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# Synthesis, Structure and Reactivity of a Stable Phosphonium-Sulfinyl Yldiide

Azucena Garduno-Alva,<sup>[a]</sup> Romaric Lenk,<sup>[a]</sup> Yannick Escudié,<sup>[a]</sup> Mariana Lozano González,<sup>[a]</sup> Laura Bousquet,<sup>[a]</sup> Nathalie Saffon-Merceron,<sup>[b]</sup> Cecilio Alvarez Toledano,<sup>[c]</sup> Xavier Bagan,<sup>[d]</sup> Vicenç Branchadell,<sup>[d]</sup> Eddy Maerten,<sup>\*[a]</sup> Antoine Baceiredo<sup>\*[a]</sup>

On the occasion of the 50th anniversary of Laboratoire Hétérochimie Fondamentale et Appliquée, LHFA

**Abstract:** The synthesis of a stable lithium phosphonium-sulfinyl yldiide is reported. The compound has been fully characterized by NMR spectroscopy and by X-Ray crystallography. Electronic structure of **2** was analysed by DFT calculations indicating strong yldiic character. Yldiide **2** is enough stable to catalyse the hydroacylation of benzaldehyde. More interestingly, the Wittig reaction with activated ketones proceeded smoothly at room temperature due to the presence of the lithium cation.

#### Introduction

Since more than a century, ylide chemistry attracts considerable interests<sup>[1]</sup> and without any doubt, the Wittig reaction is widely recognized as one of the most important reactions in organic chemistry.<sup>[2]</sup> Bis-ylide derivatives I are species containing two cumulated ylide functions, and formally possess a central carbon atom with two negative charges, which are stabilized by two positively charged fragments.<sup>[3]</sup> Recently, considerable work on their electronic structure has brought new lights on these compounds.<sup>[4]</sup> Indeed rather than the classical zwitterionic representation, their description as divalent carbon(0) complexes featuring two L ligands seems to fit better with their reactivity.<sup>[5]</sup>

The replacement of a neutral L ligand by an anionic moiety (R) gives the metalated congeners **II**,<sup>[6]</sup> which are called yldiides or metalated ylides (Figure 1). Despite limited examples (only 3 yldiides have been isolated),<sup>[7]</sup> some interesting applications were already described for organic synthesis as highly reactive Wittig-type reagents for sterically hindered ketones,<sup>[8]</sup> in transition-metal chemistry as ligands,<sup>[9]</sup> or in main group chemistry for the synthesis of stable borenium cations.<sup>[10]</sup>

Following our work on neutral mixed phosphonium-

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sulfonium bis-ylides,<sup>[11]</sup> which demonstrates their utility as asymmetric atomic carbon sources, we got interested in the synthesis and the reactivity study of the corresponding anionic phosphonium-sulfinyl yldiide.



Figure 1. Bis-ylides, yldiides and isolated yldiides.

### **Results and Discussion**

The precursor phosphonium sulfinyl ylide **1** has been prepared in good yield (66 %) by reaction of chlorophosphonium salts with methyl(tri*iso*propylphenyl) sulfoxide in presence of 2 equivalents of a non-nucleophilic strong base (LDA). Deprotonation of **1** with butyllithium cleanly affords the desired lithium yldiide **2** (70 % yield) as white solid (Scheme 1). As expected, the <sup>31</sup>P NMR chemical shift of **2** (18.0 ppm) appears at higher field than **1** (46.8 ppm). In the <sup>13</sup>C NMR spectrum, the metalated central carbon exhibits a characteristic doublet at  $\delta = 48.3$  ppm ( $J_{PC} =$ 30.6 Hz), which is in the same range as that of the related sulfonyl-yldiide reported by Gessner et al.<sup>[7c]</sup>



Scheme 1. Synthesis of lithium yldiide 2.

Both compounds were isolated in the crystalline form, from a toluene/pentane solution at -20°C for 1, and from a pentane solution with a minimum amount of THF for 2, and both structures were confirmed by X-ray diffraction analysis (Figures 2 and 3).  $^{\left[ 12\right] }$ 

oxygen atoms coordinate less strongly to Li2 (O1-Li2: 2.065 and O2-Li2: 2.074 Å) than the two THF molecules to Li1 (O4-Li1: 1.965 and O3-Li1: 1.972 Å). More classical interactions are observed with Li1 (O2-Li1: 1.894 and O1-Li1: 1.896 Å).



Figure 2. Molecular structure of 1. Thermal ellipsoids represent 30 % probability. H (except on C1) and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-C1 1.677(2), P1-C10 1.811(2), S1-O1 1.500(2), S1-C1 1.736(2), S1-C16 1.8162, P1-C1-S1 120.83(13).



Figure 3. Molecular structure of [2•THF]<sub>2</sub>. Thermal ellipsoids represent 30 % probability. H, solvent and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]:O1-Li1 1.896(6), O1-Li2 2.065(6), O2-Li1 1.894(6), O2-Li2 2.074(6), Li1-O4 1.965(7), Li1-O3 1.972(10), Li1-Li2 2.716(8), C1-Li2 2.158(6), C2-Li2 2.139(7), P1-C1 1.649(3), P1-C11 1.823(3), P2-C2 1.649(3), P2-C40 1.826(4), S1-O1 1.546(2), S1-C1 1.682(3), S2-O2 1.554(2), S2-C2 1.693(3), P1-C1-S1 117.51(18), P2-C2-S2 115.53(19), S1-C1-Li2 85.6(2), Li2-C1-P1 142.3(3), S2-C2-Li2 86.0(2), Li2-C2-P2 142.8(3).

The X-ray analysis of **2** confirms the metalation of the central carbon atom, and reveals a dimeric structure incorporating a Li<sub>2</sub>O<sub>2</sub> core. The Li1-Li2 interatomic distance is greater (2.716 Å) than the sum of the covalent radii (2.68 Å).<sup>[13]</sup> The C-Li2 bond lengths (C1-Li2: 2.158 and C2-Li2: 2.139 Å) are slightly longer than those reported in the previously described lithium yldiides (2.060 - 2.085 Å) probably due to the coordination of oxygen atoms. It is worth noting that sulfinyl-

Table 1. Selected geometrical parameters of the experimental crystal structures (1 and [2-THF]<sub>2</sub>) and the related optimized structures (distances in Å, Angles in deg).

	1	1 <sup>calcd</sup>	[2•THF]2	2 <sup>calcd</sup>	
P-C	1.677(2)	1.687	1.649(3) 1.649(3)	1.642	
S-C	1.736(2)	1.750	1.682(3) 1.693(3)	1.720	
P-C-S	120.83(13)	117.7	117.51(18) 115.53(19)	113.4	

The P-C distance (1.649 Å) of [2.THF]2 is shorter than that in 1 (1.677 Å) and the value is consistent with those previously reported for metalated ylides III-V (1.630-1.646 Å).<sup>[7]</sup> The S-C bond length also undergoes a shortening on going from 1 (1.736 Å) to [2-THF]<sub>2</sub> (1.682-1.693 Å) and the P-C-S angle decreases significantly upon metalation from 120.82° (1) to 117.51-115.53°([2•THF]<sub>2</sub>). To gain more insight into electronic structures of 1 and 2, DFT calculations were performed at the M06-2X/6-31+G(d,p) level of theory (see Sup. Info). The structure of 2 was considered with and without counter cation. In the presence of the cation, two minima were found depending on the coordination of the lithium ion either on the central carbon atom (the most stable), or on the oxygen atom ( $\Delta E = 5.1$ kcal/mol and  $\Delta G = 5.9$  kcal/mol, see Sup. Info). We finally have considered 2<sup>calcd</sup> without cation for the rest of the discussion since the ionic character of the C-Li bond have a minor influence on the rest of the electronic parameters. The optimized geometries 1<sup>calcd</sup> and anionic 2<sup>calcd</sup> agree quite well with the experimental crystal structures (Table 1). The only noticeable difference concerns the S-C bond length which is overestimated by 0.04 Å in the calculation. The variation of the Wiberg bond indices ongoing from 1<sup>calcd</sup> to 2<sup>calcd</sup> (P-C, +0.36; C-S, +0.11) is in good agreement with an increase of the negative charge on vlidic-carbon atom. The value obtained for the atomic population on the central carbon (-1.358) is reminiscent of that reported by Gessner and al (-1.33).<sup>[7c]</sup> The two highest occupied molecular orbitals (Figure.4) correspond to the two lone pairs at the central carbon in 2, the HOMO-1 and the HOMO present respectively σand  $\pi$ -symmetry.



Figure 4. HOMO-1 (left, - 2.86 eV) and HOMO (right, - 2.10 eV) of 2<sup>calcd</sup> calculated at the M06-2X/6-31+G(d,p) level of theory (±0.05 isosurfaces).

The nucleophilic character of yldiide 2 was confirmed by a quantitative reaction with methyl iodide affording cleanly the corresponding C-methylated ylide 3, which has been isolated as white solid in 95 % yield (Scheme 2). The <sup>31</sup>P NMR spectrum exhibits a singlet at  $\delta$  = 48.6 ppm, and the C-methyl protons appear as a characteristic doublet signal at  $\delta = 2.02$  ppm ( $J_{PH} =$ 13.2 Hz) in the <sup>1</sup>H NMR spectrum. The central carbon atom displays a high-field doublet at  $\delta = 11$  ppm ( $J_{CP} = 12.2$  Hz) in the <sup>13</sup>C NMR spectrum. In the same vein, yldiide 2 can be easily reprotonated, and the addition of one equivalent of water quantitatively affords immediately and the precursor phosphonium-sulfinyl ylide 1.



Scheme 2. Nucleophilic character yldiide 2, and Wittig reaction with trifluoroacetophenone.

Interestingly, one equivalent of trifluoroacetophenone readily reacts with **2**, as indicated by the immediate appearance of a new signal at  $\delta = -39$  ppm in the <sup>31</sup>P NMR spectrum, which slowly evolves over 24 h at room temperature toward a new signal at  $\delta = 22$  ppm. This high-field chemical shift is in good agreement with the formation of oxaphosphetane **4** with a penta-coordinate phosphorus atom, which is the key intermediate of the Wittig reaction. The new signal in <sup>31</sup>P NMR spectroscopy was assigned as the corresponding phosphine oxide by comparison with an authentic sample, and after work-up *cis*-vinylsulfoxide **5** *wa*s isolated in 68 % yield (Scheme 2). It is important to note that the decomposition of related oxaphosphetane, obtained by reaction of P,S-bis-ylide with trifluoroacetophenone, requires much stronger thermal activation

(150°C).<sup>[11b]</sup> The evolution of **4** at much lower temperature (rt) can be explained by the interaction of the lithium cation with the carbanion center which triggers the Wittig reaction.<sup>[14]</sup>

In marked contrast, the reaction of **2** with one equivalent of benzaldehyde did not afford the Wittig reaction but <sup>1</sup>H NMR spectroscopy revealed the formation of benzylbenzoate that exhibits a characteristic signal at  $\delta = 5.4$  ppm. The formation of benzylbenzoate can be rationalized by the hydroacylation of benzaldehyde, this transformation can be performed using catalytic amounts of yldiide **2** (see Sup. Info. for kinetic studies). The reaction probably proceeds *via* an hydride transfer that is generated upon the formation of **6** and trapped by a second equivalent of aldehyde to generate lithium alcoholate **7**. Then, the reaction between **6** and **7** gives rise to the benzylbenzoate and regenerates the catalyst **2** (Scheme 3). A similar catalytic transformation has already been reported using NHCs or P,S-bis-(ylide) as catalysts.<sup>[11b,15]</sup>



Scheme 3. Proposed mechanism for catalytic transformation of benzaldehyde to benzylbenzoate.

#### Conclusions

In conclusion, a stable lithium phosphonium-sulfinyl yldiide has has been synthesized and structurally characterized by X-ray crystallography. DFT calculations evidenced a strong nucleophilic character which was experimentally confirmed. When compared with neutral P,S-bis-ylide analogue, the metalation of the central carbon induces some chemical behaviour differences, and particularly, Wittig type reactions can be performed at room temperature without any additives. Detailed reactivity of **2** and its applications in synthesis are under active investigation.

#### Acknowledgements

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#### Keywords: Ylide • Yldiide • Metalated Ylide • Phosphorus • Wittig

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### Entry for the Table of Contents (Please choose one layout)

Layout 1:

## COMMUNICATION

A stable lithium phosphonium-sulfinyl yldiide was isolated and fully characterized by NMR spectroscopy and by X-Ray crystallography. In between methandiides and bis-ylides, the metalated center allows Wittigtype reaction in soft conditions. Theoretical calculations indicate strong ylidic character that was experimentally confirmed through addition reaction with alkylhalide or as catalyst for hydroacylation of benzaldehyde.



#### Yldiide

A. Garduno-Alva, R. Lenk, Y. Escudié, M. Lozano González, L. Bousquet, N. Saffon-Merceron, C. Alvarez Toledano, X. Bagan, V. Branchadell, E. Maerten,\* A. Baceiredo\*

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