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In memoriam prof. dr. Ioan A. Silberg

TOWARDS NEW DOUBLE-BONDED ORGANOPHOSPHORUS DERIVATIVES OF C=P=C=P TYPE

GABRIELA NEMEŞ, RALUCA ŞEPTELEAN, PETRONELA M. PETRAR, LUMINIȚA SILAGHI-DUMITRESCU, IOAN SILAGHI-DUMITRESCU[a]

ABSTRACT. New potential precursors for diphosphaallenes with C=P=C=P skeleton have been synthesized. Compounds 2-4 (bearing a 2,4,6-tri-*tert*-butylphenyl group bound to phosphorus) are stabilized by the large steric hindrance which prevents the approach of monomers to form dimers or oligomers.

Keywords: *heteroallenes, diphosphaallenes, organophosphorus compounds*

INTRODUCTION

Sterical protected heterocumulenes [1-5] containing multiple double bonds of the heavier main group elements, such phospha-, or diphosphaallenes [6a, 7] are currently the focus of many research groups. Using bulky substituents like Mes* (2,4,6-tri-*tert*-butylphenyl), $C(SiMe_3)_2$ or *t*-Bu we have reported some precursors of diphosphaallenes with the C=P=C-P skeleton which are expected to be useful as starting materials for new organophosphorus compounds [6].

Due to the multiple possibilities to coordinate the C=P=C-P unit to an organometallic ML_n fragment, such systems are excellent ligands in coordination compounds with potential catalytic action. Thus, there were obtained complexes with P=C=P units attached to $M(CO)_n$ fragments, M = W, Cr [8-12] or Pd, Cr [12, 13]. Some of these systems have interesting catalytic properties, exhibited for example in the direct conversion of the alcohols in allylic compounds [14, 15].

Herein we report the synthesis of diphosphaallenic systems $(Me_3Si)_2C=P(Mes^*)=C(Cl)-PCl_2$ **2,** $(Me_3Si)_2C=P(Mes^*)=C(Cl)-PCl(t\text{-}Bu)$ **3,** and $(Me_3Si)_2C=P(Mes^*)=C(Cl)-P(O)Cl_2$ **4,** with C=P=C-P skeleton. Due to the polytopal coordination abilities, such ligands might be used in the synthesis of various interesting coordination compounds.

[a] *Universitatea Babeş-Bolyai, Facultatea de Chimie şi Inginerie Chimică, Str. Kogălniceanu Nr. 1, RO-400084 Cluj-Napoca, Romania, isi@chem.ubbcluj.ro*

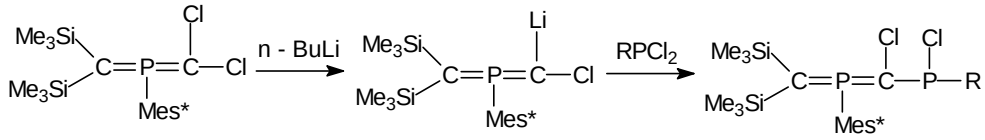
RESULTS AND DISCUSSION

Diphosphaallene derivatives **2**-**4** have been prepared starting from phosphaallene **1** (Scheme 1) in the presence of butyl lithium and the corresponding dihalophospha derivatives $RPCl_2$.

Bis(trimethylsilane)phosphorane **1** was obtained with a very good yield (98 %) by resorting to a modified version [16] of Niecke's method.

Diphosphaallenes **2** and **3** were prepared by reaction of **1** with $RPCl_2$ (R = Cl, *t*-Bu). Note however that if R = Mes*, due to the high steric demands, the formation of corresponding diphosphaalene has never been observed.

Addition of phosphorus trichloride to the lithium derivative of **1** afforded the expected diphosphaallene $(Me_3Si)_2C=P(Mes^*)=C(Cl)-PCl_2$ **2**, (Scheme 1):



1

Scheme 1

R = Cl (2)
R = t-Bu (3)

The *Z* and *E* isomers, **2a** and **2b** are formed in a 5 : 1 ratio. Both isomers **2a** and **2b** have been characterized in solution by NMR spectroscopy. The ^{31}P NMR spectra of **2a** show two signals at 165.41 ppm (d) and at 151.75 ppm (d) respectively.

3 is obtained nearly quantitatively from **1**, by the route shown in Scheme 1. $(Me_3Si)_2C=P(Mes^*)=C(Cl)-P(t-Bu)Cl$ **3** was characterized by NMR spectroscopy and mass spectrometry. The ^{31}P NMR spectrum show two signals for the phosphorus atoms at 166.08 ppm (d) and 112.7 ppm (d) (Figure 1). The high-field shift in the ^{31}P NMR is in the expected range for *t*-Bu group bonded to a $\lambda^3\sigma^2$-P atom [6].

Due to the presence of only one chlorine atom in **3** versus two chlorine atoms at $\lambda^3\sigma^2$-P phosphorus in **2**, the ^{31}P NMR shift in **3** is shifted by 40 ppm up-field.

In the presence of air, compound **2** is oxidized at the $\lambda^3\sigma^2$-P phosphorus atom giving $(Me_3Si)_2C=P(Mes^*)=C(Cl)-P(O)Cl_2$ **4** (^{31}P NMR: 195.17 ppm (d) and 69.48 ppm (d)) (Scheme 2).

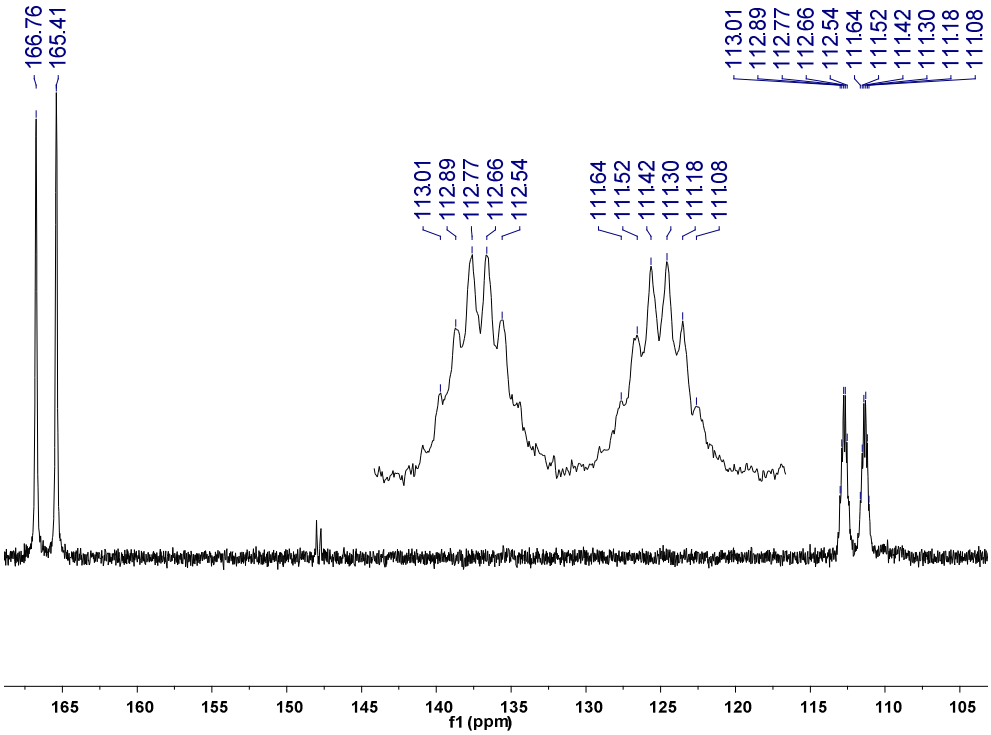
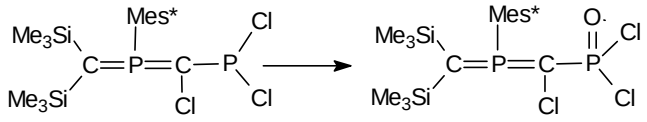


Figure 1. ^{31}P NMR (coupled with hydrogen) spectrum of $(Me_3Si)_2C=P(Mes^*)=C(Cl)-P(t\text{-}Bu)Cl$ **3**



2 Z/E **4 Z/E**

Scheme 2

The *Z* and *E* isomers, **4a** and **4b** are identified in the same ratio like the *Z/E* ratio for **2**.

CONCLUSION

Three new diphosphaallenes have been synthesized and characterized by NMR spectroscopy. Their coordinative properties are under current investigation.

EXPERIMENTAL SECTION

All experiments were carried out in flame-dried glassware under argon atmosphere using high-vacuum line techniques. Solvents were dried and freshly distilled from sodium benzophenone ketyl and carefully deoxygenated on the vacuum line by several freeze-pump-thaw cycles. NMR spectra were recorded in $CDCl_3$ and C_6D_6 by using a Bruker AC300 spectrometer (^{1}H: 300 MHz; ^{13}C: 75 MHz, reference TMS; ^{31}P: 121.49 MHz, reference H_3PO_4). Mass spectra were obtained with Hewlett-Packard 5989A spectrometer by EI at 70 eV. BuLi (1.6 M in hexane), PCl_3 and t-BuPCl_2 commercially available (Merck) were used.

Synthesis of $(Me_3Si)_2C=P(Mes^*)=CCl_2$ 1 [14]

To a solution of $CHCl_3$ (1 mL, 1.3 g) in THF (50 mL) cooled at –90 ℃ were added 6.9 mL of a solution of n-BuLi (0 .7 g). After 1 h of stirring to –78 ℃, the brown solution of CCl_3Li was frozen at -120 ℃. A solution of $Mes^*P=C(SiMe_3)_2$ (5.5 g) in THF (50 mL) cooled at – 78 ℃ was canul ated to the frozen CCl_3Li. The reaction mixture was allowed to warm at room temperature. After removal of the lithium salts, recrystallization from pentane afforded a white powder of pure **1,** the yield 98 % [14].

Synthesis of $(Me_3Si)_2C=P(Mes^*)=C(Cl)\text{-}PCl_2$ 2

To a solution of **1** (0.75 g) in THF (20 mL) cooled at –100 ℃ were added 1.9 mL of a solution of n-BuLi. After 1 h of stirring at –78 ℃ the brown liquid was canulated to a solution of trichlorophosphine (0.2 g, 0.13 mL) in THF (40 mL) cooled at –78 ℃. After stirring the mi xture at 20 ℃ for 2h, LiCl was eliminated by filtration, the solvent was removed in vacuum and the residue dissolved in 15 mL of pentane. The product was unambiguously characterized by NMR spectroscopy but could not be isolated in pure form by crystallization. We obtained the mixture of **2a** and **2b** in 5 : 1 ratio.

NMR ^{31}P **2a**: 165.41 ppm (d, $^2J_{PP}$: 178.8 Hz, $\lambda^5\sigma^3$-*P*), 151.75 ppm (d, $^2J_{PP}$: 178.5 Hz, $\lambda^3\sigma^2$-*P*).

NMR ^{31}P **2b**: 163.88 ppm (d, $^2J_{PP}$: 179.9 Hz, $\lambda^5\sigma^3$-*P*), 150.26 ppm (d, $^2J_{PP}$: 179.9 Hz, $\lambda^3\sigma^2$-*P*).

Oxidation of 2 to $(Me_3Si)_2C=P(Mes^*)=C(Cl)\text{-}P(O)Cl_2$ 4

In normal condition after 7 hours, compound **1** is oxidized to $(Me_3Si)_2C=P(Mes^*)=C(Cl)\text{-}P(O)Cl_2$ **4**. A mixture of **4a** and **4b** in the 5:1 ratio has been obtained. The reaction product was unambiguously characterized by NMR spectroscopy but could not be isolated in pure form by crystallization.

NMR ^{31}P **4a**: 195.17 ppm (d, $^2J_{PP}$: 342.6 Hz, $\lambda^5\sigma^3$-*P*), 69.48 ppm (d, $^2J_{PP}$: 342.6 Hz, $\lambda^5\sigma^3$-*P*=*O*).

NMR ^{31}P **4b**: 195.30 ppm (d, $^2J_{PP}$: 342.6 Hz, $\lambda^5\sigma^3$-*P*), 69.61 ppm (d, $^2J_{PP}$: 342.6 Hz, $\lambda^5\sigma^3$-*P*=*O*).

Synthesis of $(Me_3Si)_2C=P(Mes^*)=C(Cl)-PCl(t\text{-}Bu)$ 3

To a solution of **1** (2.1 g, 4.06 mmol) in THF (50 mL) cooled at –100 °C were added 1.82 mL of a solution of t -BuLi 1.7 M. After 1h of stirring at -78 ℃ the brown solution of $(Me_3Si)_2C=P(Mes^*)=CClLi$ was canulated to a solution of dichloro-*tert*-butylphosphine (0.66 g, 4.2 mmol) in THF (50 mL) cooled at – 78 ℃. After stirring the mixture at 20 ℃ for 10 h, LiCl was eliminated by filtration, the solvent was removed in vacuum and the residue dissolved in 25 mL of pentane. The product was unambiguously characterized by NMR spectroscopy but could not be isolated in pure form by crystallization.

NMR ^{31}P ($CDCl_3$) 2: 166.08 ppm (d, $^2J_{PP}$:164.25 Hz, $\lambda^5\sigma^3$-P), 112 ppm (dm, $^2J_{PP}$:164.25 Hz, $^3J_{PH}$: 13.4 Hz, $\lambda^3\sigma^2$-P).

NMR ^1H ($CDCl_3$) 2: 7.57 (dd, J = 4.92, 1.63 Hz, 1H), 7.51 (dd, J = 4.70, 1.88 Hz, 1H), 1.70 (d, J = 0.55 Hz, 1H 9H), 1.32 (s, 1H 9H), 1.67 (s, 1H 9H), 1.24 (d, J = 14.70 Hz, 1H 9H), 0.39 (s, 1H 9H), -0.16 (s, 1H 9H)

NMR ^{13}C (C_6D_6): 155.41 (d, J = 7.81 Hz,1C, C orto), 154.69 (d, J = 3.15 Hz,1C, C para), 125.47 (d, J = 13.24 Hz,1C, C meta), 121.07 (d, J = 93.29 Hz,1C, C ipso), 90.04 (d, J = 156.10 Hz, 1C, $PCCl_2$ CP_2Cl), 54.36 (d, J = 48.74 Hz, 1C, $PC(SiMe_3)_2$), 40.22 (d, J = 2.81 Hz,1C, orto $C(CH_3)_3$), 35.23 (d, J = 0.92 Hz,1C, para $C(CH_3)_3$), 34.02 (s,1C, orto CH_3), 30.96 (s, 1C, para CH_3), 4.34 (dd, J = 44.09, 4.76 Hz,1C, $C(SiMe_3)_2$).

MS (EI): m/z (%) = 604 (1) [M]+, 589 (1) [M – Me]+, 569 (20) [M – Cl]+, 547 (18) [M – tBu]+.

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