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Synthesis of heavier alkali metal phospholides. Crystal structure of caesium 2,3,4,5-tetramethylphospholide, an ionic solid

François Nief *, Louis Ricard

Laboratoire Hétéroéléments et Coordination, CNRS UMR 7653, DCPH, Ecole Polytechnique, 91128 Palaiseau, France

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Abstract

The reaction of rubidium or caesium metals with 2,3,4,5,2′,3′,4′,5′-octamethylbi-1,1′-phospholyl (**3**) in THF, respectively, afforded rubidium 2,3,4,5-tetramethylphospholide (**1**) and caesium 2,3,4,5-tetramethylphospholide (**2**). While the physical properties of **1** are very similar to that of the already described potassium 2,3,4,5-tetramethylphospholide, in particular as far as solubility is concerned, **2** on the contrary is very slightly soluble even in polar solvents such as dimethoxyethane (DME) or THF. Crystals of **2** suitable for X-ray analysis have been obtained by high-temperature recrystallisation in DME at 170 °C. The three-dimensional polymeric structure of **2**, where all the phospholyl rings are parallel, has the characteristics of an ionic solid.

Keywords: Caesium; Rubidium; Phosphanide; Phosphole

1. Introduction

Alkali metal phospholides have been widely used as precursors of phospholyl complexes of transition metals [1], including rare earth elements [2]. Their synthesis classically involves the reaction of a lithium or potassium phospholide (for instance [LiTmp] [3] or [KTmp] [4] (Tmp, 2,3,4,5-tetramethylphospholyl)) with a transition metal halide. In rare earth chemistry, however, ate-complexes with the alkali metal as counterion are frequently observed, for instance in [$(Tmp)_2LnCl_2K(Et_2O)$] (Ln = Nd, Sm) [5]. Even when the metathesis reaction is conducted in the absence of a coordinating solvent, an alkali metal can still be retained in the structure of the final product: when [KTmp] was reacted with $SmCl_3$ in a 3:1 ratio in toluene at 110 °C, the expected [$(Tmp)_3Sm$] was not formed, but instead a bi-dimensional polymer of composition [$\{(Tmp)_3SmClK(toluene)\}_n$] was isolated, in which the potassium atom is η^6-bonded to toluene [6]. We thought that a better anionic precursor of the Tmp ligand could be [RbTmp] (**1**) or [CsTmp] (**2**), where a larger alkali metal as counterion could (a) boost the reactivity of the Tmp anion and (b) decrease the probability of obtaining ate-complexes because of the weaker coordination properties of rubidium or caesium. In addition, there has been considerable recent interest in the structural chemistry of heavier alkali metal phosphanides that often form oligomeric complexes with no oxygenated ancillary ligands [7]. Therefore, we report here on the synthesis of rubidium 2,3,4,5-tetramethylphospholide (**1**) and of caesium 2,3,4,5-tetramethylphospholide (**2**) together with a crystal structure of this latter complex.

2. Results and discussion

*2.1. Synthesis of rubidium 2,3,4,5-tetramethylphospholide (**1**), and of caesium 2,3,4,5-tetramethylphospholide (**2**)*

Lithium and potassium phospholides can been prepared by lithium or potassium metal cleavage of the P-phenyl bond of 1-phenylphospholes [3,4]. However, the reaction also affords one equivalent of phenyl anion in the form of phenyllithium or phenylpotassium, which

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* Corresponding author. Tel.: + 33-1-69334794; fax: + 33-1-69333990.

E-mail address: nief@poly.polytechnique.fr (F. Nief).

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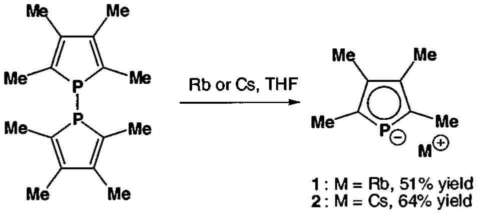
have to be eliminated. This could be a problem in the case of heavier alkali metals and particularly caesium which is highly reactive since it is known to attack toluene at or slightly above room temperature [8]. However, it has also been shown that [TmpLi] could be cleanly prepared by one-electron reduction of 2,3,4,5,2′,3′,4′,5′-octamethylbi-1,1′-phospholyl (**3**) by lithium metal [9]. So, in order to prepare **1** and **2**, we decided to transpose this reaction using rubidium and caesium as metals; we thus reacted **3** with stoichiometric amounts of rubidium or caesium metals in THF (in fact, a slight excess of **3** was used in order to ensure complete consumption of the metals). The reaction did not proceed with appreciable speed unless the reaction mixture was heated above the melting points of the metals (≈45 °C for rubidium or 30 °C for caesium) where it started as indicated by the progressive appearance of a white precipitate (Scheme 1).

After 4 h, compounds **1** and **2** were obtained in fair yields as white, air sensitive powders.

The solution behaviour of the two compounds appears quite different. While **1** is soluble in dimethoxyethane (DME) and in THF (although a bit less), **2** is only very slightly soluble in DME and almost insoluble in THF: it was necessary to use a 9:1 DME–C_4D_8O mixture as NMR solvent in order to observe the ^{13}C spectrum in a reasonable amount of time. ^1H and ^{31}P spectra of **2** could be obtained in C_4D_8O but we could not decide from its proton spectrum whether **2** was solvated by THF or not, because of the very important relative intensities of residual C_4D_7HO due to the low solubility of **2**; on the other hand, proton NMR showed that the rubidium compound **1** was unsolvated.



Scheme 1.

Table 1
Crystal data and data collection parameters for **2**

Empirical formula	$C_8H_{12}CsP$
Formula weight	272.06
Crystal habit and size (mm)	Colourless, 0.06 × 0.08 × 0.11
Crystal system and space group	Orthorhombic, *Cmcm* (no. 63)
a (Å)	6.4280(3)
b (Å)	11.3410(4)
c (Å)	12.7910(4)
V (Å^3)	932.46(7)
Z	4
F(000)	520
D_{calc} (g cm^{-3})	1.938
μ (cm^{-1})	12.1
Temperature (K)	−150.0(1)
Maximum θ (°)	26.28
Number of independent reflections	320
Reflections included	318 with $I > 2\sigma(I)$
R_1	0.0129
wR_2 (all data)	0.0326
Goodness-of-fit on F^2	1.196

The NMR parameters of **1** and **2** can be compared with that of TmpLi and of TmpK. Whereas the proton and ^{13}C resonances do not significantly vary with the alkali metal cation, there is a steady downfield shift of the ^{31}P resonances (in THF) when this cation is varied from Li (δ $^{31}P = 63.0$ in [TmpLi]) [3] to K (δ $^{31}P = 74.1$ in [TmpK]) [4], Rb (δ $^{31}P = 77.7$ in **1**) and Cs (δ $^{31}P = 82.7$ in **2**). A similar effect has been observed by Rabe et al. in a series of alkali metal salts of supermesitylphosphane [10] (supermesityl = 2,4,6-t-$Bu_3C_6H_2$). The origin of the (paramagnetic) downfield shift in phospholyl anions has been studied by Chesnut and Quin [11], and has been linked to the energy difference between the π* orbitals and the lone pair on phosphorus (the smaller the difference, the larger the shift). The larger downfield shift for the heavier alkali metal phospholyl complexes is consistent with this observation since the energy level of the phosphorus lone pair is likely to be higher in these complexes because of the weaker coordination properties of the heavier alkali metals.

Since ^{133}Cs is an easily observed NMR nucleus, its resonance was recorded in **2**. The chemical shift (−172.5 ppm vs. 0.1 M CsCl in D_2O) is quite different from that reported by Rabe et al. for [Cs(2,6-$Mes_2C_6H_3PH$)] [12] ($\delta = 34.8$) (Mes, 2,4,6-$Me_3C_6H_2$). No ^{31}P–^{133}Cs coupling constant was observed in **2**.

2.2. Crystal structure of **2**

Microscopic investigation of bulk **2** revealed that this compound appeared to be microcrystalline. After several unsuccessful attempts, X-ray quality crystals of **2** could be grown by a 'solvothermal' method: in a sealed tube, a suspension of crude **2** in DME was heated in an oven at 170 °C, and allowed to cool down slowly at room temperature (during 24 h). Crystal data and the data collection parameters are listed in Table 1, and selected bond lengths and angles are presented in Table 2. Fig. 1 represents an ORTEP plot of the coordination sphere of the caesium atom in **2** together with the numbering scheme used. Fig. 2 shows an ORTEP plot of the unit cell contents. There are only four independent atoms in the phospholyl ring, since there is a crystallographic mirror plane perpendicular to it. The structure shows several characteristics found in other caesium

Table 2
Selected bond lengths and angles for compound **2** (numbering as in Fig. 1)

Bond lengths			
Cs(1)–P(1)	3.6957(6)	Cs(1)–C(1)	3.503(1)
Cs(1)–C(2)	3.365(1)	P(1)–C(1)	1.768(4)
C(1)–C(2)	1.389(5)	C(1)–C(3)	1.506(5)
C(2)–C(2) # 4	1.435(7)	C(2)–C(4)	1.519(4)
Bond angles			
C(1)–P(1)–C(1) # 4	91.1(2)	C(2)–C(1)–P(1)	111.3(3)
C(1)–C(2)–C(2) # 4	113.1(2)		

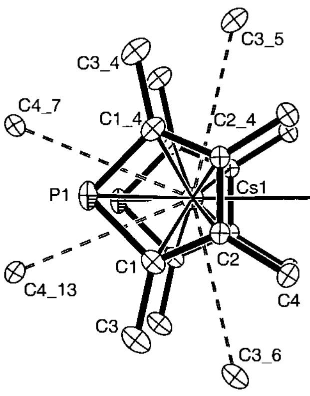


Fig. 1. An ORTEP plot of the coordination around caesium in **2** (50% ellipsoids).

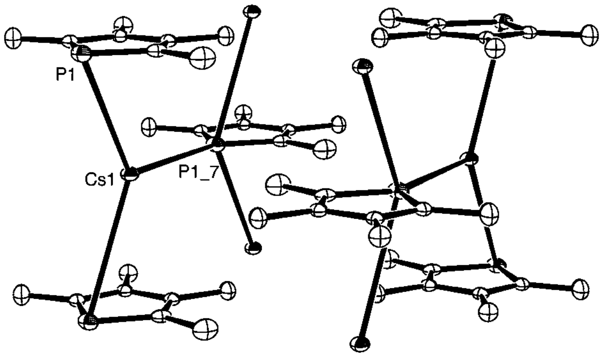


Fig. 2. An ORTEP plot of the contents of one orthorhombic unit cell of **2** (50% ellipsoids).

phosphanides: (a) the absence of donor solvent coordinated to caesium (even though **2** has been recrystallised from DME); (b) the regular tri-dimensional polymeric arrangement of the solid. A striking feature is the parallelism of the phospholyl rings between which, as shown in Fig. 1, the caesium atom appears symmetrically sandwiched. The two Cs(1)–C(2) and Cs(1)–C(1) distances are different and in particular the latter is found outside the range of 3.3–3.4 Å found in other cyclopentadienylcaesium compounds [13,14]. However, there are also a number of caesium phosphanide structures [10,12,15,16], in which there is a marked interaction of caesium with aromatic ring carbons; the limits within which these distances are found is somewhat higher (3.40–4.05 Å). The Cs–C distances of a [TmpCs] unit fit within these limits, but inside this interval are also found four caesium to carbon close contacts, two of them concern the β-methyls of another [TmpCs] unit [d(Cs(1)–C(4) # 7 = d(Cs(1)–C(4) # 13 = 3.992(2)], and the other two concern α-methyls belonging to two distinct, different [TmpCs] units [d(Cs(1)–C(3) # 5 = d(Cs(1)–C(3) # 6 = 3.767(2)]. The Cs–P bond of a [TmpCs] unit is in the range of other Cs–P bonds are published in the literature [10,12,15–17], but there is also a contact between the caesium atom and the phosphorus lone pair atom of another [TmpCs] unit [d(Cs(1)–P(1) # 7 = 3.8461(6)]. This bond is longer than the only other R_3P–Cs bond described in the literature [3.6053(6)] [18]. A comparable bonding situation has been described in a diphospholyl sodium salt [19].

So, each caesium atom can be considered to be in interaction with six different Tmp units, the formal coordination number around this atom being 15, if all bonds and close contacts are accounted for. Another noteworthy feature apparent in Fig. 1 is that the Cs atom is not aligned with the centroids of the Tmp rings (Cnt–Cs(1)–Cnt angle = 169°), it is displaced from this line towards P(1) # 7.

The overall solid-state structure of **2** is somewhat similar to that of [CsCp], also an insoluble, densely packed tri-dimensional structure with extensive metal–ligand intermolecular contacts, that was determined by high-intensity X-ray powder diffraction [14]. The main difference is that, unlike the Cp rings in [CsCp] (or even in $[Cs_2Cp_3]^-$) [13], the Tmp rings in **2** are parallel. The following characteristics of **2**, relatively large range of the bond lengths, displacement of the caesium atom from its 'ideal' position on the centroid–centroid line, intermolecular contacts, suggest that the interactions responsible for the solid-state structure of **2** are of electrostatic origin and, therefore, that the poorly soluble **2** has the characteristics of an ionic solid.

In contrast with **2**, **1** appeared amorphous on microscopic examination. Attempts to recrystallise **1** from DME were unsuccessful because of its high solubility in this solvent. Precipitation from warm THF produced colourless needles that appeared to be crystalline; however, this material turned white when mounted on the X-ray goniometre, presumably because of desolvation, and did not diffract X-rays. Thus, **1** has a very similar behaviour to that of [TmpK].

Attempts to use **1** and **2** as precursors in Group 3 metal chemistry are already under way.

3. Experimental

All reactions were performed in dry solvents under dry oxygen-free argon in a Braun Labmaster 130 glove box or on a vacuum line. NMR spectra were recorded on Bruker AC200 or ARX300 spectrometers. Chemicals shifts are expressed in parts per million (ppm) downfield from internal TMS for ^1H and ^{13}C, from external 85% H_3PO_4 for ^{31}P, and from external 0.1 M CsCl in D_2O for ^{133}Cs; coupling constants are expressed in Hz.

*3.1. Rubidium 2,3,4,5-tetramethylphospholide (**1**)*

In a 50 ml flask equipped with a glass-covered stirbar, THF (10 ml) was condensed onto a mixture of rubidium metal (0.123 g, 1.43 mmol) and **3** (0.210 g, 0.75 mmol). The mixture was stirred for 4 h at 45 °C (rubidium was liquid at this temperature) while a white precipitate progressively appeared. After 4 h, all rubidium had disappeared and the reaction mixture was cooled to room temperature. The white precipitate was filtered off, rinsed with 5 ml of cold THF and dried under vacuum. Compound **1** was obtained as a white powder (0.165 g, 0.73 mmol, 51%).

^1H-NMR (C_4D_8O): 1.93 (s, 6H, CH_3–C2), 2.16 (d, $J_{PH} = 10$, 6H, CH_3–C3). $^{13}C\{^1H\}$ (1:1 C_4D_8O–DME): 14.1 (s, CH_3–C3), 16.3 (d, $J_{PC} = 30.5$, CH_3–C2), 124.3 (s, C3), 134.9 (d, $J_{PC} = 35$, C2). $^{31}P\{^1H\}$ (C_4D_8O): 77.3.

*3.2. Caesium 2,3,4,5-tetramethylphospholide (**2**)*

In a 50 ml flask equipped with a glass-covered stirbar, THF (10 ml) was condensed onto a mixture of caesium metal (0.230 g, 1.73 mmol) and **3** (0.220 g, 0.79 mmol). The mixture was stirred for 4 h at 30 °C (caesium was liquid at this temperature) while a white precipitate progressively appeared. After 4 h, all caesium had disappeared and the reaction mixture was cooled to room temperature. The white precipitate was filtered off, rinsed with 5 ml of cold THF and dried under vacuum. Compound **1** was obtained as a white powder (0.301 g, 1.11 mmol, 64%).

^1H-NMR (C_4D_8O): 1.91 (s, 6H, CH_3–C2), 2.13 (d, $J_{PH} = 10.5$, 6H, CH_3–C3). $^{13}C\{^1H\}$ (1:9 C_4D_8O–DME): 14.2 (s, CH_3–C3), 16.3 (d, $J_{PC} = 30.5$, CH_3–C2), 126.0 (s, C3), 135.4 (d, $J_{PC} = 35$, C2). $^{31}P\{^1H\}$ (C_4D_8O): 82.5. ^{133}Cs (1:9 C_4D_8O–DME): −172.5.

3.3. X-ray data collection and processing

Crystals of **2** were obtained as described in the text. Data were collected on an Enraf–Nonius KappaCCD diffractometer using Mo–K_α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structure was solved by direct methods using MAXUS. While initial refinements were performed with the latter, final least-squares were conducted with SHELXL97 (full-matrix on F^2). No absorption corrections were applied. A mixed model was used for the treatment of the hydrogen atoms while using anisotropic temperature factors for all other atoms.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 167582 for compound **2**. Copies of this information can be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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