents [9] and recently they have studied factors controlling the pathways observed in such reactions [10]. In our own research group, we have prepared the first examples of ethynylferrocene derived cyclophosphazenes and pheny/ferrocenyl butadiyne derived fluorinated cyclophosphazenes [11] and showed the usefulness of alkyne derived cyclophosphazenes in realizing novel phosphazene derived triazoles, cobalt sandwich compounds, cobaltacyclopentadienes and multiphosphazenyl assemblies by cycloaddition reactions [12].

Recent studies by Allen and coworkers on the hydrogenation of ethynylphosphazene derivatives provide a new pathway for the preparation of alkyl substituted phosphazenes, starting from the easily accessible alkynyl derivatives of cyclophosphazenes [10]. To explore the versatility of these hydrogenation reactions and to see whether similar hydrogenation is possible with mono and geminally disubstituted conjugated butadiynyl cyclophosphazenes, we have attempted reduction reactions of cyclophosphazenes having ethynyl, butadiynyl as well as both to realize ferrocene and phenyl groups tethered to the heterocycle by alkyl chain units. Such derivatives are also model compounds for

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polyphosphazenes with terminal pendant groups having flexible alkyl spacer units. In addition, we have attempted partial reduction of the ethynyl ferrocene derived cyclophosphazene ($FcC{\equiv}C)P_3N_3F_5$ to alkene derived cyclophosphazene ($FcCH{=}CH)P_3N_3F_5$ using Lindlar catalyst. Details of these reactions and characterization of the new alkyl derived cyclophosphazenes are reported herein.

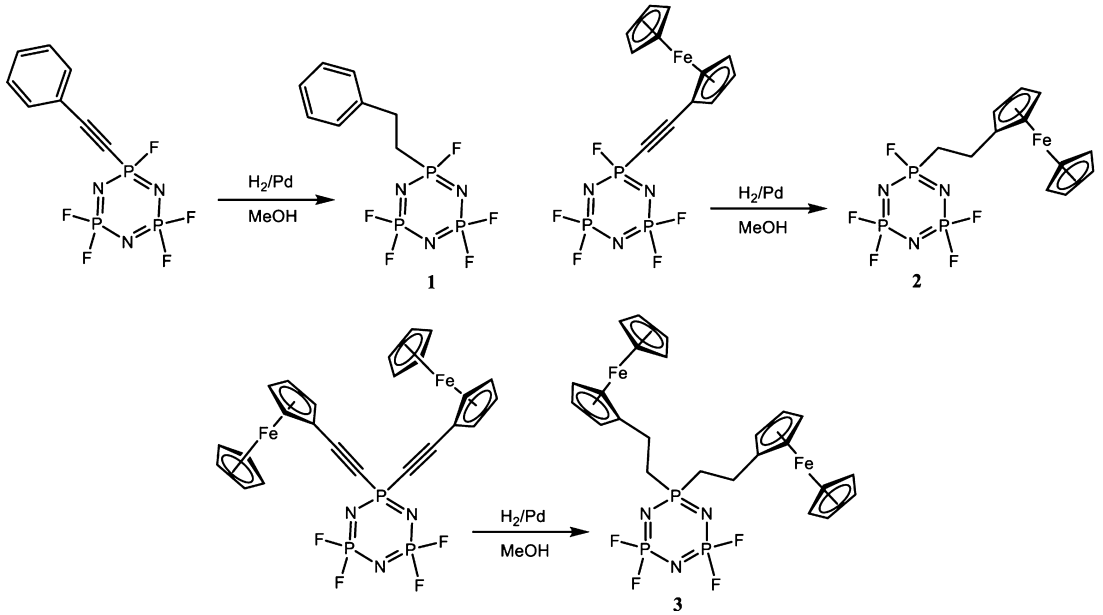
2. Results and discussion

Studies done by Allen and coworkers on the hydrogenation of the aliphatic ethynyl derived cyclophosphazene derivatives, $N_3P_3F_5(C{\equiv}CR)$ and $N_3P_3F_4(C{\equiv}CR)(C{\equiv}CR')$ (R,R′=CH_3, n-C_4H_9) resulted in the corresponding alkyl derivatives. Cyclophosphazenes having ferrocene moiety directly bound to the phosphorus atom are used for the synthesis of electro-active polyphosphazenes having unique properties [13] and it is now established that the larger the distance of bulky pendant groups such as ferrocene from the polymeric backbone, the better are the polymer properties especially molecular weight [14]. Since introducing alkyl chains of varying chain lengths directly on a phosphazene ring is cumbersome [15], we hoped that such alkyl derivatives can be accessed more easily by the hydrogenation reactions of alkyne and conjugated multi-alkyne (e.g. butadiyne) derived phosphazenes having phenyl/ferrocenyl groups at the periphery. Initial reactions were carried out on the mono and geminal disubstituted alkynyl derived fluorophosphazenes. It was observed that reduction of alkynyl units in compounds $[PhC{\equiv}C(F)PN](PNF_2)_2$, $[FcC{\equiv}C(F)PN](PNF_2)_2$ and $[(FcC{\equiv}C)_2PN](PNF_2)_2$ proceeds smoothly using 10% Pd/C in MeOH to give $Ph(CH_2)_2P_3N_3F_5$ (**1**), $Fc(CH_2)_2P_3N_3F_5$ (**2**) and $[(FcCH_2CH_2)_2PN](PNF_2)_2$ (**3**), respectively, resulting in alkyl cyclophosphazenes having phenyl or ferrocenyl units separated by two CH_2 units from the cyclophosphazene ring in very good yields (Scheme 1). These alkyl derivatives showed interesting changes in the ^{31}P and ^{19}F NMR on going from the ethynyl to the arylethyl derivatives, which will be discussed under spectral studies.

After successful reduction of ethynyl derived phosphazene derivatives, we were keen to see whether similar reduction can be made possible with our mono and geminal disubstituted conjugated butadiynes. We observed that the complete reduction of butadiyne fragment takes place very smoothly for all the three types of our derivatives, i.e., monosubstituted, geminal disubstituted and geminal alkynyl–butadiynyl substituted cyclophosphazenes. Reduction of compounds $[PhC{\equiv}C{-}C{\equiv}C(F)PN](PNF_2)_2$, $[FcC{\equiv}C{-}C{\equiv}C(F)PN](PNF_2)_2$, $[(FcC{\equiv}C{-}C{\equiv}C)_2PN](PNF_2)_2$ and $[(FcC{\equiv}C)(FcC{\equiv}C{-}C{\equiv}C)PN](F_2PN)_2$ was carried out using 10–20% Pd/C in MeOH to give the phenyl and ferrocenyl tethered phosphazene compounds $Ph(CH_2)_4P_3N_3F_5$ (**4**), $Fc(CH_2)_4P_3N_3F_5$ (**5**), $[\{Fc(CH_2)_4\}_2PN](PNF_2)_2$ (**6**) and $[\{Fc(CH_2)_4\}\{Fc(CH_2)_2\}PN](F_2PN)_2$ (**7**), respectively, having phenyl or ferrocenyl units separated by four CH_2 units from the cyclophosphazene ring (Scheme 2).

Since very few examples of alkenes directly bonded to cyclic phosphazenes are known in the literature [16], we were keen to see if partial reduction of alkyne/butadiyne derived cyclophosphazenes can be used as a method to realize alkene derived cyclophosphazenes. A few attempted reductions of butadiyne derived cyclophosphazenes using Lindlar catalyst were found to result in a complex mixture of partial and fully saturated products. To reduce the complexity, we attempted partial reduction of ethynyl ferrocene derived cyclophosphazene ($FcC{\equiv}C)P_3N_3F_5$ using Lindlar catalyst in different solvents. It was observed that partial reduction takes place smoothly to give ($FcCH{=}CH)P_3N_3F_5$ (**8**) when THF was used as the solvent. Two different sets of doublet multiplets in the ^{31}P NMR in the range of 25–40 ppm indicated the presence of both cis and trans alkene isomers, which was further confirmed by ^{1}H NMR studies as a 72:28 cis:trans mixture. On further reduction with Pd/C in MeOH, this mixture of cis/trans isomers of alkene derivatives was found to undergo complete reduction to give $Fc(CH_2)_2P_3N_3F_5$ (**2**). Compound **2**, as expected gave only one doublet of multiplet peak in ^{31}P NMR in the range of 40 to 55 ppm similar to compound **1** (Scheme 3).

Since polymerization of fluorophosphazenes is difficult compared to chlorophosphazenes, we were keen to see whether similar type of hydrogenation reactions can take place with the ethynyl units in the chlorophosphazene derivatives. When we attempted the reduction of ethynyl ferrocene derived chlorophosphazene, ($FcC{\equiv}C)P_3N_3Cl_5$ using 10% Pd/C in MeOH it resulted in a complex mixture of products having multiple substituted P–OMe compounds along with hydrogenated P–$(CH_2)_2$Fc moiety. The same hydrogenation reaction when attempted in THF and ethylacetate was not found to proceed. Finally, when a 1:1 mixture of MeOH and THF was used along with 10% Pd/C, $[(FcCH_2CH_2)(OCH_3)PN](PNCl_2)_2$ (**9**) was obtained as major product in 65% yield. A simple triplet and



Scheme 1. Hydrogenation reactions of alkynyl derived fluorophosphazenes.