Mixed Bisylides

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Synthesis of a Mixed Phosphonium–Sulfonium Bisylide $R_3P{=}C{=}SR_2$**

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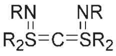
Phosphonium and sulfonium ylides are highly nucleophilic species, which feature a totally different reactivity. Whereas the former have been used extensively for olefination reactions,[1] the later have mostly been involved in epoxidation reactions.[2] Carbodiphosphoranes (**A**) contain two cumulated phosphorus ylide functions, and formally possess a carbon atom with two negative charges, which are stabilized by two phosphonium groups. Since their discovery in 1961 by Ramirez et al.,[3] their unique bonding system and reactivity have attracted considerable interest.[1a,4,5] In contrast, only one example of a sulfur-containing bisylide (**B**) has been reported.[6]

$R_3P{=}C{=}PR_3$

A



$\overset{RN}{\overset{\|}{R_2S}}{=}C{=}\overset{NR}{\overset{\|}{SR_2}}$

B

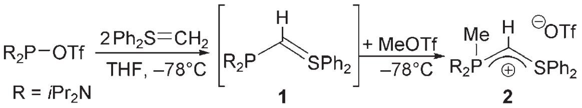
$R_3P{=}C{=}SR_2$

C

Here we report the synthesis and characterization of the first persistent mixed phosphorus–sulfur bisylide (**C**). Such compounds have never been isolated or even observed by spectroscopic methods.

Abstraction of a proton from the corresponding conjugated acid is the classical method for preparing ylides; thus, phosphonium salt **2**, (Scheme 1) which already features the phosphorus-carbon-sulfur (PCS) skeleton, appeared to be a potential precursor for the desired cumulene **C**.

Treatment of bis(diisopropylamino)phosphenium triflate[7] with two equivalents of diphenylsulfonium ylide in THF solution at −78 °C gave C-phosphonium sulfonium ylide **1** in quantitative yield, which could be characterized in solution (^{31}P NMR: $\delta = 53.0$ ppm). However, ylide **1** appeared to be thermally labile, and therefore was treated in situ with one equivalent of MeOTf at −78 °C. The P-methyl derivative **2** was isolated as a white powder in 80 % yield, and X-ray quality single crystals were grown from a CH_2Cl_2 solution at −20 °C (Scheme 1, Figure 1 a).[8]



Scheme 1. Synthesis of sulfonium phosphaylide **2**. Ph = phenyl, Tf = triflate.

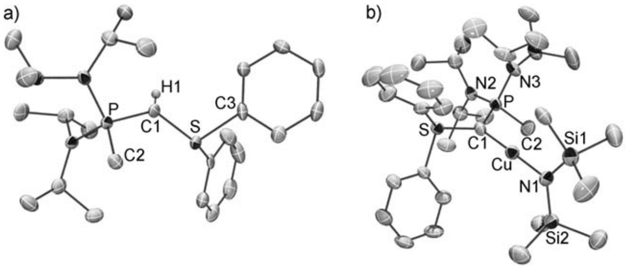


Figure 1. X-ray crystal structures of **2** (a) and **5** (b). H atoms and the triflate anion (for **2**) are omitted for clarity.[8] Thermal ellipsoids are drawn at the 50 % level. Selected bond lengths [Å] and angles [°]. **2**: P-C1 1.721(5), S-C1 1.690(4), P-C2 1.796(4), S-C3 1.810(5), P-C1-S 118.0(3). **5**: P-C1 1.709(5), S-C1 1.677(5), P-C2 1.804(5), C1-Cu 1.903(4), N1-Cu1 1.874(4), P-C1-S 115.3(2), C1-Cu-N 176.97(18), S-C1-Cu 125.7(3), P-C1-Cu 118.7(2).

The cumulene **3** was cleanly generated at −78 °C by deprotonation of the corresponding salt **2** with either potassium or sodium hexamethyldisilazane (Scheme 2). The neutral structure of **3** was indicated by its very high solubility in nonpolar solvents such as pentane. Derivative **3** displays a singlet signal at $\delta = +44.0$ ppm in the ^{31}P{1H} NMR spectrum, while the central carbon atom appears as a doublet at $\delta = 36$ ppm ($J_{PC} = 86.4$ Hz) in the ^{13}C NMR spectrum. Although **3** is stable for days at temperatures lower than −20 °C, it decomposes ($t_{1/2} = 10$ h, in C_6D_6) at room temperature to give a complex mixture.

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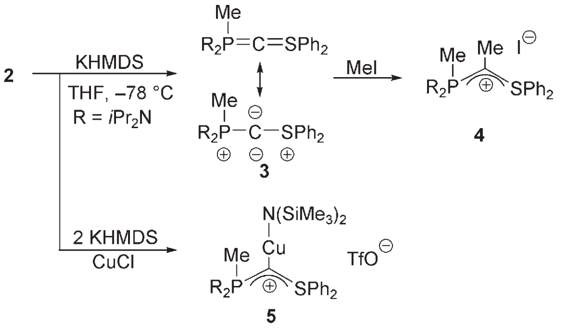


Scheme 2. Synthesis and reactivity of bisylide **3**.

All attempts to grow X-ray quality single crystals for diffraction analysis failed because of the high reactivity of **3**. However, the formation of **3** was clearly demonstrated by its chemical reactivity. Addition of MeI to a solution of **3** in THF cleanly and quantitatively gave the C-methylated salt **4**, which was fully characterized, including by X-ray diffraction analysis.[8] Furthermore, we also successfully synthesized the Cu^I complex **5** by the reaction of **2** with copper chloride in the presence of an excess of potassium hexamethyldisilazane (KHMDS). X-ray quality crystals of **5** were grown from a toluene solution, and its structure[8] (Figure 1b) showed a similar geometry to that of a carbodiphosphorane–Cu^I complex.[9] The P1–C1–S1 angle is rather acute (115.3°) and the P–C1 (1.709 Å) and S–C1 bond lengths (1.677 Å) are slightly shorter than those of the corresponding protonated cation **2**.

To gain insight into the electronic structure of **3**, calculations by geometry optimization, natural population analysis (NPA), and natural bond orbital (NBO) analysis were performed on the model compound **6** (R=NMe_2) and its protonated triflate salt **7**. The geometries of **6** and **7** are shown in Figure 2.

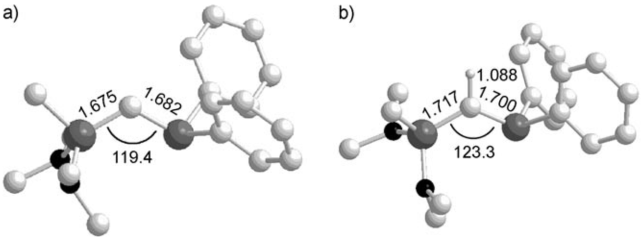


Figure 2. Structures of **6** (a) and **7** (b) optimized at the B3LYP/6-31+G(d,p) level of calculation. Interatomic distances are in Å and bond angle in degrees. H atoms and the triflate anion (for **7**) are omitted for clarity.

The optimized geometry of **7** agrees reasonably well with the experimentally obtained structure of **2**. Each molecule shows a strongly bent P–C–S arrangement. The deprotonation essentially affects only the P–C bond, as can be seen by the larger variation in bond lengths ($\Delta_{P\text{-}C} = 0.042$ Å; $\Delta_{S\text{-}C} = 0.018$ Å), and in the Wiberg bond indexes ($\Delta_{P\text{-}C}$: 0.320; $\Delta_{C\text{-}S}$: 0.134).

Figure 3 shows the two highest occupied molecular orbitals (HOMOs) of **6**. The HOMO is an orbital of σ symmetry which corresponds mainly to the in-plane lone pair of electrons on the C atom, while HOMO-1 is the π(P–C) bonding orbital, which is strongly polarized towards the C atom.

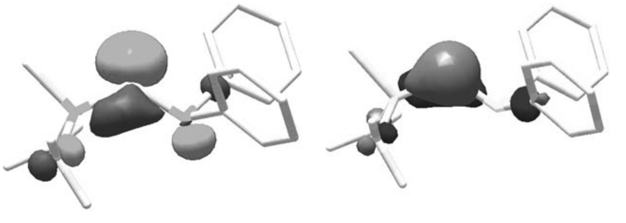
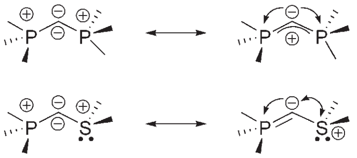


Figure 3. Highest occupied molecular orbitals of **6**: HOMO (left) and HOMO-1 (right).

In the P–C–S moiety of **6,** the NBO procedure identified a P=C bond and a C–S bond, along with lone pair electrons on C and S atoms. The π(P–C) orbital has a low occupancy (1.663) and it is strongly polarized toward the C atom (88 % of contribution), which could also be viewed as a second lone pair of electrons on the C atom. The occupancy of the corresponding antibonding orbital (with an 88 % contribution from the P atom) is 0.171.

Contrary to the carbodiphosphorane case where the n_σ orbital is stabilized by favorable interactions with $\sigma^*_{P\text{-}R}$ orbitals (negative hyperconjugation),[10] the antiperiplanar relationship between the $n_{\sigma C}$ and n_S orbitals in P,S bisylides is destabilizing.[11] This finding explains the small variation of the S–C bond length compared to that of the P–C bond after the deprotonation of **7** [Eq. (1)].



(1)

The NPA shows (Table 1) that the central carbon atom of **6** bears a strong negative charge (−1.357 a.u.), which is compensated by the positive charges of the SPh_2 and P(Me)$(NMe_2)_2$ fragments. Upon protonation, the negative charge of the central carbon atom slightly decreases and most of the positive charge (0.320 a.u.) goes to the P(Me)$(NMe_2)_2$ fragment.

Table 1: Natural population analysis[a] of **6** and **7** (R = NMe_2).

Fragment	C[b]	H	S	SPh_2	P	$PMeR_2$
6	−1.357		0.874	0.585	1.947	0.771
7	−1.235	0.315	0.926	0.797	2.055	1.049

[a] In arbitrary units (a.u.). [b] Central C atom.

As expected, because of the high negative charge density on the central carbon atom, the gas-phase proton affinity of **6** (290.3 kcal mol^{-1}) is larger than that of carbodiphosphoranes (270–280 kcal mol^{-1}).[12]

The preparation of such derivatives should be of major significance because of the synthetic impact of both types of ylides (P and S).

Experimental Section

All manipulations were performed under an inert atmosphere of argon and by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded on a Bruker WM 250 and Bruker Avance 300 spectrometers. ^{1}H and ^{13}C NMR chemical shift were reported in ppm relative to Me_4Si as an external standard. ^{31}P NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to the standard of 85 % H_3PO_4.

2: A solution of *n*BuLi (1.6 M in hexanes, 2.0 mmol) was added dropwise to a solution of diphenylmethylsulfonium triflate (0.70 g, 2.0 mmol) in THF (10 mL) at −78 °C. After 15 min at −78 °C, a solution of bis(diisopropylamino)phosphonium triflate (0.38 g, 1.0 mmol) in THF (20 mL) was added, and the mixture was then stirred at the same temperature for 2 h. Then, methyl triflate (0.16 g, 1.0 mmol) was added and the reaction mixture was slowly warmed to room temperature over 12 h. After removal of all volatiles under vacuum, the product was extracted with CH_2Cl_2. Derivative **2** was obtained in the solid state after crystallization from CH_2Cl_2/Et_2O at −30 °C (0.54 g, 91 %). M.p. 102–103 °C; ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121 Hz): $\delta = 53.0$ ppm; ^{1}H NMR ($CDCl_3$, 25 °C, 300 Hz): $\delta = 1.17$ (d, $^4J_{HH} = 7$ Hz, 24 H, CH_3), 2.02 (d, $^2J_{PH} = 12.9$ Hz, 3 H, PCH_3), 2.42 (d, $^2J_{PH} = 13.9$ Hz, 1 H, CH), 3.52–3.74 (m, 4 H, CH), 7.43–7.52 ppm (m, 10 H, CH_{arom}); ^{13}C NMR ($CDCl_3$, 25 °C, 75 Hz): $\delta = 15.9$ (d, $^1J_{CP} = 109.0$ Hz, CH_3), 18.4 (d, $^1J_{CP} = 41.6$ Hz, PCH), 23.4 (s, CH_3), 46.9 (d, $^2J_{CP} = 5.5$ Hz, NCH), 121.6 (q, $^1J_{CF} = 319$ Hz, CF_3), 127.1, 130.5, 131.7 (s, CH_{arom}), 137.5 ppm (s, C_{ipso}).

3: C_6D_6 (1 mL) was added to a mixture of KHMDS (0.12 g, 0.6 mmol) and phosphoniosulfonium ylide **2** (0.28 g, 0.5 mmol) at 0 °C, and the mixture was then warmed to room temperature. The product **3** was characterized without any purification. ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121 Hz): $\delta = 44.6$ ppm; ^{1}H NMR ($CDCl_3$, 25 °C, 300 Hz): $\delta = 1.17$ (d, $^4J_{HH} = 6.0$ Hz, 12 H, CH_3), 1.36 (d, $^4J_{HH} = 6.0$ Hz, 12 H, CH_3), 1.79 (d, $^2J_{PH} = 12.0$ Hz, 3 H, PCH_3), 3.44 (d-sept, $^3J_{PH} = 15.0$ Hz, $^3J_{HH} = 6.0$ Hz, 4 H, CH), 7.01 (t, $^3J_{HH} = 9.0$ Hz, 2 H, CH_{arom}), 7.19 (m, 4 H, CH_{arom}), 8.00 ppm (d, $^3J_{HH} = 6.0$ Hz, 4 H, CH_{arom}); ^{13}C NMR ($CDCl_3$, 25 °C, 75 Hz): $\delta = 21.5$ (d, $^1J_{CP} = 75.7$ Hz, PCH_3), 23.4 (d, $^2J_{CP} < 1$ Hz, CH_3), 24.0 (s, CH_3), 35.9 (d, $^1J_{CP} = 86.6$ Hz, PCS), 45.5 (s, NCH), 123.0, 128.3, 128.6 (s, CH_{arom}), 151.2 ppm (d, $^3J_{CP} = 23.7$ Hz, C_{ipso}).

4: Methyl iodide (0.14 g, 1.0 mmol) was added to the solution of **2** in THF (2 mL), generated from **3** (0.59 g, 1.0 mmol) in the presence of KHMDS (0.24 g, 1.2 mmol) at −78 °C. After warming the solution to room temperature, all volatiles were removed under vacuum. The product was extracted with CH_2Cl_2 and the pure product **5** was obtained after drying under vacuum (0.35 g, 57 %). X-ray quality crystals were grown from CH_2Cl_2/Et_2O solution at −30 °C; ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121 Hz): $\delta = 66.1$ ppm; ^{1}H NMR ($CDCl_3$, 25 °C, 300 Hz): $\delta = 1.19$ (d, $^3J_{HH} = 7$ Hz, 12 H, CH_3), 1.23 (d, $^3J_{HH} = 7$ Hz, 12 H, CH_3), 1.54 (d, $^3J_{PH} = 11.9$ Hz, 3 H, PCH_3), 2.10 (d, $^3J_{PH} = 13.5$ Hz, 3 H, CCH_3), 3.44 (d-sept, $^3J_{PH} = 12.4$ Hz, $^3J_{HH} = 6.7$ Hz, 4 H, CH), 7.34–7.53 ppm (m, 10 H, CH_{arom}); ^{13}C NMR ($CDCl_3$, 25 °C, 75 Hz): $\delta = 11.3$ (d, $^2J_{CP} = 11.1$ Hz, CH_3), 17.9 (d, $^1J_{CP} = 96.1$ Hz, PCH_3), 24.3 (d, $^3J_{CP} = 2.8$ Hz, CH_3), 24.7 (d, $^3J_{CP} = 2.8$ Hz, CH_3), 48.0 (d, $^2J_{CP} = 6.5$ Hz, NCH), 48.9 (d, $^2J_{CP} = 6$ Hz, NCH), 121.6 (q, $^1J_{CF} = 319$ Hz, CF_3), 128.5, 130.5, 131.9 (s, CH_{arom}), 132.2 ppm (s, C_{ipso}).

5: A mixture of phosphonium salt **2** (0.20 g, 3.31 mmol), excess KHMDS (0.20 g, 9.94 mmol), and anhydrous copper(I) chloride (0.033 g, 3.31 mmol) were cooled to −78 °C and then THF (4 mL) was added. The mixture was stirred and warmed to room temperature over 12 h. All volatiles were removed under vacuum and the product was extracted with toluene (3 mL). Pale yellow crystals were grown from a concentrated toluene solution (139 mg, 63 %). M.p. 78–79 °C; ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121 Hz): $\delta = 66.5$ ppm; ^{1}H NMR (C_6D_6, 25 °C, 300 Hz): $\delta = 0.63$ (s, 18 H, $SiCH_3$), 1.07 (d, $^3J_{HH} = 6.7$ Hz, 12 H, CH_3), 1.25 (d, $^3J_{HH} = 6.7$ Hz, 12 H, CH_3), 2.04 (d, $^3J_{PH} = 12.4$ Hz, 3 H, PCH_3), 7.07–7.24 (m, 6 H, CH_{arom}), 8.07–8.10 ppm (m, 4 H, CH_{arom}); ^{13}C NMR ($CDCl_3$, 25 °C, 75 Hz): $\delta = 11.3$ (d, $^2J_{CP} = 11.1$ Hz, CH_3), 17.9 (d, $^1J_{CP} = 96.1$ Hz, PCH_3), 24.3 (d, $^3J_{CP} = 2.8$ Hz, CH_3), 24.7 (d, $^3J_{CP} = 2.8$ Hz, CH_3), 48.0 (d, $^2J_{CP} = 6.5$ Hz, NCH), 48.9 (d, $^2J_{CP} = 6$ Hz, NCH), 121.6 (q, $^1J_{CF} = 319$ Hz, CF_3), 128.5, 130.5, 131.9 (s, CH_{arom}), 132.2 ppm (s, C_{ipso}).

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