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New insight into the reactivity of S,S-bis-ylide

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Abstract: The present work focuses on the reactivity of S,S-bis-ylide **2**, which presents a strong nucleophilic character as evidenced by reactions with methyl iodide and CO₂ affording C-methylated salts **3** and betaine **4**, respectively. Derivatization of betaine **4** affords the corresponding ester derivative **6** which was fully characterized by NMR spectroscopy and X-ray diffraction analysis. Furthermore, an original reaction with phosphonium ions leads to the formation of a transient push-pull phosphino(sulfonio)carbene **8** which rearranges to give stabilized sulfonium ylide derivative **7**.

Keywords: bis-ylides; ylide; carbene; phosphonium; carbene.

1. Introduction

Since the discovery of ylides in the 1920s [1,2], their chemistry has experienced an important growth [3-5] and they have become very important synthetic tools [6-9]. Bis-ylides, which are the combination of two ylide functions on a single carbon atom, have attracted significant attention from many research groups [10-16]. Indeed, since the first synthesis of carbodiphosphanes **I** by Ramirez in the 60s [17], many models have been developed (Figure 1). Among them, we can mention carbodicarbenes **II** prepared by Bertrand's group [18] after initial theoretical predictions by Frenking [19], the mixed carbo-phosphinocarbene **III** initially synthesized by Fürstner and Alcarazo and later by Ong et al. [20,21,22] and mixed phosphonio/sulfonio **IV** and phosphonio/sulfoxonio **V** (X = O) bis-ylides prepared by our group [23-25]. Finally, major contributions were made by Fujii's group with various combinations of selenium/sulfur or sulfur/sulfur stabilized carbones **V-VIII** [26-30]. Naturally, this diversity of structures has brought considerable knowledge on these species that exhibit a very diverse reactivity ranging from their use as ligands in organometallic chemistry [15] to activation of small molecules [21] and even application as atomic carbon sources [23]. Bis-ylides main application remains their use as ligands because of the peculiar environment of the central carbon atom. In particular, the presence of two lone pairs located on a single carbon atom [10-16] offers unique coordination modes for transition metals. Indeed, Stephen took advantage of the presence of the two lone pairs to stabilize certain transition metals, achieving high efficiency in hydrogenation reactions [31]. Ong's group has evidenced that the unexpected accepting character of carbodicarbenes at the N-heterocyclic carbene fragments was beneficial for an ambiphilic-type reactivity allowing the activation of small molecules [32,33]. It is obvious that the reactivity and applications of bis-ylides are directly linked to the combination of the two ylide functions, but overall remain rare.

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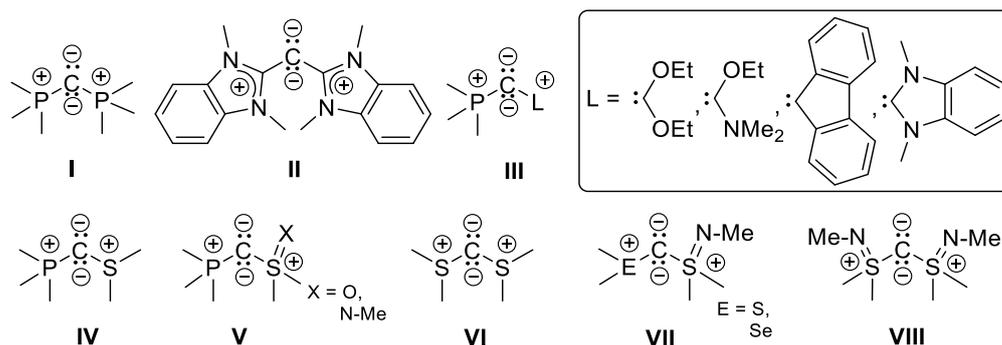
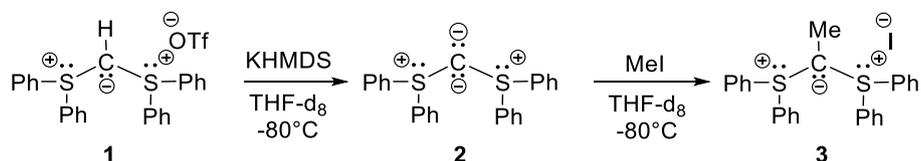


Figure 1. Carbodiphosphoranes **I**, carbodicarbenes **II**, carbophosphinocarbenes **III**, phosphonio/sulfonio bis-ylides **IV**, phosphonio/sulfoxonio or phosphonio/iminosulfonio bis-ylides **V**, sulfonio/sulfonio bis-ylides **VI**, selenio- or sulfonio-/iminosulfonio **VII** and bis iminosulfanebis-ylides **VIII**.

In 2010, we have reported the first stable and isolable mixed P,S-bis-ylide **IV** [23] which can be used as atomic carbon reagent to introduce one carbon atom into various organic molecules [34]. In particular, the labile character of sulfide ligand in **IV** facilitates substitution reactions at the central carbon atom and thus atomic carbon transfer reactions. Therefore, S,S-bis-ylide **VI** constituted of two labile sulfide moieties should be an excellent atomic carbon reagent. However, probably due to the thermal instability of **VI**, only a few reactions with Au(I), demonstrating its carbene character were described [30] and no reaction with organic reagents has been reported to date. In this article, we report original reactions of S,S-bis-ylide **VI** with CO₂ and phosphonium ions (Figure 1).

2. Results and Discussion

Monoprotonated precursor **1** (Scheme 1) has been prepared according to the method previously described by Fujii [30]. The spectroscopic data are in good agreement with the reported values. In particular, the central proton and carbon resonances of **1** appear at $\delta = 3.88$ ppm and $\delta = 19.4$ ppm, respectively in ¹H and ¹³C NMR spectra. Because of the thermal instability of S,S-bis-ylide **2**, the deprotonation was then realized in THF-d₈ using potassium hexamethyldisilazane at -80 °C and was analyzed at low temperature, in situ, in the presence of conjugated acid. With the appearance of a bright yellow color, in the ¹H NMR spectrum the C-H signal in disappeared while the central carbon in the ¹³C NMR spectrum was lower field shifted at $\delta = 39.0$ ppm compared to **1**. Bis-ylide **2** starts to decompose at -30 °C to afford black carbon precipitate and diphenyl sulfide.



Scheme 1. Synthesis of S,S-bis-ylide **2** and alkylation reaction with MeI.

The formation of S,S-bis-ylide **2** was unambiguously confirmed by its methylation reaction (Scheme 1). Indeed, upon addition of one equivalent of methyl iodide to a THF solution of **2** at -80 °C, the yellow color immediately disappeared concomitantly with the precipitation of a white solid. After treatment, the desired C-methylated salt **3** was isolated in 85% yield. The methylation was confirmed by the presence of two characteristic signals for the methyl group at $\delta = 1.67$ ppm and $\delta = 10.2$ ppm in the ¹H and ¹³C NMR spectra, respectively. C-methylated salt **3** was isolated in the crystalline form layering

diethyl ether onto a saturated dichloromethane solution and its structure was confirmed by X-ray diffraction analysis (Figure 2). As expected, the S-C bond lengths in **3** (1.682 and 1.687 Å) are very similar to those of the protonated bis-ylide precursor **1** (1.685 Å and 1.676 Å) [30] and much shorter than a S-C single bond length (1.81 Å), showing the delocalization of the negative charge from the central carbon atom to the SPh₂ fragments, and justifying the planar environment around the C1 atom ($\Sigma^\circ = 359.7^\circ$). The S1-C1-S2 angle is also almost identical to that of **1**.

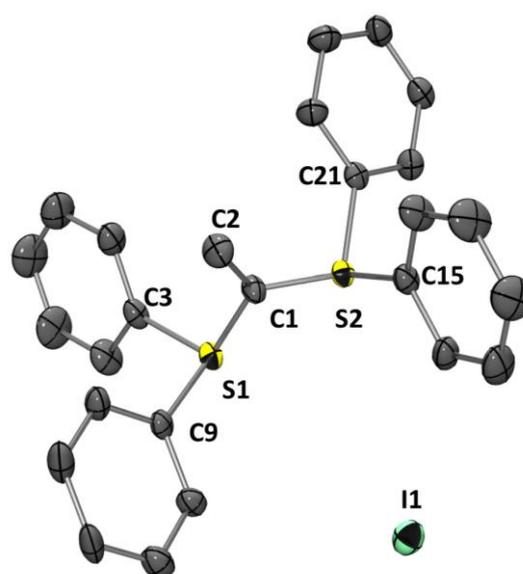
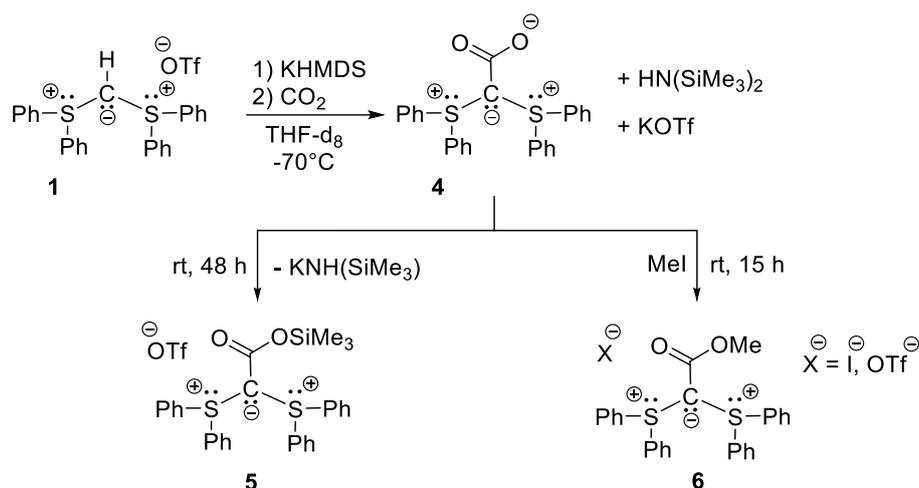


Figure 2. Molecular structure of C-methylated salt **3**. Ellipsoids are drawn at the 30% probability level; hydrogen and disordered atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): S1-C1 1.682(9), C1-S2 1.687(9), C1-C2 1.525(12), S1-C3 1.794(4), S1-C9 1.759(3), S2-C21 1.772(4), S2-C15 1.776(3). S1-C1-S2 111.6(6), S2-C1-C2 123.8(6), C2-C1-S1 124.3(6), C9-S1-C1 107.4(3), C1-S1-C3 111.6(4), C3-S1-C9 100.2(2), C1-S2-C15 107.6(3), C15-S2-C21 101.5(2), C21-S2-C1 111.9(4).

It is well known that carbodiphosporanes (P,P-bis-ylides) react with CO₂ to form zwitterionic donor-acceptor complexes that can coordinate transition metals or evolve upon heating towards phosphine oxide and phosphoranylidene ketene [35–39]. The sulfur analogue **2** also reacts with CO₂ (3 bars) at -70°C affording the corresponding CO₂ adduct **4** (Scheme 2). ¹³C NMR analysis of the resulting solution at -20°C shows two broad signals appearing at $\delta = 167.2$ ppm and $\delta = 40.16$ ppm corresponding to the coordinated CO₂ fragment and the central carbon atom, respectively, in good agreement with the formation of betaine **4**. However, at room temperature, zwitterionic CO₂ adduct **4** reacts slowly with hexamethyldisilazane byproduct to afford the O-silylated ester **5** [40]. Alternatively, CO₂ adduct **4** can be trapped by adding one equivalent of MeI to generate the O-methylated salt **6**, which is stable and was easily isolated in 80% yield. Compound **6** has been fully characterized by NMR spectroscopy (see experimental section and supporting information). Single crystals of **6** were grown layering pentane onto a saturated DCM at room temperature [41] and then analyzed by X-ray diffraction confirming the expected structure (Figure 3). The S1-C2 and S2-C2 bond lengths (1.720(2) Å and 1.713(3) Å, respectively) are slightly longer than in those of **3** (1.682 Å and 1.687 Å). The central carbon C1 shows a planar environment and the C1-C2 bond length is short 1.437(4) Å. This bonding pattern can be explained by a major contribution of the ester fragment to stabilize the negative charge [42].



Scheme 2. Reactivity of *S,S*-bis-ylide **2** with CO_2 and corresponding esters **5** and **6**.

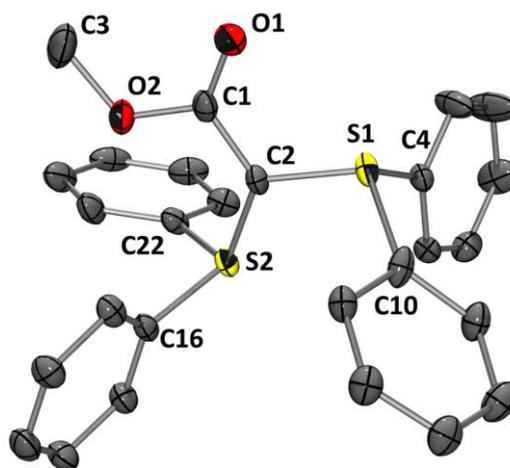
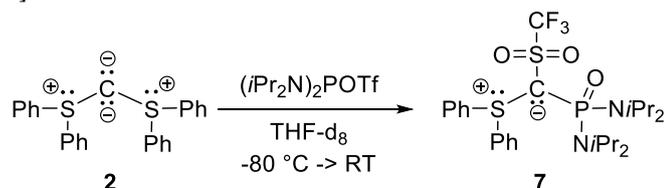


Figure 3. Cationic part of **6**. Ellipsoids are drawn at the 30% probability level; hydrogen and disordered atoms and counter ion (**1**) were omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): S1-C2 1.720(2), C2-S2 1.713(3), C1-C2 1.437(4), C1-O1 1.214(3), C1-O2 1.351(3), O2-C3 1.438(4), S1-C4 1.783(3), S1-C10 1.803(5), S2-C22 1.793(3), S2-C16 1.794(3). S1-C2-S2 117.5(1), S2-C2-C1 127.6(2), C1-C2-S1 114.1(2), C2-C1-O2 110.8(2), O2-C1-O1 122.6(3), O1-C1-C2 126.6(2).

In order to demonstrate the leaving group ability of sulfide group, we have considered the reaction of *S,S*-bis-ylide **2** with an electrophile bearing a lone pair such as a phosphonium ion (Scheme 3) [43]. The reaction of **2** with bis(diisopropylamino)phosphonium ion at -80°C affords ylide **7** with a good selectivity when the reaction mixture is rapidly brought to room temperature [44]. The structure of **7** was established by X-ray diffraction analysis (Figure 4). Variable temperature NMR analysis indicate the formation of adduct **8** ($\delta = 48.3$ ppm in ^{31}P NMR) at -70°C that starts to evolve towards sulfonium ylide **7** ($\delta = 25.7$ ppm in ^{31}P NMR) above -40°C (carbene intermediate **9** was not detected). The process can be explained by the initial attack of nucleophilic bis-ylide **2** on the positively charged phosphonium salt generating a phosphino cationic ylide intermediate **8** (Scheme 4). The π -donation of phosphine lone pair induces sulfide elimination and formation of phosphino(sulfonio)carbene **9**. This push-pull carbene, substituted by a π -donating phosphino- and a π -accepting sulfonio-group, exhibits a strong electrophilic character on the phosphorus center [45], and therefore reacts with triflate anion to afford **10**. Finally, rearrangement, starting with the nucleophilic attack of central carbon to the

sulfoxide moiety, occurs to afford sulfonium ylide **7** which is stabilized by two π -accepting substituents such as trifluoromethanesulfonyl and phosphonyl groups, as indicated by the short C1-S2 and C1-P1 bond lengths [1.694(2) and 1.807(2) Å, respectively]. Thanks to the high leaving group ability of sulfide ligand, such a strongly electrophilic phosphino(sulfonio)carbene **9**, which reacts even with the generally non-coordinating triflate anion, can be generated from **8** by elimination of diphenyl sulfide. It should be noted that, in the case of carbodiphosphoranes, such an addition-elimination reaction does not take place. Instead, they react with a chlorophosphine to form a stable adduct similar to **8** [46,47].



Scheme 3. Reactivity of S,S-bis-ylide **2** with a phosphonium ion.

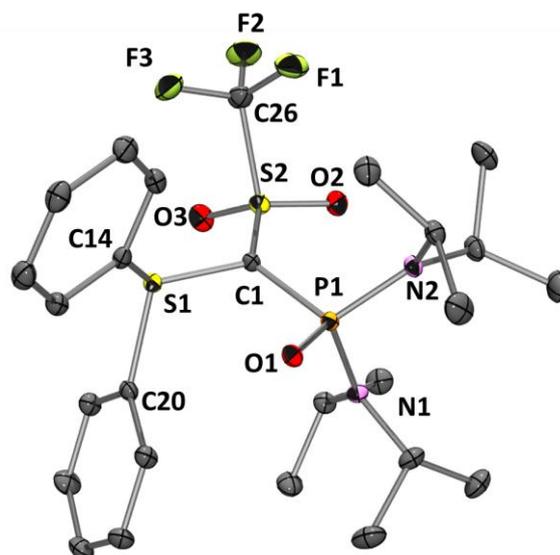
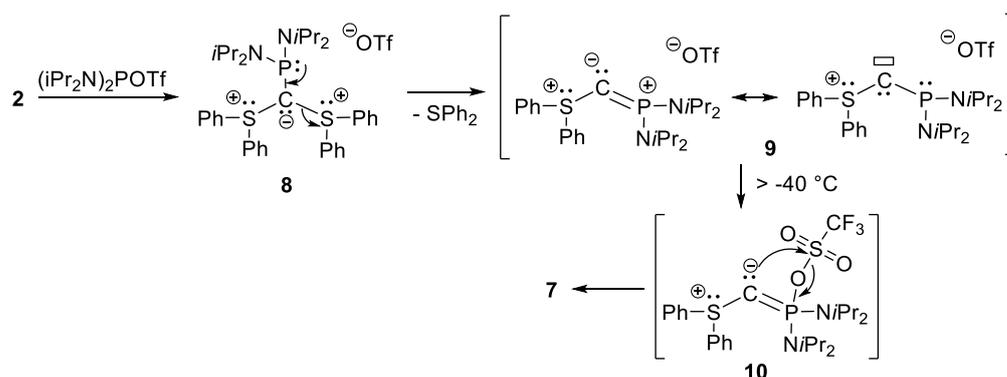


Figure 4 Molecular structure of **7**. Ellipsoids are drawn at the 30% probability level; hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): S1-C1 1.724(2), C1-S2 1.694(2), C1-P1 1.807(2), S1-C14 1.803(2), S1-C20 1.788(2), P1-O1 1.487(1), P1-N1 1.669(2), P1-N2 1.656(2), S2-O2 1.434(2), S2-O3 1.437(1), S2-C26 1.841(2), C26-F1 1.327(2), C26-F2 1.336(2), C26-F3 1.333(2). S1-C1-P1 120.80(10), S1-C1-S2 109.97(10), P1-C1-S2 127.57(11).



Scheme 4. Proposed mechanism.

3. Materials and Methods

3.1. General Comments

All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques or high-pressure NMR tube techniques. Dry and oxygen-free solvents were used. ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra were recorded on Bruker Avance II 300 MHz, Avance III HD 400 MHz and Avance I and II 500 MHz spectrometers (Bruker, Karlsruhe, Germany). Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (^1H and $^{13}\text{C}\{^1\text{H}\}$). ^{19}F and ^{31}P NMR chemical shifts were reported in ppm relative to CFCl_3 and 85% H_3PO_4 , respectively. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; hept, heptuplet; m, multiplet. ^1H and ^{13}C resonance signals were attributed by means of 2D COSY, HSQC and HMBC experiments. Mass spectra were recorded on a Hewlett Packard 5989A spectrometer (Hewlett-Packard, Palo Alto, CA, United States). HRMS was realized on a Xevo G2 QToF apparatus (Waters, Milford, United States). Melting points were measured in a sealed glass tube on a Stuart SMP-30 melting point apparatus. All commercially available reagents were used without further purification otherwise noted. **1** was prepared following previously reported procedure [30].

3.2. Synthesis

S,S-Bis-ylide 2: In a J. Young NMR tube, protonated precursor of bis-ylide **1** (50 mg, 0.094 mmol, 1 eq.) was dissolved in THF-*d*₈ (0.2 mL). At $-80\text{ }^\circ\text{C}$, a solution of KHMDS (19 mg, 0.095 mmol, 1 eq.) in 0.2 mL of THF-*d*₈ was added. The NMR tube was then closed and carefully shaken the mixture while remaining at low temperature. The yellow colored solution was obtained. Because of thermal instability of **2**, the product was used or characterized at low temperature in presence of hexamethyldisilazane without any purification. ^1H NMR (400 MHz, 213 K, THF-*d*₈): $\delta = 7.41\text{--}7.26$ (m, 12H, CH_{ar}), 8.02-7.90 (m, 8H, CH_{ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 213 K, THF-*d*₈): $\delta = 39.0$ (s, SCS), 127.1 (s, CH_{ar}), 129.3 (s, CH_{ar}), 129.6 (s, CH_{para}), 148.2 (s, C_{ipso}).

C-methylated salt 3: In a Schlenk flask containing bis-ylide precursor **1** (50 mg, 0.094 mmol, 1 eq.) and KHMDS (19 mg, 0.095 mmol, 1 eq.) was added 0.5 mL of THF at $-80\text{ }^\circ\text{C}$. After the yellow coloration of the solution, 1 equivalent of iodomethane (5.9 μL , 0.094 mmol, 1eq) was added at the same temperature. The solution immediately became colorless and a white precipitate appeared. After 15 min, the solution was allowed to warm up to RT, then the volatiles were removed under reduced pressure. The crude was extracted with CH_2Cl_2 (3 x 2 mL). The resulting solution was dried using MgSO_4 then evaporated to afford **3** as white solid (42 mg, 0.080 mmol, 85% yield). Crystals were grown layering diethyl ether onto a saturated CH_2Cl_2 solution. ^1H NMR (500 MHz, 298 K, CD_3CN): $\delta = 1.67$ (s, 3H, CH_3), 7.54-7.57 (m, 8H, CH_{ar}), 7.59-7.69 (m, 12H, CH_{ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 298 K, CD_3CN): $\delta = 10.2$ (s, CH_3), 23.4 (s, SCS), 129.7 (s, CH_{ar}), 131.4 (s, CH_{ar}), 132.7 (s, C_{ipso}), 133.3 (s, CH_{para}). Mp = $116\text{ }^\circ\text{C}$ (decomposition). HRMS (ESI+): m/z [M]⁺ calculated for $\text{C}_{26}\text{H}_{23}\text{S}_2 = 399.1241$ found = 399.1248.

CO₂-adduct 4: In a high-pressure NMR tube, to a solution of bis-ylide **2**, freshly prepared from the protonated precursor **1** (50 mg, 0.094 mmol, 1 eq.) and KHMDS (19 mg, 0.094 mmol, 1 eq.) in THF-*d*₈ (0.4 mL) at $-70\text{ }^\circ\text{C}$, 3 bars of CO_2 were applied. The tube was shaken carefully leading to a colorless solution. Because of thermal instability of **4**, the product was characterized at $0\text{ }^\circ\text{C}$ in presence of hexamethyldisilazane and CO_2 without any purification. ^1H NMR (400 MHz, 273 K, CD_3CN): $\delta = 7.30\text{--}7.42$ (br s, 12H, CH_{ar}), 7.65-7.88 (br s, 8H, CH_{ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 273 K, CD_3CN): $\delta = 40.2$ (br s, SCS), 130.7 (s, CH_{ar}), 130.8 (s, CH_{ar}), 132.6 (s, CH_{para}), 134.4 (s, C_{ipso}), 167.2 (br s, C- CO_2).

O-methylated CO₂ adduct 6: In a pressure NMR tube, to a solution containing freshly generated CO_2 adduct **4** by above mentioned method, at $-70\text{ }^\circ\text{C}$ then warmed up to room temperature and CO_2 pressure released. Subsequently, MeI (1.0 eq, 6 μL) was added then

precipitation occurs overnight. After removal of volatiles under reduced pressure, the crude was washed with pentane (3 x 2 mL). Then **6** was extracted from the crude using DCM. After concentration, the solution was layered with pentane affording **6** as colorless crystals at room temperature (42 mg, 0.075 mmol, 80% yield). ¹H NMR (300 MHz, 298 K, CD₂Cl₂): δ = 3.67 (s, 3H, CH₃), 7.55–7.65 (m, 16H, CH_{ar}), 7.66–7.75 (m, 4H, CH_{ar}). ¹³C{¹H} NMR (75 MHz, 298 K, CD₂Cl₂): δ = 44.0 (s, SCS), 52.6 (s, CH₃), 129.2 (s, C_{ipso}), 129.7 (s, CH_{ar}), 131.1 (s, CH_{ar}), 133.7 (s, CH_{para}), 164.2 (s, CO₂CH₃). Mp = 160 °C (decomposition). HRMS (ESI⁺): m/z [M]⁺ calculated for C₂₇H₂₃O₂S₂ = 443.1139 found = 443.1140.

Sulfonium ylide **7**: In a Schlenk flask containing bis-ylide precursor **1** (50 mg, 0.094 mmol, 1 eq.) and KHMDS (19 mg, 0.094 mmol, 1 eq.) was added 0.5 mL of THF at –80 °C. After the yellow coloration of the solution, 1 equivalent of phosphonium triflate (35.7 mg, 0.094 mmol, 1eq) was added at the same temperature. The solution was rapidly brought to room temperature then the volatiles were removed under reduced pressure. The crude was extracted with CH₂Cl₂ (3 x 2 mL). The resulting solution was dried then evaporated. The crude was purified by flash silica gel chromatography using pentane and ethyl acetate as solvents. **3** was obtained as white solid (32 mg, 0.056 mmol, 60% yield). Crystals can be grown from a saturated CHCl₃ solution. ¹H NMR (400 MHz, 298 K, C₆D₆): δ = 1.04–1.24 (bs, 12H, CH₃), 1.24–1.34 (d, J_{PC} = 7.0 Hz, 12H, CH₃), 3.80–4.10 (bs, 4H, CH), 6.80–7.00 (bs, 6H, CH_{ar}), 7.90–8.20 (bs, 4H, CH_{ar}). ¹³C{¹H} NMR (126 MHz, 203 K, THF-*d*₈): δ = 24.4 (bs, CH), 48.1 (d, J_{PC} = 6.3 Hz, CH), 55.0 (d, J_{PC} = 158.0 Hz, SCS), 122.5 (q, J_{FC} = 321.9 Hz, CF₃), 128.2 (s, CH_{ar}), 130.4 (s, CH_{ar}), 131.4 (s, CH_{ar}), 138.3 (s, C_{ipso}). ³¹P NMR (121 MHz, 298 K, C₆D₆): δ = 25.7. ¹⁹F NMR (282 MHz, 298 K, C₆D₆): δ = –76.4. HRMS (ESI⁺): m/z [M+H]⁺ calculated for C₂₆H₃₈F₃N₂O₃PS₂ = 579.2092 found = 579.2104.

Intermediate **8**: Variable temperature analysis was performed at –70 °C in THF-*d*₈. Data attributed to intermediate **8** extracted from the crude analysis. ¹H NMR (400 MHz, 203 K, THF-*d*₈): δ = 0.70–0.90 (bs, 8H, CH₃), 1.10–1.40 (bs, 16H, CH₃), 3.50–4.00 (bs, 4H, CH), 7.20–8.00 (m, 20H, CH_{ar}). ¹³C{¹H} NMR (126 MHz, 203 K, THF-*d*₈): δ = 24.4 (bs, CH₃), 24.7 (bs, CH₃), 34.5 (d, J_{PC} = 96.8 Hz, SCS), 47.1 (d, J_{PC} = 17.5 Hz CH), 49.6 (bs, CH), 122.4 (q, J_{FC} = 322.6 Hz, CF₃), 128.7 (s, CH_{ar}), 131.3 (s, CH_{ar}), 133.7 (s, CH_{ar}), 139.1 (s, C_{ipso}). ³¹P NMR (121 MHz, 203 K, THF-*d*₈): δ = 46.1.

3.3. X-ray Data

The data of the structures for **3**, **5**, **6-I**, **6-OTf** and **7** were collected at 193 K on a Bruker-AXS APEX II CCD Quazar diffractometer (**7**) equipped with a 30 W air-cooled microfocus source and on a Bruker-AXS D8-Venture diffractometer (**3**, **5**, **6-I** and **6-OTf**) equipped with a Photon III-C14 detector with MoK α radiation (wavelength = 0.71073 Å) by using phi- and omega-scans. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied [48]. The structures were solved using an intrinsic phasing method (ShelXT) [49] and refined using the least-squares method on F² (ShelXL-2014) [50]. All non-H atoms were treated anisotropically. All H atoms attached to C atoms were fixed geometrically and treated as riding on their parent atoms with C–H = 0.95 Å (aromatic), 0.98 Å (CH₃), 0.99 Å (CH₂) or 1.0 Å (CH) with U_{iso}(H) = 1.2U_{eq}(CH, CH₂) or U_{iso}(H) = 1.5U_{eq}(CH₃). The structures **3** and **6-I** were found to be disordered. Several restraints (SAME, SADI, SIMU, DELU) were applied to refine these disorders and to avoid the collapse of the structure during the least-squares refinement by the large anisotropic displacement parameters.

Supplementary crystallographic data for CCDC-2250100 (**3**), CCDC-2250101 (**5**), CCDC-2250102 (**6-I**), CCDC-2250103 (**6-OTf**), CCDC-2250104 (**7**) can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>.

4. Conclusions

In summary, *S,S*-bis-ylide **2** readily reacts with MeI to give the C-methylated salt **3**. Moreover, **2** also reacts with CO₂ to give betaine **4** which was characterized in solution by NMR spectroscopy at low temperature. CO₂ adduct **4** was still reactive and undergoes O-silylation and O-alkylation reactions, in the presence of HMDS and MeI respectively, to afford the corresponding salts **5** and **6**. Finally, the high leaving group ability of sulfide ligand in **2** was demonstrated by an original reaction with phosphonium ions, yielding a stabilized ylide **7** probably through the transient formation of a strongly electrophilic phosphino(sulfonio)carbene **9**. Efforts are currently underway to extend the potential of this type of ylides.

Supplementary Materials: The following supporting information are available online at: www.mdpi.com/xxx/s1. NMR spectra and crystallographic data

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