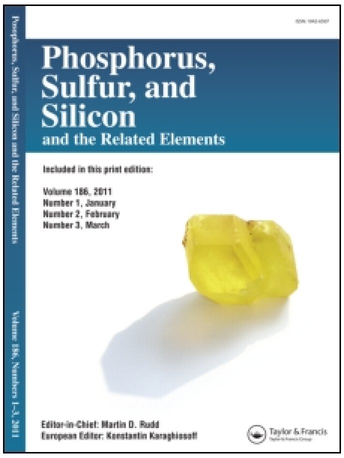

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

New Synthetic Route and Characterisation of Phosphorus and Arsenic Heterocyclic Compounds

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To cite this Article Matos, Robson M. , de Lima, Luiz Carlos Gomes , de Souza, Edward , de Souza, Ana Lúcia Americano Barcelos , de Lima, Miriam Bernardes Gomes and Raslan, Délio Soares(2002) 'New Synthetic Route and Characterisation of Phosphorus and Arsenic Heterocyclic Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 12, 2859 — 2870

To link to this Article: DOI: 10.1080/10426500214881

URL: http://dx.doi.org/10.1080/10426500214881

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:2859–2870
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1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290146901

NEW SYNTHETIC ROUTE AND CHARACTERISATION OF PHOSPHORUS AND ARSENIC HETEROCYCLIC COMPOUNDS

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(Received 2 April 2002)

Herein we report synthetic routes for the preparation of 2-chloro-1,3,2-dioxarsenane ***1****, O,O'-bis(5,5-dimethyl-1,3,2-dioxarsenane)-2,2-dimethyl-1,3-propanediol* ***3****, 2-chloro-1,3,2-dioxaphosphorinane* ***4****, and 2-fluoro-1,3,2-dioxaphosphorinane* ***5****. The new synthetic routes described here have the advantage to be simple, very clean and to lead to the desired compounds in very good yields. Compound 2-fluoro-1,3,2-dioxarsenane* ***2*** *also was prepared in good yield and is described here for the first time. Compounds* ***1–5*** *were fully characterized on the basis of NMR spectroscopic studies. Semi-empirical structural studies have been carried out and the results show that* ***1*** *and* ***2*** *exist as a mixture of two conformers, whereas only one conformer for* ***4*** *and* ***5*** *have been found. Variable temperature ^{1}H NMR studies reveal a fluxional behaviour for* ***1*** *and a mechanism for the inter-conversion between its two conformers is proposed.*

Keywords: Arsenic; conformation; NMR studies; phosphorus; semi-empirical calculations

INTRODUCTION

Heterocyclic compounds of the type shown in Scheme 1 are an important class of compounds[1] with wide application such as the development of specific immunoassays for the detection of pesticides,[2] polymerization

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We thank FAPEMIG, FINEP, PRPq-UFMG, and CNPq-Brazil for the continuing support of this work. The authors thank Dr. Wagner Batista de Almeida for his kind permission to use the workstations and others computational facilities of the LQC-MM, UFMG.

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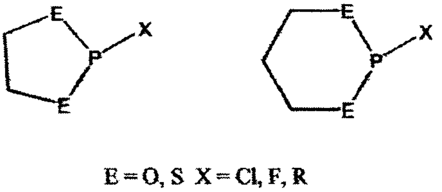
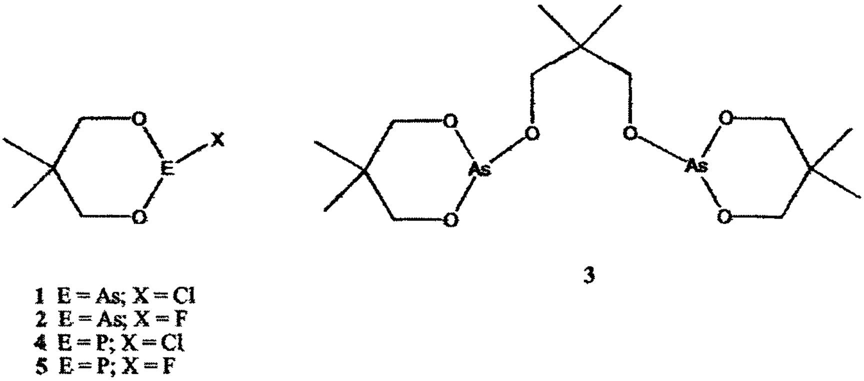


SCHEME 1

reactions,[3,4] syntheses of naturally occurring lipids,[5] and as a reagent to analyse labile hydrogen functional groups on coal materials.[6]

Recently, we have shown that the chemistry of this kind of compounds towards transition metal is very interesting, and much remains to be investigated.[7,8] However, it is necessary to develop new and simple synthetic routes that lead to this type of compounds in better yields. We already have shown that 5-membered rings such as 2-chloro-1,3,2-dioxaphospholane, 2-chloro-4,5-benzodioxaphospholane,[9] and 2-chloro-1,3,2-dithiaphospholane[10] can be obtained in very good yields by treating the corresponding diol or dithiol with PCl_3. More recently, we have shown that 2-chloro-1,3,2-dithiastibolane can be formed via skeletal substitution reaction.[11] Now, we report new routes for the preparation of 6-membered rings containing P and As and the preparation of the novel 2-fluoro-5,5-dimethyl-1,3,2-dioxarsenane.

RESULTS AND DISCUSSION



SCHEME 2

a) 2-Chloro-5,5-dimethyl-1,3,2-dioxarsenane 1

Compound **1** has been prepared by treatment of $AsCl_3$ with the diol in the presence of triethylamine using ether as a solvent in 75%

yield,[12,13] and more recently Said et al.[14] reported the preparation of the same compound, in 95% yield, by treatment of the diol with $AsCl_3$ in dichloromethane. Herein we report that addition of 2,2-dimethyl-1,3-propanediol, as a solid, to neat $AsCl_3$ affords 2-chloro-5,5-dimethyl-1,3,2-dioxarsenane **1** as the only product, also in a very good yield (97%).

Compound **1** was formed as a mixture of two conformers, as evidenced by its ^1H and $^{13}C\{^1H\}$ NMR studies. At room temperature, the ^1H NMR spectrum of **1** shows one broad singlet at δ 3.87 corresponding to methylene hydrogens and a singlet at δ 0.98 corresponding to the methyl hydrogens. At −50°C the signal at δ 3.87 starts to split into two doublets at δ 4.26 and δ 3.65, whereas the signal at δ 0.98 starts to split into two singlets at δ 1.21 and δ 0.79 revealing a spectrum corresponding to an [AA'BB'] spin system. Typically, hydrogens in axial positions on cyclohexanes are more shielded than the equatorial hydrogens,[15] however, studies on 1,3-dioxanes show the opposite result.[16] This is believed to be caused by the interaction between the H_e and the p-orbital of the oxygen atoms.[17] A deshieldding of the axial hydrogens relative to their equatorial counterparts also has been observed for six-membered ring systems containing phosphorus[18–20] and arsenic.[21–23] In this case, the effect might be caused by the presence of an axial halogen on phosphorus or arsenic. Based on this, the resonance signals at δ 0.79 and δ 3.65 on the ^1H NMR spectrum of **1** are assigned to the equatorial methyl group and equatorial hydrogens respectively.

The $^{13}C\{^1H\}$ NMR spectrum of **1** at room temperature also reveals its fluxional behaviour since broad signals are observed. This spectrum shows a singlet due to the CH_3 groups at δ 21.70, and at δ 71.97 corresponding to the CH_2, and a rather broad singlet at δ 35.4 attributed to the $C(Me)_2$.

Aksnes and coworkers[21–24] proposed that **1** could be present, in solution, as two different chair conformations, that is, the chlorine is on an axial position in the more stable conformer and on an equatorial position in the other conformer. Furthermore, they proposed an intermolecular halogen exchange process to account for the fluxional behaviour of **1**, since it is a well known fact that the inversion energy barrier between the two conformers would be prohibitively high. On the other hand, Arbuzov et al.[25] showed that the similar 2-chloro-4-methyl-1,3,2-dioxarsenane has a chair conformation with an axial chlorine and equatorial methyl, based on measurements of its dipole moments and Kerr constants. All these hypotheses have been approached in this work, employing semi-empirical calculations, PM3, coordinate driving and conformational search resources. First of all, an intramolecular inversion of **1** was simulated and, as expected, a very high inversion energy barrier (110 kcal mol^{-1}) was found. Attempt to simulate a reaction path

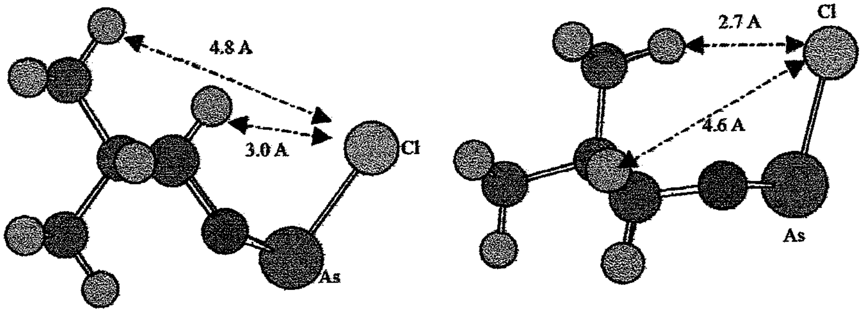


FIGURE 1 Lateral view of the chair (left) and the twisted-boat (right) conformers of **1**.

involving an intermolecular chlorine exchange process leading to the formation of an isomer with the chlorine on a equatorial position also gives a high inversion energy barrier, up to 60 kcal mol^{-1}. Due to these results, a conformational search of **1** was carried out which pointed to the existence of two conformers, that is, a chair and twisted-boat (Figure 1). The energy for the process of conversion chair/twisted-boat for **1** was found to be 7 kcal mol^{-1} (Table I).

Further conformational searches employing ab initio quantum mechanical calculations, 3-21G* (Table II), gave the same results as the semi-empirical approach, that is, the possible coexistence of the chair and the twisted-boat conformers. However, attempts to unequivocally characterize the transition state between them and to quantitate the conformational energy barrier were not satisfactory with that basis set.

b) 2-Fluoro-5,5-dimethyl-1,3,2-dioxarsenane 2

To the best of our knowledge this compound has not been reported before and its synthesis is a modification of the procedure described by Verkade et al.[20] to prepare 2-fluoro-5,5-dimethyl-1,3,2-dioxaphophorinane **5**. Evidence that **2** exists as a mixture of two conformers in solution comes from the ^1H NMR spectrum at room temperature, which consists of two subspectra corresponding to [AA'BB'] spin system. One of the sub

TABLE I Calculated PM3 Enthalpy of Formation for the Conformers of **1**

Conformer	Description	$\Delta H/(kcal\cdot mol^{-1})$
Maximum	Twisted-boat (bt)	−120
Minimum	Chair (ch)	−124
Transition state	50% bt-ch	−117

TABLE II Calculated ab initio Enthalpy of Formation for the Conformers of **1**

Conformer	Description	Energy/a.u.	ΔE/a.u.	ΔH/(kcal·mol^{-1})
Minimum	Chair (ch)	−3024.11640	0	0
Maximum	Twisted-boat (bt)	−3024.10273	0.01367	8.6
Transition state	50% bt-ch	−3024.09013	0.026272	16.5

spectra shows two doublets at δ 4.33 and δ 3.63 attributed to H_a and H_e respectively, and two singlets at δ 0.81 (equatorial CH_3) and δ 1.25 (axial CH_3). The other subspectrum shows two doublets at δ 4.30 and δ 3.51 (H_a and H_e) and two singlets at δ 0.78 (equatorial CH_3) and δ 1.28 (axial CH_3). Conformational studies for **2** employing semi-empirical PM3 calculations have been carried out and the results were similar to those found for **1**, that is, a coexistence of a chair and a twisted-boat conformers (Figure 2) with their conversion energy barrier around 12 kcal mol^{-1} (Table III). Similarly to **1**, conformation searches using ab initio quantum mechanical calculations (3-21G*) presented the same results as the semi-empirical approach (Table IV). Again, it was not possible, with that basis set, to unequivocally characterize the transition state and to quantitate the conformational energy barrier between the conformers.

Interestingly, no C–F coupling constants have been observed on the $^{13}C\{^1H\}$ NMR spectrum of **2**, as observed for **5** (vide infra). This might be due to the bigger size of the arsenic compared to the phosphorus atom. Likewise, the difference of size of oxygen and sulphur has been used to account for the decrease of $^2J_{(CP)}$ found for 2-chloro-1,3,2-dioxaphospholane (8.7 Hz)[9] and for 2-chloro-1,3,2-dithiaphospholane (2.2 Hz).[10] The two singlets at δ 22.0 and δ 23.2 are attributed

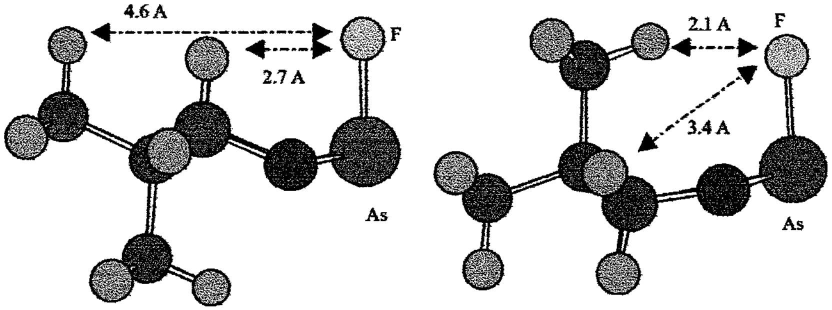


FIGURE 2 Lateral view of the chair (left) and the twisted-boat (right) conformers of **2**.

TABLE III Calculated PM3 Enthalpy of Formation for the Conformers of **2**

Conformer	Description	ΔH/(kcal·mol^{-1})
Maximum	Twisted-boat (bt)	−157
Minimum	Chair (ch)	−163
Transition state	50% bt-ch	−152

respectively to the CH_3 at the equatorial and axial positions. The $^{13}C\{^1H\}$ NMR spectrum of **2** also shows singlets at δ 33.6 (CMe_2) and δ 72.8 (CH_2).

c) O,O′-bis(5,5-dimethyl-1,3,2-dioxarsenane)-2,2-dimethyl-1,3-propanediol 3

Said and coworkers[14] recently have reported the preparation of **3** in a low yield (40%) by treatment of **1** with sodium. The same group has also reported that **3** was isolated along several impurities from the reaction of **1** with cyclohexylamine.[14] The synthetic method herein reported has the advantage to be a very clean one and to give **3** in a very high yield (96%). It consists of addition of neat $AsCl_3$ to the solid 2,2-dimethyl-1,3-propanediol. Compound **3** was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The ^1H NMR spectrum exhibits two doublets at δ 4.29 and δ 3.60 corresponding to the hydrogens from the OCH_2 group on the ring and a singlet at δ 3.91 due to the equivalent hydrogens from the bridging OCH_2 groups. The coupling constant between the axial and equatorial hydrogens on the ring is 11.2 Hz. Three other singlets are observed for **3** at δ 1.24, δ 0.77, and δ 0.99. The latter is attributed to the equivalent CH_3 groups in the bridge and the first two attributed to the CH_3 groups on the ring. The signals at δ 4.29 and δ 1.24 are most likely to be due to the axial hydrogens from the OCH_2 and from the axial CH_3 groups, respectively. The $^{13}C\{^1H\}$ NMR spectrum shows signals at δ 72.3 and δ 72.2 corresponding to the CH_2 on the ring and in the bridge, respectively, according to the integration of these peaks (4:2). The signals observed at δ 36.8 and δ 33.2 are attributed to

TABLE IV Calculated ab initio Enthalpy of Formation for the Conformers of **2**

Conformer	Description	Energy/a.u.	ΔE/a.u.	ΔH/(kcal·mol^{-1})
Minimum	Chair (ch)	−2665.62450	0	0
Maximum	Twisted-boat (tb)	−2665.61822	0.00627	3.9
Transition state	50% bt-ch	−2665.61058	0.01392	8.7

quaternary carbons and, by use of the integration of the peaks. The first can be attributed to the bridging carbon, whereas the latter to the carbons on the ring. Another way to undoubtedly attribute these two signals would be by comparison with data found for **1**. However, since **1** has a fluxional behavior and, unfortunately, a low temperature $^{13}C\{^1H\}$ NMR spectrum has not been recorded, the attribution had to be made based on the data found for its phosphorus analogue compounds **4** and **5** and for its closely related fluoro compound **2** (vide infra), which show signals for the Me_2C at δ 32.8, δ 32.4, and δ 33.6 respectively. Thus, one would speculate that the signal at δ 33.2 corresponds to the quaternary carbons on the ring whereas the signal at δ 36.8 is due to the quaternary carbon on the bridge. From the integration of the peaks at δ 22.8, δ 21.8, and δ 21.4 it can be said, undoubtedly, that the first two correspond to the carbon of the methyl groups on the ring whereas the latter corresponds to the one in the bridge. Unfortunately, our $^{13}C\{^1H\}$ NMR data, with respect to the CH_2 resonance signals, do not match those reported by Said et. al[14] (δ 68.3 (bridge) and δ 71.2 (ring)). However, the authors do not provide details such as the solvent used for the NMR spectrum.

d) 2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane 4

Treatment of 2,2-dimethyl-1,3-propanediol with PCl_3 affords the title compound in 95% yield. Compound **4** has been prepared by treatment of the diol with PCl_3 in presence of pyridine and ether as a solvent,[20] but the authors did not report the yield. The $^{31}P\{^1H\}$ NMR spectrum of **4** shows a singlet at δ 145 and it is in accordance with data found by others.[20,25] Its ^1H NMR spectrum corresponds to an [AA'BB'X] spin system; the data are shown in Table V. The $^{13}C\{^1H\}$ NMR spectrum of **4** shows two singlets at δ 22.4 and δ 22.3 corresponding to the CH_3 groups, a doublet at δ 32.8 corresponding to the quaternary carbon and another doublet at δ 70.8 due to the methylene carbon. The $^2J_{CP}$ (2.7 Hz) and $^3J_{CP}$ (4.7 Hz) coupling constants are in the range expected for this kind of compounds.

TABLE V ^1H NMR Data for **4** and **5**

	4	**5**
$\delta_{H(a)} = \delta_{H'(a)}$	4.30	4.10
$\delta_{H(e)} = \delta_{H'(e)}$	3.56	3.43
$J_{H(a)H(e)} = J_{H'(a)H'(e)}$	9.46	9.12
$J_{H(a)H'(a)}$	0.90	0.85
$J_{H(e)H'(e)}$	0.10	0.35
$J_{H(a)P} = J_{H'(a)P}$	3.11	2.85
$J_{H(e)P} = J_{H'(e)P}$	1.62	2.52

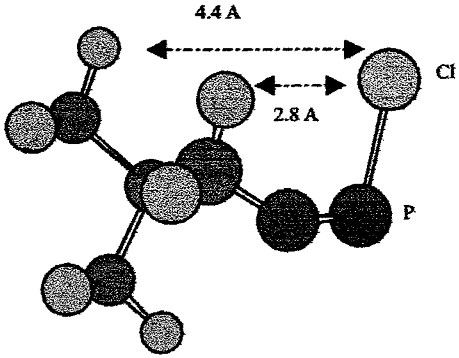


FIGURE 3 Lateral view of **4**.

Semi-empirical calculations, PM3, followed by conformational studies agreed with experimental data, leading to the conclusion that **4** resides only in a chair conformation at room temperature ($\Delta H_f = -169$ kcal mol^{-1}) with the chlorine in an axial position and 2.8 Å from the axial hydrogens and 4.4 Å from the hydrogens of the equatorial methyl group (Figure 3). Both chair and twisted-boat conformations have been reported for similar six-membered ring compounds, showing that the their conformational properties will depend on heteroatoms and on the group bonded through the phosphorus.[26–28]

e) 2-Fluoro-5,5-dimethyl-1,3,2-dioxaphosphorinane 5

Treatment of **4** with SbF_3 affords **5** in 71% yield. The $^{31}P\{_1H\}$ NMR spectrum of **5** consists of a doublet at δ 110 showing the expected P-F coupling constant ($^1J_{PF}$ = 1179.7 Hz). Its ^1H NMR spectrum corresponds to an [AA'BB'XY] spin system and data are shown in Table V.

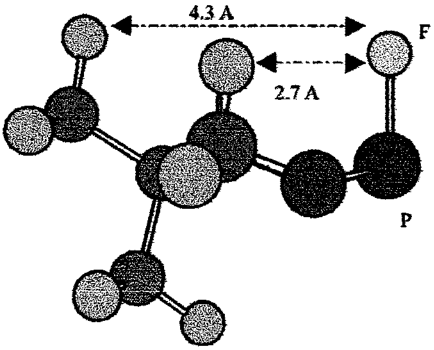


FIGURE 4 Lateral view of **5**.

The $^{13}C\{^1H\}$ NMR spectrum of **5** shows two signals for the methyl groups at δ 22.0 (singlet) and δ 22.4 (doublet). Since the signal at δ 22.4 corresponds to the axial CH_3, it can be said that the coupling of this signal is due to the phosphorus nucleus. The other signals observed at the $^{13}C\{^1H\}$ NMR spectrum of **5** are as expected (vide infra).

Similar for compound **4**, semi-empirical calculations, PM3, followed by conformational studies agreed with experimental data, leading to the conclusion that **5** would exist only in a its chair conformation at room temperature, $\Delta H_f = -220$ kcal mol^{-1}, with the fluorine in an axial position and 2.7 Å from the axial hydrogens and 4.3 Å from the hydrogens of the equatorial methyl group (Figure 4).

CONCLUSIONS

We have shown that the synthetic routes developed for the preparation of compounds **1–5** are simple, reliable, and lead to excellent yields of the desired compound. Semi-empirical calculations show that the arsenic compounds **1** and **2** exist as two conformers, in solution, whereas their phosphorus analogues, **4** and **5**, exist in only one conformation, consistent with the NMR spectroscopic data. It is believed that the existence of two conformers of **1** and **2** is due to the larger size of the arsenic atom relative to phosphorus. We have shown that semi-empirical calculations (PM3 method) can be used along with spectroscopic characterization with success for this type of system.

EXPERIMENTAL

All reactions were carried out either under dry dinitrogen in Schlenk tubes or by use of high-vacuum techniques. Glassware was flame-dried in vacuum. 2,2-Dimethyl-1,3-propanediol, arsenic trichloride and phosphorus trichloride are commercially available from Aldrich, and only the latter was purified prior to its use. (*Caution*: $AsCl_3$ and the arsenic compounds herein described must be manipulated in a well ventilated hood, and one should avoid contact with the skin.) The NMR spectra were recorded on a Varian VRX400 spectrometer at 400.13 MHz for ^1H, at 100.61 MHz for ^{13}C and 376.5 MHz for ^{19}F or on a Bruker AC200 operating at 200.13 MHz for ^1H and 81.02 MHz for ^{31}P. A Bruker BVT1000 variable temperature unit was used to control the temperature. All chemical shifts data are quoted in ppm with positive values to high frequency of the indicated reference (external 85% H_3PO_4 for ^{31}P; $SiMe_4$ for ^1H and ^{13}C and $CFCl_3$ for ^{19}F) and corrected with respect to the appropriate deuterium frequency. Coupling constants are quoted in Hertz. The theoretical calculations were accomplished utilising the SPARTAN^{TM} suite, V. 4.0, running on a IRIX 6.2 SILICON GRAPHICS workstation.

Synthesis of 2-Chloro-5,5-dimethyl-1,3,2-dioxarsenane 1

To neat $AsCl_3$(12.9 g, 71.2 mmol) was added, over a period of 5 min, 2,2-dimethyl-1,3-propanediol (1.4 g, 13.5 mmol). The mixture was stirred for 1 h and the excess of $AsCl_3$ was distilled to afford pure **1** (2.8 g; 97%). $^{13}C\{^1H\}$ NMR data (100.61 MHz; $CDCl_3$; 25°C): δ 21.7 (s; CH_3); δ 35.4 (bs; $C(CH_3)_2$) δ 71.97 (s; CH_2); ^1H NMR data (400.13 MHz; $CDCl_3$; 25°C): δ 0.98 (bs; CH_3; 6H); δ 3.87 (bs; CH_2; 4H); ^1H NMR data (400.13 MHz; $CDCl_3$; −50°C): δ 0.79 (s; CH_3(equatorial); 3H); δ 1.21 (s; CH_3(axial) 3H); δ 3.65 (d; CH_2(equatorial); 2H; $^2J_{HH} = 9.8$ Hz); δ 4.26 (d; CH_2(axial); 2H; $^2J_{HH} = 9.8$ Hz).

Synthesis of 2-Fluoro-5,5-dimethyl-1,3,2-dioxarsenane 2

To a flask containing SbF_3 (2.8 g, 15.5 mmol) **1** was added (3.3 g, 15.5 mmol) and the mixture stirred for 30 min. The product was distilled under reduced pressure to yield **2** (2.9 g, 75%). $^{13}C\{^1H\}$ NMR data (100.61 MHz; $CDCl_3$; 25°C): δ 22.0 (s; CH_3(axial)); δ 23.2 (s; CH_3(equatorial)); δ 33.6 (s; $C(CH_3)_2$); δ 72.8 (s; CH_2); ^1H NMR data (400.13 MHz; $CDCl_3$; 25°C): δ 0.81 (s; CH_3(equatorial); 3H); δ 1.25 (s; CH_3(axial); 3H); δ 3.63 (d; CH_2(equatorial); 2H; $^2J_{HH} = 11.2$ Hz); δ 4.33 (d; CH_2(axial); 2H; $^2J_{HH} = 11.2$ Hz); $^{19}F\{^1H\}$ NMR data (376.51 MHz ; $CDCl_3$; 25°C): −44.5 (s).

Synthesis of O,O′-bis(5,5-dimethyl-1,3,2-dioxarsenane)-2,2-dimethyl-1,3-propanediol 3

Neat $AsCl_3$ (12.9 g, 71.6 mmol) was added to a flask containing 2,2-dimethyl-1,3-propanediol (1.4 g, 13.5 mmol). The mixture was stirred for 1 h, and the excess of $AsCl_3$ was evaporated under reduced pressure to yield a colorless oil (5.9 g, 96%). $^{13}C\{^1H\}$ NMR data (100.61 MHz; $CDCl_3$; 25°C): δ 21.4 (s; CH_3(bridge)); 21.8 (s; CH_3(ring)); δ 22.8 (s; CH_3(ring)); δ 33.2 (s; $C(CH_3)_2$(ring)); δ 36.8(s; $C(CH_3)_2$(bridge)); δ 72.2 (s; CH_2(bridge)); 72.3 (s; CH_2(ring)); ^1H NMR data (400.13 MHz; $CDCl_3$; 25°C): δ 0.77 (s; CH_3(equatorial); 6H); δ 0.99 (s; CH_3(bridge); 6H); δ 1.24 (s; CH_3(axial); 6H); δ 3.60 (d; CH_2(equatorial); 2H; $^2J_{HH} =$ 11.2 Hz); δ 3.91 (s; CH_2(bridge); 2H) δ 4.29 (d; CH_2(axial); 2H; $^2J_{HH} =$ 11.2 Hz).

Synthesis of 2-Chloro 5,5-Dimethyl-1,3,2-dioxaphosphorinane 4

To 2,2-dimethyl-1,3-propanediol (3.0 g, 28.8 mmol) neat fresh distilled PCl_3 (8 g; 58.2 mmol) was added and the mixture was stirred for 1 h. Then the excess of PCl_3 was evaporated and the product distilled under reduced pressure to yield a colorless viscous oil (4.7 g, 95%). $^{31}P\{^1H\}$ NMR data (81.01 MHz; $CDCl_3$; 25°C): δ 145 (s); $^{13}C\{^1H\}$ NMR data (100.61 MHz; $CDCl_3$; 25°C): δ 22.3 (s; CH_3); δ 22.4 (s; CH_3); δ 32.8 (d; $C(CH_3)_2$; $^3J_{CP} = 4.7$ Hz); δ 70.8 (d; CH_2; $^2J_{CP} = 2.7$ Hz); ^1H NMR data (400.13 MHz; $CDCl_3$; 25°C): δ 0.83 (s; CH_3(equatorial); 3H); δ 1.26 (s; CH_3(axial); 3H); δ 3.59–3.52 (m; CH_2(equatorial); 2H); δ 4.33–4.27 (m; CH_2(axial); 2H).

Synthesis of 2-Fluoro-5,5-dimethyl-1,3,2-dioxaphosphorinane 5

To a flask containing SbF_3 (1.2 g, 6.7 mmol) **4** was added (1.1 g, 6.7 mmol) and the mixture was stirred for 30 min. The product was distilled under reduced pressure to yield **5** (0.7%, 71%). $^{31}P\{^1H\}$ NMR data (81.01 MHz; $CDCl_3$; 25°C): δ 110 (d; $^1J_{PF} = 1179.7$ Hz); $^{13}C\{^1H\}$ NMR data (100.61 MHz; $CDCl_3$; 25°C): δ 22.0 (s; CH_3); δ 22.4 (d; CH_3; $J_{CF} = 1.06$ Hz); 32.4 (d; $C(CH_3)_2$; $^3J_{CP} = 4.83$ Hz); δ 70.8 (dd; CH_2; $^2J_{CP} = 7.62$ Hz); ^1H NMR data (400.13 MHz; $CDCl_3$; 25°C): δ 0.78 (s; CH_3(equatorial); 3H); δ 1.26 (s; CH_3(axial); 3H); δ 3.47–3.39 (m; CH_2(equatorial); 2H); δ 4.13–4.09 (m; CH_2(axial); 2H) ; $^{19}F\{^1H\}$ NMR data (376.51 MHz; $CDCl_3$; 25°C): δ-64.9 (d; $^1J_{PF} = 1177.8$ Hz).

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