Pergamon

Tetrahedron Letters, Vol. 37, No. 50, pp. 9025-9028, 1996
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0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)02118-1

Aromatic Phosphenium Cations

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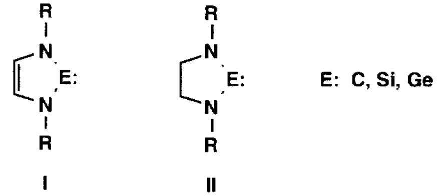
Abstract: The ionic chlorophosphane $[L'P]^+ Cl^-$ (**1**) was obtained for the ligand L' = N,N´-bis(*tert*-butyl)-1,4-diaza-2-butene. By contrast, the CC-saturated analog LP-Cl (**2**, L = N,N´-bis(*tert*-butyl)-1,4-diaza-2-butane) is covalent. This remarkable difference can be attributed to the fact that the phosphenium cation derived from **1** possesses aromatic 6π-stabilization. As expected, the two chlorophosphanes differ sharply in their volatility and solubility in organic solvents. Copyright © 1996 Elsevier Science Ltd

Introduction

The recent isolation of stable amido-carbenes [1], amido-silylenes [2] and amido-germylenes [3] of the structural types **I** and **II** raised the question whether aromaticity plays a crucial role in stabilizing the CC-unsaturated compounds **I** vs. their saturated counterparts **II**. Carbenes, silylenes and germylenes of type **II** have recently been isolated as stable compounds but they are typically more reactive and less thermostable than their CC-unsaturated counterparts **I**.

For E = Si and E = Ge [2,3] we presented evidence that compounds of type **I** possess aromatic delocalization. For E = C, interpretation of the bonding situation was controversial. A study by Arduengo *et al.* ruled out π-bonding between the divalent carbon and the nitrogen atoms,[1] while Nyulászi *et al.* came to the conclusion that compounds of type **I** are aromatic.[4]

Scheme 1



Most recently, two independent computational studies performed by the groups of Apeloig[5], Schwarz[5] and Frenking[6] confirmed the findings of Nyulászi that stable carbenes of type **II** do have strong C(II)-N π-bonding and substantial aromatic stabilization. In this publication we describe the synthesis of phosphenium cations of type **I** and **II** and present evidence for aromatic stabilization in the former.

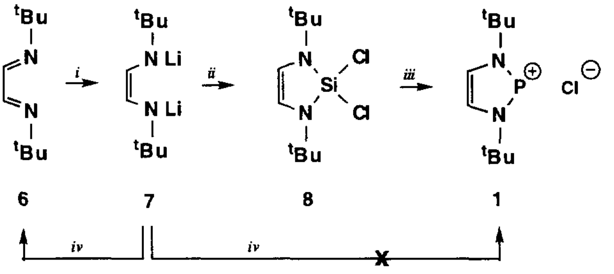
Results and Discussion.

Phosphenium cations $[R_2P]^+$ were first characterized in solution[7] but can also be isolated in favorable cases.[8] Recent research, notably by the groups of Burford[9] and Reed[10] has focused on the complexation of the phosphorus center by the counterion and the role that this complexation plays in the stability and reactivity of phosphenium cations. Phosphenium cations stabilized by π-delocalization were studied by the group of Schmidpeter.[11] The role of aromaticity in these systems is difficult to evaluate as no saturated counterparts were described.[11]

Phosphenium cations $[R_2P]^+$ are typically generated from chlorophosphanes R_2P-Cl by two different methods: Extraction of the chloride with Lewis acids such as $GaCl_3$ or $AlCl_3$. or metathesis of the chlorophosphanes with silver salts of weakly coordinating anions, especially $AgPF_6$ and $AgBF_4$.[8]

We expected that phosphenium cations of the novel structure type **I** would posses enhanced stability as a result of aromatic delocalization and decided to compare these phosphenium cations with their non-aromatic counterparts of structure type **II**. To simplify comparison with the isoelectronic carbenes, silylenes and germylenes, all of which have been described for R = ^{t}Bu, we decided to study the ^{t}Bu-substituted phosphenium cations.

Synthesis. The two chlorophosphanes **1** and **2** were needed as starting materials for the phosphenium cations. Compound **2** was obtained from N,N'-di-*tert*-butylethylenediamine (**5**) [12] and PCl_3.[13] The CC-unsaturated phosphane **1**, as well as simple alkyl or aryl derivatives was unknown. This surprising absence may be rooted in the synthetic difficulties in obtaining the compound via the obvious route from the lithium amide and PCl_3.



6 7 8 1

i) 2 eq. Li in THF, r. t.
ii) 1 eq. $SiCl_4$ in THF, r. t. (-2LiCl)
iii) 1 eq. PCl_3, C_6H_6, 5d reflux, (-$SiCl_4$)
iv) 1 eq. PCl_3, THF, r. t. -$\{PCl\}_n$, (-2 LiCl)

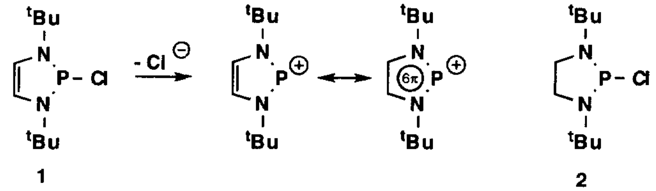
Scheme 2

While reaction of **7** (from **6** [14] + 2 eq. of Li in THF) with $SiCl_4$ is a high yielding synthesis for the dichlorosilane **8** [14], the analogous reaction with PCl_3 did not result in the formation of **1**. (Scheme 2). Instead, we observed a clean redox reaction leading to $\{PCl\}_n$ and the diazadiene **6**. This presumably reflects the relative ease of reduction of PCl_3 *vs.* $SiCl_4$ and characterizes the dilithium salt **7** as a powerful reducing agent. Metathesis of the silicon-amide **8**[14] with PCl_3 in refluxing benzene, however, gave us the desired chlorophosphane **1** in high yield.

Much to our surprise, the two chlorophosphanes differ significantly in their physical properties: Compound **2** is soluble in benzene and hexanes, while **1** is insoluble in hexanes and only sparingly soluble in benzene. **2** is quite volatile and sublimes readily at 80 °C / 0.1 Torr while **1** requires 180 °C / 0.1 Torr. The remarkably different physical properties suggest that **2** is a covalent compound while **1** is ionic. [15]

The crucial role of the CC-double bond in creating an ionic PCl bond is obvious.

Scheme 3



To substantiate our assumption that **1** is indeed ionic it was necessary to investigate derivatives of **1** that unambiguously contain phosphenium cations. The tetrachlorogallates [L'P][$GaCl_4$] (**3**) and [LP][$GaCl_4$] (**4**) were obtained in quantitative yield by reacting the chlorophosphanes **1** and **2** with $GaCl_3$ in CH_2Cl_2 or benzene. Both are indefinitely stable at r. t. in solution ($CHCl_3$, CH_2Cl_2) or as solids. The tetrachlorogallates are insoluble in hexanes and benzene but moderately soluble in CH_2Cl_2 and $CHCl_3$. Analytically pure samples (C,H,N) were obtained by recrystallization from CH_2Cl_2 .

^{31}P NMR spectroscopy is a sensitive tool for probing the electronic environment of phosphorus atoms. The degree of ionicity in **1** / **2** was studied by comparing their ^{31}P chemical shifts with those of the fully ionic tetrachlorogallates **3** and **4**. The phosphorus atom in the C-C saturated chlorophosphane **2** ($\delta^{31}P$ +166.8) experiences strong deshielding ($\Delta\delta$ of 107.9) upon extraction of the chloride by $GaCl_3$ (formation of **4**, $\delta^{31}P$ = +274.7). As expected, extraction of the chloride ion from the ionic chlorophosphane **1** ($\delta^{31}P$ +168.7) to form the tetrachlorogallate **3** ($\delta^{31}P$ +192.0 ppm) does not lead to a dramatic deshielding ($\Delta\delta$ = 23.3). Although one might ideally expect identical shifts for **1** and **3** even weakly coordinating counterions such as PF_6^-, BF_4^- and $GaCl_4^-$ produce variations of up to 30 ppm in the ^{31}P chemical shifts of the phosphenium cations[8, 9]. The similarity of chemical shifts in **1** / **3** therefore suggests that **1** is indeed ionic (in contrast to **2**) but is still loosely coordinated by the counterion Cl^- in solution.

Aromatic delocalization in **1** / **3** should manifest itself in characteristic deshielding of the ring protons. This is indeed observed [16] for both **1** (δ^1H = 6.97) and **3** (δ^1H = 7.86). Coordination of the phosphorus atom by the counterion should disrupt aromaticity and it seems noteworthy in that context that the exchange of $GaCl_4^-$ for the stronger coordinating Cl^- leads to diminished deshielding of the ring protons.

***Synthesis of* 1 - 4**. All operations were performed under argon and with anhydrous solvents. NMR-spectra[15] were recorded in CD_2Cl_2 with a 200 MHz spectrometer ($\delta^{31}P$ vs. 85 % H_3PO_4). **1**: A solution of **8**[14] (20.00 g,74.93 mmol) and PCl_3 (9.80 mL, 15.4 g, 112 mmol) in benzene (300 mL) is boiled under reflux for 5 days. The cold reaction mixture is layered with hexanes (300 mL). Yellow microcrystalline **1** is collected after 4 days by filtration over a glass frit and washed with hexanes (3 x 40 mL). The product contains varying amounts of benzene that are removed by simple pumping at r. t. for 4 h. Yield: 11.43 g (65%) of analytically pure **1**. The product can be sublimed at 180 - 200 °C (oilbath temperature) under vacuum (0.1 Torr). Large amounts are best purified by recrystallization from CH_2Cl_2 : hexanes (20 : 1). **3** : Reaction of **1** in CH_2Cl_2 with one equivalent of $GaCl_3$ and stirring at r. t. for 15 min followed by the addition of the same volume of hexanes gave analytically pure **3** as colorless crystals in quantitative yield. **4** was obtained in the same fashion from $GaCl_3$ and **2**.

Spectroscopic characterization **$[\mathrm{L'P}]^+\mathrm{Cl}^-$ (1)**: NMR $\delta^1\mathrm{H}$ 6.97 (d, $^3J(\mathrm{P,H})$ = 1.5 Hz, 2H, $\mathrm{C\underline{H}}$) 1.63 (d, $^4J(\mathrm{P,H})$ = 1.8 Hz, 18H, $\mathrm{C\underline{H}_3}$); $\delta^{13}\mathrm{C}$: 30.41 (d, $^3J(\mathrm{C,P})$ = 10.3 Hz, $\mathrm{\underline{C}H_3}$) 57.83 (d, $^2J(\mathrm{C,P})$ = 7.4 Hz, $\mathrm{\underline{C}Me_3}$) 121.34 (d, 2J(C,P) = 8.8 Hz, $=\mathrm{\underline{C}H}$); $\delta^{31}\mathrm{P}$: 168.7 (br, s). **$[\mathrm{L'P}]^+[\mathrm{GaCl_4}]^-$ (3)**: NMR $\delta^1\mathrm{H}$ 7.86 (s, 2H, CH) 1.77 (d, $^4J(\mathrm{P,H})$ = 1.8 Hz, 18H, $\mathrm{CH_3}$); $\delta^{13}\mathrm{C}$: 31.47 (d, $^3J(\mathrm{P,C})$ = 9.5 Hz, $\mathrm{\underline{C}H_3}$) 62.71 (d, $^2J(\mathrm{P,C})$ = 7.3 Hz, $\mathrm{\underline{C}Me_3}$) 131.38 (d, $^2J(\mathrm{P,C})$ = 3.6 Hz, $=\mathrm{\underline{C}H}$); $\delta^{31}\mathrm{P}$: 192.0 (br, s). **LP-Cl (2)**: NMR $\delta^1\mathrm{H}$ 1.39 (d, $^4J(\mathrm{P,H})$ = 1.8 Hz, 18H, $\mathrm{C\underline{H}_3}$) 3.37 (d, $^3J(\mathrm{P,H})$ = 6.6 Hz, 4H, $\mathrm{C\underline{H}_2}$); $\delta^{13}\mathrm{C}$ 28.97 (d, $^3J(\mathrm{C,P})$ = 11.7 Hz, $\mathrm{\underline{C}H_3}$) 45.78 (d, $^2J(\mathrm{C,P})$ = 6.6 Hz, , $\mathrm{\underline{C}H_2}$) 54.10 ($^2J(\mathrm{C,P})$ = 11 Hz, $\mathrm{\underline{C}Me_3}$); $\delta^{31}\mathrm{P}$ 166.8 (s, br). **$[\mathrm{LP}]^+[\mathrm{GaCl_4}]^-$ (4)**: NMR $\delta^1\mathrm{H}$ 4.10 (d, $^3J(\mathrm{P,H})$ = 4.5 Hz, 4H, $\mathrm{C\underline{H}_2}$) 1.58 (d, $^4J(\mathrm{P,H})$ = 2.2 Hz, 18H, $\mathrm{C\underline{H}_3}$); $\delta^{13}\mathrm{C}$ 29.75 (d,$^3J(\mathrm{P,C})$ = 9.5 Hz, $\mathrm{\underline{C}H_3}$) 49.72 (d, $^2J(\mathrm{P,C})$ = 8.0 Hz, $\mathrm{\underline{C}H_2}$) 59.21 (d, $^2J(\mathrm{P,C})$ = 10.3 Hz, $\mathrm{\underline{C}Me_3}$); $\delta^{31}\mathrm{P}$ 274.7 (br, s).

Acknowledgment: The authors wish to thank NSERC and Mirotech Inc. (Mississauga) for financial support of this research.

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15. Preliminary results from single crystal x-ray studies of **1** and **2** further support this interpretation: d(PCl) = 276 pm (**1**), 231 pm (**2**).
16. Compare $\mathrm{L'SiCl_2}$: 5.75 ppm. [12,14]

(*Received in USA* 4 *September* 1996; *revised* 14 *October* 1996; *accepted* 15 *October* 1996)