Formation of a stable dicarbenoid and an unsaturated $C_2P_2S_2$ ring from two-electron oxidation of the $[C(PPh_2S)_2]^{2-}$ dianion†

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Two-electron oxidation of the $[C(PPh_2S)_2]^{2-}$ dianion with iodine afforded an unexpected mixture of a dimeric Li–I carbenoid $[(Et_2O)(\mu\text{-}Li)][(\mu_4\text{-}Li)\{IC(PPh_2S)_2\}_2]$ and a novel, unsaturated six-membered $C_2P_2S_2$ ring in $[(SPh_2P)_2C_2(PPh_2)_2S_2]$.

Our recent systematic studies of the oxidation of dichalcogenidoimidodiphosphinate monoanions $[(EPR_2)_2N]^-$ (**1**, E = S, Se, Te; R = ^{i}Pr, ^{t}Bu, Chart 1) have revealed new and unanticipated aspects of the chemistry of these well-studied anions.[1] We have shown that one-electron oxidation with iodine produces dimeric dichalcogenides $EPR_2NR_2PE\text{–}EPR_2NPR_2E$ (**2**) with elongated central E–E bonds.[2,3] In one case (E = Te, R = ^{t}Bu) a structural isomer comprised of a contact ion pair in which a $[(\text{TeP}^t\text{Bu}_2)_2\text{N}]^-$ anion is *Te,Te′*-chelated to one Te atom of an incipient cyclic cation $[(\text{TeP}^t\text{Bu}_2)_2\text{N}]^+$ was identified.[3] The formally 6π-electron five-membered cations $[(EPR_2)_2N]^+$ (E = S, Se, Te; R = ^{i}Pr, ^{t}Bu) are obtained as iodide salts by two-electron oxidation of the corresponding anions.[3–5] By contrast, the oxidation of the phenyl-substituted derivatives $[(EPPh_2)_2N]^-$ (E = Se, Te) with one equivalent of iodine was found to be chalcogen-dependent; the five-membered ring $[(TePPh_2)_2N]^+$ was obtained for tellurium, whereas the unusual six-membered ring $[(\mu\text{-}Se)(SePPh_2)_2N]^+$ was the major product in the case of selenium.[5]

In the context of these intriguing and diverse results we turned our attention to the oxidative behaviour of the isoelectronic $[C(PPh_2S)_2]^{2-}$ dianion (**3**), which is prepared from bis(thiodiphenylphosphinoyl)methane upon treatment with two equivalents of methyl-lithium.[6] Le Floch and co-workers have reported recently that mild oxidation of Li_2**3** with hexachloroethane produces the remarkably stable carbenoid $[ClC(PPh_2S)_2]Li(OEt_2)_2$ (**4**).[7,8] In this communication we give details of our complementary investigations of the oxidation of Li_2**3** with iodine, which have led to the structural and spectroscopic characterisation of the stable dicarbenoid $[(Et_2O)(\mu\text{-}Li)][(\mu_4\text{-}Li)\{IC(PPh_2S)_2\}_2]$ (**5**) and the novel, unsaturated six-membered $C_2P_2S_2$ ring in $[(SPh_2P)_2C_2(PPh_2)_2S_2]$ (**6**).

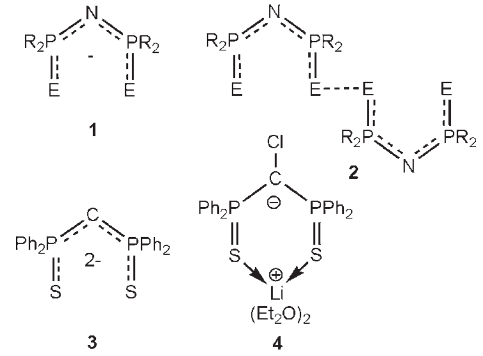
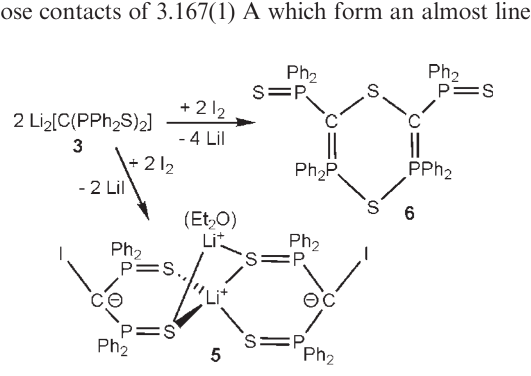


Chart 1

The reaction between Li_2**3** and one equivalent of I_2 was initially performed in a toluene–Et_2O mixture at −80 °C (Scheme 1).‡ The ^{31}P NMR spectrum of the product in d_8-THF revealed a major component (*ca.* 75%) that exhibits a singlet at δ 48.2 and a minor product (*ca.* 25%), which gives rise to two mutually coupled doublets at δ 46.4 and 42.1 $[^2J(^{31}P,^{31}P) = 97\ Hz]$. Both of the new compounds were identified in the solid state by their X-ray crystal structures.†§

Single crystals of the major component were obtained from a toluene solution of the product mixture and identified as the dicarbenoid $[(Et_2O)(\mu\text{-}Li)][(\mu_4\text{-}Li)\{IC(PPh_2S)_2\}_2]$ (**5**) (Scheme 1). In contrast to the monomeric structure of **4**, the iodide derivative **5** adopts a dimeric arrangement of two molecules of the carbene $[:C(PPh_2S)_2]$ and two molecules of LiI. The two five-atom SPCPS fragments in the C_2-symmetric dicarbenoid **5**, each of which contains a C–I bond, are connected by a tetrahedral Li^+ cation and a three-coordinate Li^+ cation solvated by Et_2O (Fig. 1). The spirocyclic Li^+ cation Li(1) has S–Li–S bond angles spanning a range of 99.8(1) to 119.5(3)°, while the 3-coordinate lithium is in a trigonal planar environment ($\sum \angle$Li(2) 359.9°). The Li(2) centre also engages in significant Li···I close contacts of 3.167(1) Å which form an almost linear



Scheme 1 Formation of **5** and **6** by two-electron oxidation of the dianion $[C(PPh_2S)_2]^{2-}$ (**3**) with iodine.

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† Electronic supplementary information (ESI) available: Experimental and crystallographic data in pdf format. CCDC reference numbers 692935 (**5**) and 692936 (**6**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b810796c

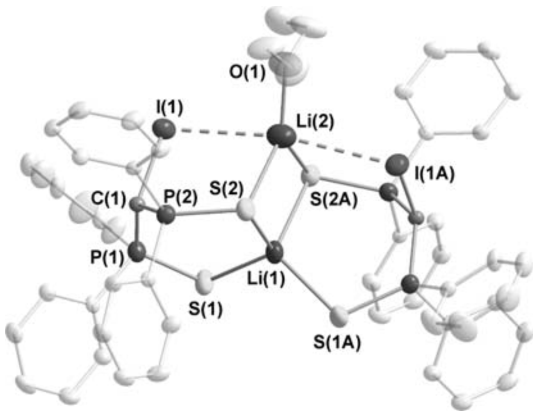


Fig. 1 Crystal structure of **5** with thermal ellipsoid at 50% probability level. Hydrogen atoms have been omitted for clarity. Relevant bond parameters (in Å and °): C(1)–I(1) 2.147(3), C(1)–P(1) 1.750(3), C(1)–P(2) 1.745(3), P(1)–S(1) 1.997(1), P(2)–S(2) 2.022(1), Li(1)–S(1) 2.466(4), Li(1)–S(2) 2.512(5), Li(2)–S(2) 2.461(5), Li(2)···I(1) 3.167(1), P(1)–C(1)–P(2) 123.8(2), P(1)–C(1)–I(1) 111.8(2), P(2)–C(1)–I(1) 107.3(2). Symmetry operation (A): $-x$, y, $0.5 - z$.

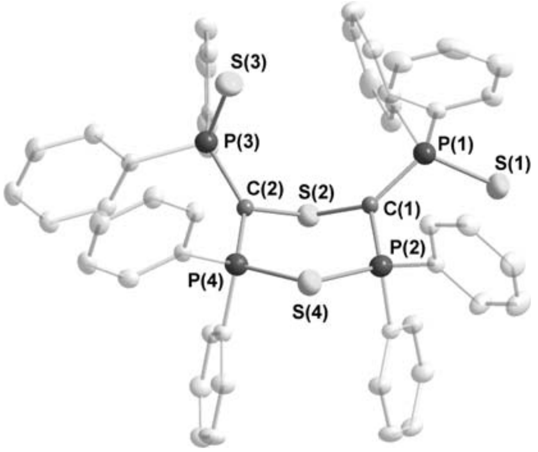


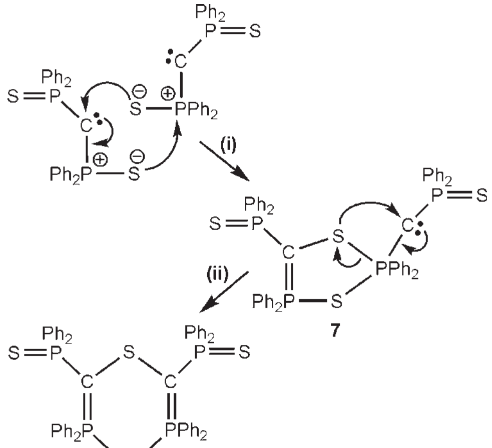
Fig. 2 Molecular structure of **6**·Et$_2$O with thermal ellipsoids at 50% probability level. Hydrogen atoms and Et$_2$O solvate have been omitted for clarity. Pertinent bond lengths (in Å): C(1)–P(1) 1.762(3), C(1)–P(2) 1.692(3), C(1)–S(2) 1.775(3), C(2)–P(3) 1.766(3), C(2)–P(4) 1.692(3), C(2)–S(2) 1.769(3), P(1)–S(1) 1.975(1), P(2)–S(4) 2.133(1), P(3)–S(3) 1.969(1), P(4)–S(4) 2.137(1).

arrangement [∠I(1)–Li(2)–I(1A) = 169.6(3)°]. Consequently, the carbon atom in the PCP unit in **5** is pyramidally distorted with the sum of bond angles being 342.9°, *cf.* 359.9° in **4**.[7] Despite the disparity in the geometry around the carbon center in **4** and **5**, and the strength of the different carbon–halogen bonds, the calculated bond orders for the C–Cl and C–I bonds in **4** and **5**, respectively, are essentially identical (0.90 and 0.92, respectively).[9] The endocyclic P–C and P–S bond distances in **5** are slightly elongated (by *ca.* 0.02 Å), compared to those in **4**.[12]

Notwithstanding the two inequivalent lithium and phosphorus environments in **5**, only a single resonance was observed in both the ^{7}Li (δ 0.73) and ^{31}P NMR spectra at 23 °C indicating fluctionality in solution. Indeed, when a CD$_2$Cl$_2$ solution of the product is cooled to −90 °C, two singlets are observed in the ^{7}Li NMR at δ 2.20 and 1.16. The broadness of the latter singlet, however, suggests that unresolved fluctionality persists even at low temperature affording a broad singlet for the 3-coordinate lithium. Consistently, the ^{31}P NMR spectrum of **5** exhibits two broad, overlapping singlets rather than the expected two mutually coupled doublets at −90 °C. The ^{13}C{^{1}H} NMR spectrum of **5** in d$_8$-THF shows a broad triplet at δ 2.4 ppm [$^1J(^{13}C,^{31}P) = ca.$ 60 Hz] for the PCP-carbon at 23 °C. The triplet of the PCP-carbon in **5** is shifted to higher field by *ca.* 36 ppm compared to that in **4** (38.5 ppm).[7] This upfield shift can be attributed primarily to the greater shielding effect of iodine compared to chlorine,[13] although the change of hybridization (towards sp^3) in **5** compared to that in **4** (carbon lone pair in a pure p orbital)[7] may also be a contributing factor.

Single crystals of the minor product formed in the reaction depicted in Scheme 1 were obtained from a diethyl ether solution. This compound was identified by X-ray crystallography as [(SPh$_2$P)$_2$C$_2$(PPh$_2$)$_2$S$_2$] (**6**), which contains a novel, unsaturated six-membered C$_2$P$_2$S$_2$ ring in a chair conformation (Fig. 2).†§ This heterocycle can be viewed to result from the union of two [:C(PPh$_2$S)$_2$] carbenes without the incorporation of LiI. The crystal structure of **6**·Et$_2$O contains exocyclic Ph$_2$P═S units attached to each carbon, one of which is inclined towards the centre of the ring while the second unit is bent away from the ring. The structure exhibits both endo- and exo-cyclic P–C and P–S bonds with inequivalent bond lengths; the exocyclic P–C bonds are *ca.* 0.07 Å longer and the exocyclic P–S bonds are *ca.* 0.16 Å shorter than the corresponding endocyclic bond lengths, indicating significant double bond character in the endocyclic P═C and exocyclic P═S bonds, respectively, as illustrated in Scheme 1. The exocyclic P═S distances are similar to those reported for the related compounds [Ph$_2$C═C(PPh$_2$S)$_2$][14] and [H(Cl)C(PPh$_2$S)$_2$].[7] The C(1) and C(2) atoms in **6** are only slightly distorted from planarity with the sum of bond angles being 356.2 and 358.5°, respectively.

The formation of the C$_2$P$_2$S$_2$ ring in **6**·Et$_2$O from the two-electron oxidation of **3** involves a sulfur transfer process to generate a CSC unit. A tentative explanation of this observation is shown in Scheme 2. The first step (i) invokes an *inter*molecular nucleophilic attack of a sulfur atom of the initially formed carbene [:C(PPh$_2$S)$_2$] on the electron-deficient carbon centre of another carbene to create a C–S bond, accompanied by a



Scheme 2 Suggested reaction mechanism for the formation of the six-membered C$_2$P$_2$S$_2$ ring in **6**.

rearrangement to afford a five-membered CSPSP ring **7**. Step (ii) involves an *intra*molecular attack of a sulfur atom of the five-membered ring on the exocyclic carbene center in **7** with subsequent ring expansion to give the final product **6**.

Attempts were made to improve the yield of **6** by carrying out the oxidation of Li_2**3** with a mixture of iodine and 12-crown-4 (to remove LiI) at −80 °C.† Although this procedure prevented the formation of **5** and increased the yield of **6** to *ca.* 50% (^{31}P NMR) it was not possible to separate pure samples of **6** from the other products $H_2C(PPh_2S)_2$ and $H(I)C(PPh_2S)_2$. When the reaction of Li_2**3** with iodine was carried out at 23 °C the dicarbenoid **5** was obtained in *ca.* 90% yield (^{31}P NMR), together with $H_2C(PPh_2S)_2$ from which it is difficult to separate; the six-membered ring **6** is not formed under these conditions.†

In summary, participation of the LiI by-product in the two-electron oxidation of Li_2**3** results in the formation of the dimeric carbenoid **5**, which exhibits distorted pyramidal carbon centers and a thermal stability comparable to that found in the monomeric Li–Cl carbenoid **4**.[15] In the absence of LiI incorporation, this oxidation process produces the novel unsaturated six-membered $C_2P_2S_2$ ring in **6**.

Notes and references

‡ Formation of **5** and **6** from Li_2**3** and I_2: $Li_2[C(PPh_2S)_2]$ was synthesized according to the literature.[6,7] A solution of $H_2C(PPh_2S)_2$ (0.287 g, 0.64 mmol) in 30 mL of toluene was cooled to −80 °C and 0.80 mL of MeLi (1.6 M in Et_2O, 1.28 mmol) was added *via* syringe. The reaction mixture was stirred for 15 min at −80 °C and $2\frac{1}{2}$ h at room temperature.

The turbid solution of $Li_2[C(PPh_2S)_2]$ was cooled to −80 °C and a solution of I_2 (0.162 g, 0.64 mmol) in 30 mL of Et_2O was added *via* cannula. The reaction mixture was stirred for $\frac{1}{2}$ h at −80 °C and 3 h at room temperature giving an orange-yellow solution. The solvents were evaporated under vacuum and the resulting tarry product was dissolved to 50 mL of Et_2O. White LiI powder was filtered with a PTFE-disk and the solvent was evaporated *in vacuo* to give a yellow, amorphous powder (0.335 g, 91% calculated as a 75 : 25 mixture of **5** and **6** based on ^{31}P NMR data).

NMR data of **5**: ^{1}H NMR (THF-d_8, 23 °C): δ 7.17–8.02 [m, 40H, C_6H_5]. $^{13}C\{^{1}H\}$ NMR: δ 139.5 [(dd) AXX′, $J(^{13}C,^{31}P) = 101$ Hz; C_{ipso} of C_6H_5], 133.8 [t, $^{2}J(^{13}C,^{31}P) = 5.0$ Hz; C_{ortho} of C_6H_5], 130.2 [s; C_{para} of C_6H_5], 127.8 [t, $^{3}J(^{13}C,^{31}P) = 6.1$ Hz; C_{meta} of C_6H_5], 2.4 [br, t, $^{1}J(^{13}C,^{31}P) =$ *ca.* 60 Hz; PCP-carbon]. ^{31}P NMR: δ 48.2 ppm. ^{7}Li NMR: δ 0.73 ppm. ^{31}P NMR (CD_2Cl_2, −90 °C): δ 50.0 and 49.9 ppm (br, overlapping). ^{7}Li NMR (CD_2Cl_2, −90 °C): δ 2.20 and 1.16 (br) ppm.

NMR data of **6**: ^{31}P NMR (THF-d_8, 23 °C): δ 46.4 [d, $^{2}J(^{31}P,^{31}P) = 97$ Hz] and 42.1 [d, $^{2}J(^{31}P,^{31}P) = 97$ Hz] ppm. ^{1}H and $^{13}C\{^{1}H\}$ NMR data for **6** could not be obtained due to the small quantity of the compound in the product mixture.

§ Crystal data of **5**: $C_{54}H_{50}I_2Li_2OP_4S_4$, $M_r = 1234.74$, monoclinic, space group $C2/c$, $a = 26.997(5)$, $b = 10.517(2)$, $c = 20.050(4)$ Å, $\beta = 109.28(3)°$, $V = 5373(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.526$ g cm^{-3}, $\mu = 1.483$ mm^{-1}, $T = 173(2)$ K, 8595 reflections collected (θ range = 2.99–25.03°), 4 707 unique ($R_{int} = 0.0284$), $R_1 = 0.0312$ [for 3 694 reflections with $I > 2\sigma(I)$] and $wR_2 = 0.0629$ (for all data). Crystal data of **6**·Et_2O: $C_{54}H_{50}OP_4S_4$, $M_r = 967.06$, monoclinic, space group $P2_1/c$, $a = 18.496(4)$, $b = 11.907(2)$, $c = 23.533(5)$ Å, $\beta = 108.68(3)°$, $V = 4910(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.308$ g cm^{-3}, $\mu = 0.363$ mm^{-1}, $T = 173(2)$ K, 16 547 reflections collected (θ range = 2.46–25.03°), 8 634 unique ($R_{int} = 0.0432$), $R_1 = 0.0484$ [for 6 137 reflections with $I > 2\sigma(I)$] and $wR_2 = 0.1149$ (for all data). The structures were solved and refined by using SHELXS-97 and SHELXL-97.[16]

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