

Dedicated to Professor Ionel Haiduc  
on the occasion of his 70th anniversary

## SYNTHESIS AND CHARACTERIZATION OF THE FIRST ARSANYLBIS(METHYLENE)PHOSPHORANE (Me<sub>3</sub>Si)<sub>2</sub>C=P(Mes\*)=C(Cl)-As(F)Mes\*

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The first arsanylbis(methylene)phosphorane, (Me<sub>3</sub>Si)<sub>2</sub>C=P(Mes\*)=C(Cl)-As(F)Mes\* **2** (Mes\* = 2,4,6-tri-*tert*-butylphenyl, called supermesityl) has been synthesized by addition of the difluoroarsane Mes\*AsF<sub>2</sub> to the supermesityl[bis(trimethylsilyl)methylene](lithiochloro- methylene)phosphorane **3**. Compound **2** was characterized by its NMR spectra and its solid state structure was determined by X-ray diffraction.

### INTRODUCTION

The first low-coordinate phosphorus compound containing the C=P=C unit was described only in 1982<sup>1</sup>. Some other stable representatives have also been prepared whereas those lacking steric protection isomerized to the corresponding phosphiranes.<sup>2–6</sup> Bis(methylene)phosphoranes are of interest as building blocks in phosphorus chemistry, and due to their multiple coordination sites, as versatile ligands in the synthesis of transition metal complexes. So far, several complexes in which either the P atom or the P=C bonds are coordinated to transition metals like Fe, Ni or Pt have been reported.<sup>7,8</sup> Our research has been focused on the functionalisation of C=P=C derivatives with substituents containing group 15 elements, which by electronic effects can modify the properties of this unit. We also target the synthesis of cumulenenic derivatives of the type >C=P=C=E< (E = group 15 element).

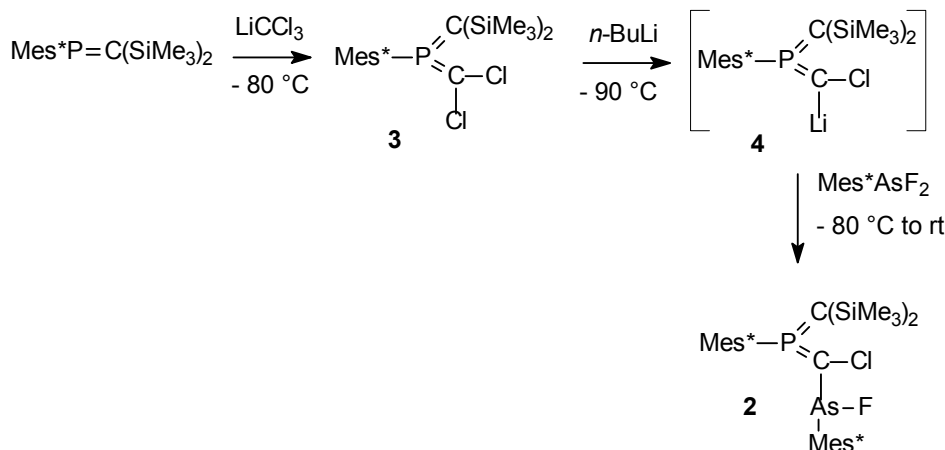
The dihalophosphaarsapropene Mes\*P=C(Br)-As(F)Mes\* **1**<sup>9</sup> containing a λ<sup>3</sup>σ<sup>2</sup> phosphorus atom, was obtained by reaction of Mes\*AsF<sub>2</sub> with the

phosphacarbenoid Mes\*P=C(Br)Li<sup>10</sup>. Other -P=C(X)-E derivatives (X = halogen, E = Mg, Zn, Hg<sup>11</sup>, P<sup>12</sup>, Si<sup>10,13</sup>, Ge<sup>10,14</sup>) have also been obtained by a similar route starting from Mes\*P=C(X)Li. This prompted us to extend this method to the synthesis of a closely related compound containing a λ<sup>3</sup>σ<sup>3</sup> phosphorus atom.

Here, we report the synthesis and characterization of the first arsanylbis(methylene)phosphorane (Me<sub>3</sub>Si)<sub>2</sub>C=P(Mes\*)=C(Cl)-As(F)Mes\*

### RESULTS AND DISCUSSION

This synthesis involves the initial preparation of the bis(methylene)phosphorane **3**<sup>15</sup> (Scheme 1). The latter was already described in the literature,<sup>15</sup> but we improved the yield by slightly modifying the procedure (see experimental section), so that the overall yield of **3** increased from 78%<sup>15</sup> to 92%. The lithiation of **3** with *n*-BuLi gave the carbenoid **4**<sup>15</sup> which yielded the first arsanylbis(methylene)phosphorane **2** by coupling with Mes\*AsF<sub>2</sub>.<sup>16</sup>



Scheme 1

A single isomer of **2** was formed according to its NMR spectrum. The X-ray structural studies revealed it to correspond to the *E*-configuration with the arsenic moiety in a *cis* position with respect to the supermesityl group. This finding indicates an attack of *n*-BuLi on the less sterically hindered side of the P=C double bond. The preferential formation of the *Z* isomer **4** was also reported by Niecke<sup>15</sup>. By quenching **4** with water and warming up over 0 °C, these authors observed that the resulting *Z*- $(\text{Me}_3\text{Si})_2\text{C}=\text{P}(\text{Mes}^*)=\text{C}(\text{Cl})\text{H}$  derivative undergoes a rearrangement into the thermodynamically more stable *E*-derivative (H atom in trans position with respect to the Mes\* group)<sup>15</sup>. By contrast, in the case of compound **2**, which possesses the very bulky Mes\*AsF group instead of the hydrogen atom, such an isomerization did not occur since only the *E* isomer (As *cis* to Mes\* group) is observed.

The structure of **2** in solution was confirmed through <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy which reveal that rotation around the (Mes\*)C-P bond is hindered. In the <sup>1</sup>H NMR spectrum, the non equivalent aromatic protons of the Mes\* group bonded to phosphorus appear as two doublets of doublets due to the coupling with the phosphorus atom (see Figure 1): the greater coupling constant (4.5 Hz) is attributed to the <sup>4</sup>J<sub>HP</sub> by comparison with similar values found in Mes\*P(O)=C=PMes\*<sup>17</sup>. By contrast, the aromatic protons on the Mes\* group bonded to the arsenic atom give a singlet since a free rotation around the (Mes\*)C-As bond is observed in the NMR time scale. This result is not surprising since the same phenomenon (hindered and free rotation for the Mes\* groups bonded to P and As respectively) was observed in **1**<sup>9</sup> which contains a similar Mes\*(F)As moiety and a less encumbered phosphorus atom.

The same non equivalence is observed for the *ortho tert*-butyl groups of the Mes\* bonded to P; due to slow or hindered rotation of the Mes\* groups, *ortho tert*-butyl groups give broader signals than do *para tert*-butyl groups allowing an easy assignment.

In the <sup>19</sup>F and <sup>31</sup>P NMR spectra of **2**, doublets are observed at -151.4 ppm and 157 ppm respectively with a <sup>3</sup>J<sub>PF</sub> coupling constant of 4.5 Hz much smaller than in **1** (23.3 Hz) which has a λ<sup>3</sup>σ<sup>2</sup> phosphorus atom. Similar chemical shifts have been reported in closely related derivatives (**3**: δ<sup>31</sup>P = 127 ppm<sup>15</sup>; PhP[=C(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, δ<sup>31</sup>P = 174 ppm<sup>1</sup>; **1**: δ<sup>19</sup>F = -175.6 ppm<sup>9</sup>).

The <sup>13</sup>C NMR spectrum also displays the great steric congestion around the phosphorus atom with two doublets (coupling with P) for the *ortho tert*-butyl groups and the *ortho* and *meta* carbon atoms of the Mes\* group on P, whereas only one doublet (coupling with F) and two singlets are observed for the Mes\* groups bonded to As. The different chemical environment of the carbon atoms C(1) and C(38) leads to an asymmetric charge distribution with the negative charge on C(38) since the silyl groups are more capable of stabilizing a negative charge; thus the corresponding <sup>13</sup>C NMR signal is observed at high field (72.33 ppm) with a small <sup>1</sup>J<sub>CP</sub> coupling constant as previously observed in similar derivatives.<sup>15</sup>

In mass spectrometry, the molecular peak was observed by electronic impact. The most abundant fragment corresponds to the loss of a Mes\* group.

Some relevant NMR data are given in Table 1.

Compound **2** was crystallized from pentane as yellow needles and was characterized by X-ray diffraction. Its molecular structure is represented in Figure 2, together with selected values for significant geometrical parameters.

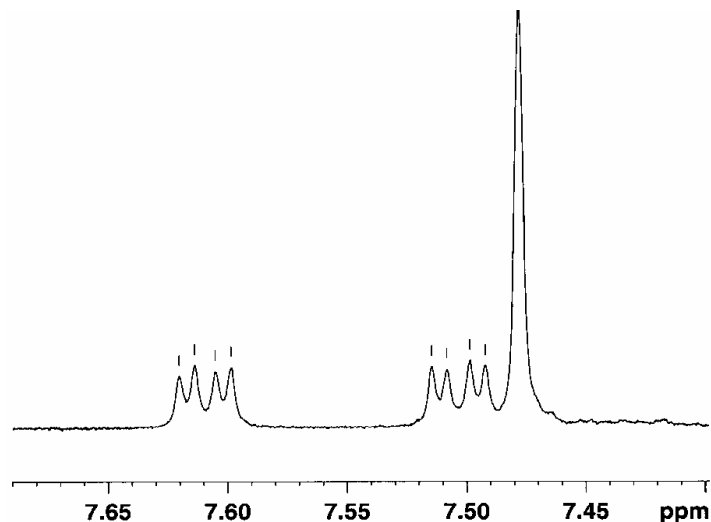


Fig. 1 – Detail of the aromatic range in the  $^1\text{H}$ -NMR spectrum for  $(\text{Me}_3\text{Si})_2\text{C}=\text{P}(\text{Mes}^*)=\text{C}(\text{Cl})-\text{As}(\text{F})\text{Mes}^* \mathbf{2}$

Table 1

Relevant NMR data for  $(\text{Me}_3\text{Si})_2\text{C}=\text{P}(\text{Mes}^*)=\text{C}(\text{Cl})-\text{As}(\text{F})\text{Mes}^* \mathbf{2}$

$^{13}\text{C}$ NMR	$^{19}\text{F}$ NMR	$^{31}\text{P}$ NMR
$\delta^{13}\text{C}$ : 95.2 ppm (P=C-As), ( $J_{\text{CF}}$ : 34.1 Hz, $J_{\text{CP}}$ : 74.0 Hz); $\delta^{13}\text{C}$ : 72.3 ppm (P=C(SiMe <sub>3</sub> ) <sub>2</sub> ), ( $J_{\text{CP}}$ : 49.0 Hz, $J_{\text{CF}}$ : 5.3 Hz).	$\delta^{19}\text{F}$ : -151.4 ppm, ( $J_{\text{PF}}$ : 4.5 Hz)	$\delta^{31}\text{P}$ : 157.0 ppm ( $J_{\text{PF}}$ : 4.5 Hz)

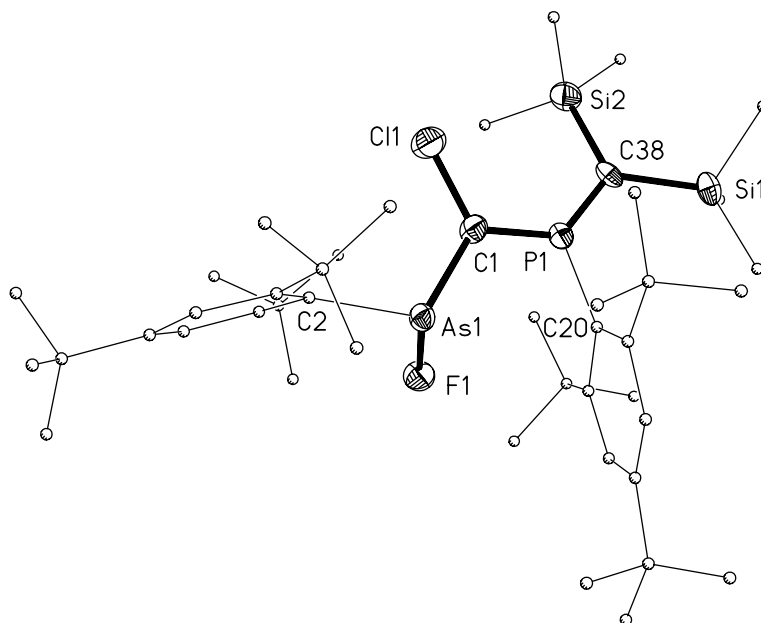


Fig. 2 – Molecular structure of  $(\text{Me}_3\text{Si})_2\text{C}=\text{P}(\text{Mes}^*)=\text{C}(\text{Cl})-\text{As}(\text{F})\text{Mes}^* \mathbf{2}$  (thermal ellipsoids drawn at the 50% probability level); hydrogen atoms are omitted for clarity; selected bond lengths (Å) and angles (°).  
 As-F: 1.783(8); As-C(2): 1.999(9); As-C(1): 1.951(9); C(1)-Cl: 1.730(8); C(1)-P: 1.684(8);  
 P-C(20): 1.803(7); P-C(38): 1.661(8); C(38)-Si(1): 1.884(8); C(38)-Si(2): 1.857(8);  
 FAsC(1): 101.3(4); AsC(1)Cl: 119.0(4); ClC(1)P: 119.8(5); C(1)PC(20): 106.7(4);  
 C(1)PC(38): 129.6(4); C(20)PC(38): 123.6(4); AsC(1)PC(38): 175.4; FAsC(1)Cl: 120.7;  
 FAsC(1)P: 63.8; ClC(1)PC(38): 9.2.

Like in other bis(methylene)phosphoranes,<sup>15</sup> the phosphorus atom has a trigonal-planar arrangement (sum of angles at P: 359.9°) as are the marginal C atoms C(1) and C(38) in the C=P=C unit. The Mes\* group bonded to the phosphorus atom presents an almost orthogonal alignment with regard to the PC<sub>2</sub> unit (torsion angles C(25)C(20)PC(38) = 78.57° and C(21)C(20)PC(1) = 93.29°). The lengths of the PC(1) and PC(38) bonds (1.684(8) and 1.684(8) Å, respectively) are in the normal range for P=C double bonds.<sup>2,18</sup>

## EXPERIMENTAL

All manipulations were carried out under N<sub>2</sub> or Ar using standard Schlenk techniques with solvents freshly distilled from sodium benzophenone. Mass spectra were measured on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV. Melting points were determined on a Leitz microscope, heating stage 250. NMR spectra were recorded on a Bruker Varian 300 MHz machine at 300.13 MHz (<sup>1</sup>H), at 75.48 MHz (<sup>13</sup>C), at 282.40 MHz (<sup>19</sup>F, ref CFCl<sub>3</sub>) and at 121.49 MHz (<sup>31</sup>P); CDCl<sub>3</sub> was used as a solvent for **3** and C<sub>6</sub>D<sub>6</sub> for <sup>1</sup>H, <sup>19</sup>F and <sup>31</sup>P NMR spectrum of **2**; due to its rather poor solubility in C<sub>6</sub>D<sub>6</sub>, THF d8 was used for the <sup>13</sup>C NMR spectrum of **2**.

**Synthesis of 2,4,6-tri-tert-butylphenyl[bis(trimethylsilyl)methylene]dichloromethylene-phosphorane 3:** A solution of 1.2 ml of CHCl<sub>3</sub> (0.015 mol) in 20 ml of THF and 5 ml of Et<sub>2</sub>O was cooled down at -100 °C and 10 ml of *n*-BuLi 1.6 M in hexane (1 equiv) were added dropwise. The reaction mixture was left under stirring for an hour. The synthesis described in the literature<sup>15</sup> involves cannulating the resulted LiCCl<sub>3</sub> to Mes\*P=C(SiMe<sub>3</sub>)<sub>2</sub>.<sup>19</sup> We found that the reverse addition, the dropwise addition of a solution of 6 g of Mes\*P=C(SiMe<sub>3</sub>)<sub>2</sub> (0.014 mol) in 100 ml of Et<sub>2</sub>O to a CHCl<sub>3</sub>/*n*-BuLi mixture cooled down at -120 °C, increased the yield by 14%.

The resulting mixture was allowed to warm up to room temperature. The solvent was removed under vacuum and replaced by 70 ml of pentane. The lithium salts were filtrated off and the solution was concentrated under vacuum and cooled to -25 °C. After 24 hours, **3** precipitated as a yellow powder (η=92%). <sup>31</sup>P-NMR: 128 ppm (s), <sup>1</sup>H-NMR: 0.21 ppm (s, 9H, SiCH<sub>3</sub>), 0.26 ppm (s, 9H, SiCH<sub>3</sub>), 1.26 ppm (s, 9H, *p*-t-Bu), 1.61 (d, 18H, <sup>4</sup>J<sub>PH</sub> = 0.7 Hz, *o*-t-Bu), 7.49 ppm (d, <sup>4</sup>J<sub>PH</sub> = 5.0 Hz, arom H).

**Synthesis of 2,4,6-tri-tert-butylphenyl[bis(trimethylsilyl)methylene] [(2,4,6-tri-tert-butylphenyl)arsanylchloromethylene] phosphorane 2:** A solution of 1g (0.0019 mol) of **3** in 50 ml of THF was cooled down to -90 °C and 1.2 ml *n*-BuLi 1.6 M in hexane (1 equiv) was added dropwise. The mixture was stirred for 15 minutes and then 0.72 g of Mes\*AsF<sub>2</sub> (0.0019 mols) in 30 ml of THF were added by canulation. After warming up to room temperature, the solvent was evaporated and replaced by 50 ml of pentane. The salts were removed by filtration and the filtrate was kept

at -25 °C. After several hours, yellow crystals (m.p. = 147°C) were collected (η=66%).

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): 0.21 and 0.43 (2s, 2 x 9H, Me<sub>3</sub>Si), 1.09 and 1.20 (2s, 2 x 9H, *p*-t-Bu of Mes\*As and Mes\*P), 1.53 (d, J<sub>HF</sub> = 0.6 Hz, 18H, *o*-t-Bu of Mes\*As), 1.75 and 1.85 (2s, 2 x 9H, *o*-t-Bu of Mes\*P), 7.07 (s, 2H, arom H of Mes\*As), 7.50 and 7.61 (2dd, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, <sup>4</sup>J<sub>HP</sub> = 4.5 Hz, arom H of Mes\*P).

<sup>13</sup>C-NMR (THF d8): 3.54 (d, <sup>3</sup>J<sub>CP</sub> = 5.2 Hz, SiMe<sub>3</sub>), 5.21 (d, <sup>3</sup>J<sub>CP</sub> = 4.5 Hz, SiMe<sub>3</sub>), 29.67, 30.57 and 34.48 (*p*-Me<sub>3</sub>C of Mes\*P and Mes\*As, *o*-Me<sub>3</sub>C of Mes\*As), 33.27 (d, <sup>4</sup>J<sub>CP</sub> = 4.5 Hz, *o*-Me<sub>3</sub>C of Mes\*P), 34.00 (d, <sup>4</sup>J<sub>CP</sub> = 3.0 Hz, *o*-Me<sub>3</sub>C of Mes\*P), 34.38 and 34.79 (2s, *p*-Me<sub>3</sub>C of Mes\*As and Mes\*P), 38.83 (*o*-Me<sub>3</sub>C of Mes\*As), 40.58 and 40.97 (2d, <sup>3</sup>J<sub>CP</sub> = 2.3 Hz, *o*-Me<sub>3</sub>C of Mes\*P), 72.33 (dd, <sup>1</sup>J<sub>CP</sub> = 49.1 Hz, <sup>4</sup>J<sub>CF</sub> = 5.3 Hz, P=C(SiMe<sub>3</sub>)<sub>2</sub>), 94.96 (dd, <sup>1</sup>J<sub>CP</sub> = 74.0 Hz, <sup>2</sup>J<sub>CF</sub> = 24.2 Hz, P=C-As), 119.39 (d, <sup>1</sup>J<sub>CP</sub> = 83.8 Hz, *ipso*-C of Mes\*P), 123.05 (s, *m*-C of Mes\*As), 126.63 (d, <sup>3</sup>J<sub>CP</sub> = 12.8 Hz, *m*-C of Mes\*P), 127.43 (d, <sup>3</sup>J<sub>CP</sub> = 12.1 Hz, *m*-C of Mes\*P), 140.06 (t, <sup>3</sup>J<sub>CP</sub> and <sup>2</sup>J<sub>CF</sub> = 10.2 Hz, *ipso*-C of Mes\*As), 149.85, 153.23 (d, J<sub>CP</sub> = 9.1 Hz), 153.83 (d, J<sub>CP</sub> = 3.0 Hz), 155.74 and 156.04 (d, J<sub>CP</sub> = 6.8 Hz) *o*- and *p*-C of Mes\*P and Mes\*As.

<sup>19</sup>F-NMR: -151.4 ppm (d, <sup>3</sup>J<sub>PF</sub> = 4.5 Hz).

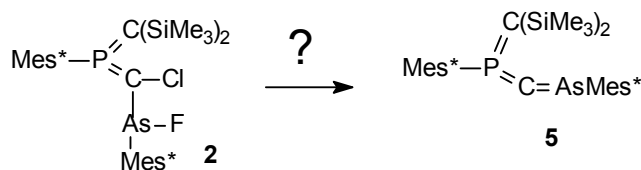
<sup>31</sup>P-NMR: 157.0 ppm (d, <sup>3</sup>J<sub>PF</sub> = 4.5 Hz).

MS (EI, m/z): 820 (M, 5), 800 (M - F - H, 15), 763 (M - t-Bu, 40), 729 (M - t-Bu - Cl - H, 25), 656 (M - t-Bu - Cl - SiMe<sub>3</sub>, 25), 641 (M - t-Bu - Cl - SiMe<sub>3</sub> - Me, 35), 575 (M - Mes\*, 100).

**Crystal data:** Compound **2** [C<sub>44</sub>H<sub>76</sub>AsClFPSi<sub>2</sub>], with the molecular weight M = 821.57 crystallizes in the triclinic space group *P* $\bar{1}$ . The cell parameters are *a* = 10.206(6) Å, *b* = 14.094(7) Å, *c* = 16.386(9) Å,  $\alpha$  = 84.57(2)°,  $\beta$  = 86.05(1)°,  $\gamma$  = 88.44(2)°, *V* = 2340(2) Å<sup>3</sup>, *Z* = 2. 5386 independent reflections were collected at low temperatures (T = 173(2) K) using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structure was solved by direct methods<sup>20</sup> and 543 parameters were refined using the least-squares method on *F*<sup>2</sup>.<sup>21</sup> All non hydrogen atoms were refined anisotropically. The largest electron density residue is 0.411 eÅ<sup>-3</sup> and *R*<sub>i</sub> (for *I* > 2σ(*I*)) = 0.0798 and *wR*<sub>2</sub> = 0.1930 (all data) with *R*<sub>i</sub> = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>| and *wR*<sub>2</sub> = (Σw(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>/Σw(*F*<sub>o</sub><sup>2</sup>)<sup>0.5</sup>). CCDC 631667 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

## CONCLUSION

The first arsanylbis(methylene)phosphorane (Me<sub>3</sub>Si)<sub>2</sub>C=P(Mes\*)=C(Cl)-As(F)Mes\* **2**, an arsenic-containing derivative with two P=C double bonds, was obtained as a stable compound in the solid state. The ability of **2** to lose ClF and to give the new cumulenenic compound (Me<sub>3</sub>Si)<sub>2</sub>C=P(R)=C=As- **4** is under investigation (Scheme 2).



Scheme 2

Such derivative could be stabilized owing to the important steric hindrance exerted by the bulky organic groups. Functionalization of **2** owing to the presence of the easily substitutable Cl on the doubly-bonded carbon atom is also under active investigation.

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## REFERENCES

1. R. Appel, J. Peters, A. Westerhaus, *Angew. Chem., Int. Ed. Engl.*, **1982**, *21*, 80-81.
2. For a review, see: R. Appel in *Multiple Bonding and Low Coordination in Phosphorus Chemistry* (Eds: M. Regitz, O.J. Scherer), Thieme, **1990**, p 367-374.
3. R. Appel, K.-H. Dunker, E. Gaitzsch, T. Gaitzsch, *Z. Chem.*, **1984**, *24*, 384-385.
4. R. Appel, C. Casser, *Chem. Ber.*, **1985**, *118*, 3419-3423.
5. R. Appel, E. Gaitzsch, K.-H. Dunker, F. Knoch, *Chem. Ber.*, **1986**, *119*, 535-542.
6. R. Appel, T. Gaitzsch, F. Knoch, G. Lenz, *Chem. Ber.*, **1986**, *119*, 1977-1985.
7. H. J. Metternich, E. Niecke, *Angew. Chem., Int. Ed. Engl.*, **1991**, *30*, 312-313.
8. H. J. Metternich, E. Niecke, J. F. Nixon, R. Bartsch, P. B. Hitchcock, M. F. Meidine, *Chem. Ber.*, **1991**, *124*, 1973-1976.
9. H. Ranaivonjatovo, H. Ramdane, H. Gornitzka, J. Escudié, J. Satgé, *Organometallics*, **1998**, *17*, 1631-1633.
10. S. J. Goede, F. Bickelhaupt, *Chem. Ber.*, **1991**, *124*, 2677-2684.
11. M. Van der Sluis, J.B.M. Wit, F. Bickelhaupt, *Organometallics*, **1996**, *15*, 174-180.
12. M. Yoshifuji, S. Sasaki, N. Inamoto, *Tetrahedron Lett.*, **1989**, *30*, 839.
13. L. Rigon, H. Ranaivonjatovo, J. Escudié, A. Dubourg, J.-P. Declercq, *Chem. Eur. J.*, **1999**, *5*, 774-781.
14. H. Ramdane, H. Ranaivonjatovo, J. Escudié, S. Mathieu, N. Knouzzi, *Organometallics*, **1996**, *15*, 3070-3075.
15. E. Niecke, P. Becker, M. Nieger, D. Stalke, W. W. Schoeller, *Angew. Chem., Int. Ed. Engl.*, **1995**, *34*, 1849-1852.
16. A. H. Cowley, J. E. Kilduff, J. G. Lasch, S. K. Mehrotra, N. C. Norman, M. Pakulski, B. R. Whittlesey, J. L. Atwood, W. E. Hunter, *Inorg. Chem.*, **1984**, *23*, 2582.
17. R. Septelean, H. Ranaivonjatovo, G. Nemes, J. Escudié, I. Silaghi-Dumitrescu, L. Silaghi-Dumitrescu, S. Massou, *Eur. J. Inorg. Chem.*, **2006**, 4237-4241.
18. R. Appel, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, (Eds: M. Regitz, O.J. Scherer), Thieme, **1990**, p 157-219.
19. R. Appel, C. Casser, M. Immenkeppel, *Tetrahedron Lett.*, **1985**, *26*, 3551-3554.
20. SHELXS-97, G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467-473.
21. SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen **1997**.