

Supplementary information

Formation of a stable dicarbenoid and an unsaturated C₂P₂S₂ ring from two-electron oxidation of the [C(PPh₂S)₂]²⁻ dianion

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General Procedures. All reactions and the manipulations of products were performed under an argon atmosphere by using standard Schlenk techniques or an inert atmosphere glove box. The compounds (Ph₂P)₂CH₂ (Aldrich, 97%), MeLi (1.6 M sol. in Et₂O, Aldrich), I₂ (Aldrich, 99.99+%) and 12-Crown-4 (Alfa Aesar, 98%) were used as received. The dianion Li₂[C(PPh₂S)₂] (**3**) was prepared by a literature method and was used *in situ*.^{1,2} The solvents Et₂O and toluene were dried by distillation over Na/benzophenone under an argon atmosphere prior to use.

Spectroscopic Methods. The ¹H, ⁷Li, ¹³C and ³¹P NMR spectra were obtained in CD₂Cl₂ or d₈-THF on a Bruker DRX 400 spectrometer operating at 399.59, 155.30, 100.49 and 161.77 MHz, respectively. ¹H and ¹³C spectra are referenced to the solvent signal and the chemical shifts are reported relative to (CH₃)₄Si. ⁷Li and ³¹P NMR spectra were referenced externally and the chemical shifts are reported relative to a 1.0 M solution of LiCl in D₂O and to an 85% solution of H₃PO₄, respectively.

X-ray Crystallography. Yellow, plate-shaped crystals of [(Et₂O)(μ-Li)][(μ₄-Li){IC(PPh₂S)₂}]₂ (**5**) were obtained from toluene after 24 h at 5 °C while yellow, block-like crystals of [(SPh₂P)₂C₂(PPh₂)₂S₂]·Et₂O (**6**·Et₂O) were grown from Et₂O after 3 d at 23 °C. The crystals were coated with Paratone 8277 oil and mounted on a glass fiber. Diffraction data were collected on a Nonius KappaCCD diffractometer using monochromated MoK_α radiation (λ = 0.71073 Å) at -100 °C. The data sets were corrected for Lorentz and polarization effects, and empirical absorption correction was applied to the net intensities. The structures were solved by direct methods using SHELXS-97³ and refined using SHELXL-97.⁴ After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions (C-H = 0.95, 0.98 and 0.99 Å for phenyl, CH₃ and CH₂ hydrogens,

respectively). The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times to that of the corresponding carbon for phenyl and CH_2 hydrogens, and 1.5 times for CH_3 hydrogens. In the final refinement the hydrogen atoms were riding on their respective carbon atoms. Crystallographic data are summarized in Table S1.

Improved synthesis of 5. A solution of $H_2C(PPh_2S)_2$ (0.345 g, 0.77 mmol) in 40 mL of Et_2O was cooled to $-80\text{ }^\circ C$ and 1.00 mL of MeLi (1.6 M in Et_2O , 1.60 mmol, slight excess) was added via syringe. The reaction mixture was stirred for 15 min at $-80\text{ }^\circ C$ and 2 ½ h at $23\text{ }^\circ C$. To the cloudy solution of $Li_2[C(PPh_2S)_2]$ a solution of I_2 (0.203 g, 0.80 mmol) in 30 mL of Et_2O was added at room temperature. The reaction mixture was stirred for ½ h after which a solution of 12-Crown-4 (0.141 g, 0.80 mmol) in 10 mL of Et_2O was added via cannula and stirring was continued for 3 h. The white precipitate was removed by filtration with a PTFE-disk and the solvent was evaporated in vacuo to give a yellow, amorphous powder (0.385 g). Based on ^{31}P and 1H NMR data, the product contains a ca. 9/1 mixture of **5** and $H_2C(PPh_2S)_2$, however **6** is not observed. Repeated attempts at further purification of **5** resulted in hydrogen abstraction from solvent(s) and formation of additional $H_2C(PPh_2S)_2$ as well as $H(I)C(PPh_2S)_2$.

NMR data for H(I)C(PPh₂S)₂: ^{31}P NMR (d_8 -THF): δ 49.2 ppm. 1H NMR; δ 6.05 ppm (t, 1H bonded to PCP-carbon, $^2J(^1H, ^{31}P) = 7.2$ Hz). $^{13}C\{^1H\}$ NMR; δ 26.5 ppm (t, PCP-carbon, $^1J(^{13}C, ^{31}P) = 31.2$ Hz).

cf. NMR data for $H(Cl)C(PPh_2S)_2$: ^{31}P NMR (d_8 -THF): δ 46.3 ppm. 1H NMR; δ 5.55 ppm (t, 1H bonded to PCP-carbon, $^2J(^1H, ^{31}P) = 8.9$ Hz). $^{13}C\{^1H\}$ NMR; δ 53.7 ppm (t, PCP-carbon, $^1J(^{13}C, ^{31}P) = 31.2$ Hz)].⁵

Improved synthesis of 6. A solution of $H_2C(PPh_2S)_2$ (0.169 g, 0.38 mmol) in 40 mL of Et_2O was cooled to $-80\text{ }^\circ C$ and 0.50 mL of MeLi (1.6 M in Et_2O , 0.80 mmol, slight excess) was added via syringe. The reaction mixture was stirred for 15 min at $-80\text{ }^\circ C$ and 2 ½ h at $23\text{ }^\circ C$.

The turbid solution of $Li_2[C(PPh_2S)_2]$ was cooled to $-80\text{ }^\circ C$ and a mixture of I_2 (0.102 g, 0.40 mmol) and 12-Crown-4 (0.141 g, 0.80 mmol) in 30 mL of Et_2O was added via cannula. The reaction mixture was stirred for ½ h at $-80\text{ }^\circ C$ and 3 h at $23\text{ }^\circ C$. The pale yellow precipitate was removed by filtration with a PTFE-disk and the solvent was evaporated under vacuum to give a yellow, amorphous powder (0.142 g). Based on ^{31}P and 1H NMR data, this procedure produces a mixture of **6**, $H_2C(PPh_2S)_2$ and $H(I)C(PPh_2S)_2$ in an approximately 2:1:1 ratio; the dicarbenoid **5** is not observed. However, it was not possible to separate a pure sample of **6** from the other products.

Table S1. Crystallographic data for [(Et₂O)(μ-Li)][(μ₄-Li){IC(PPh₂S)₂}₂] (**5**) and [(SPh₂P)₂C₂(PPh₂)₂S₂]₂·Et₂O (**6**·Et₂O).^a

	5	6 ·Et ₂ O
empirical formula	C ₅₄ H ₅₀ I ₂ Li ₂ OP ₄ S ₄	C ₅₄ H ₅₀ OP ₄ S ₄
fw	1234.74	967.06
cryst. system	monoclinic	monoclinic
space group	C2/c	P2 ₁ /c
<i>a</i> , Å	26.997(5)	18.496(4)
<i>b</i> , Å	10.517(2)	11.907(2)
<i>c</i> , Å	20.050(4)	23.533(5)
α, deg.	90.00	90.00
β, deg.	109.28(3)	108.68(3)
γ, deg.	90.00	90.00
<i>V</i> , Å ³	5373(2)	4910(2)
<i>Z</i>	4	4
<i>T</i> , °C	-100	-100
ρ _{calcd} , g/cm ³	1.526	1.308
μ(Mo Kα), mm ⁻¹	1.483	0.363
crystal size, mm ³	0.16x0.06x0.02	0.20x0.12x0.06
<i>F</i> (000)	2472	2024
Θ range, deg	2.99-25.03	2.46-25.03
reflns collected	8595	16547
unique reflns	4707	8634
<i>R</i> _{int}	0.0284	0.0432
reflns [<i>I</i> >2σ(<i>I</i>)]	3694	6137
<i>R</i> ₁ [<i>I</i> >2σ(<i>I</i>)] ^b	0.0312	0.0484
<i>wR</i> ₂ (all data) ^c	0.0629	0.1149
GOF on <i>F</i> ²	1.057	1.042
completeness	0.989	0.997

^a λ (MoKα) = 0.71073 Å. ^b $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$. ^c $wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2]}{\sum wF_o^4}]^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (°) in [(Et₂O)(μ-Li)][(μ₄-Li){IC(PPh₂S)₂}]₂ (**5**) and [(SPh₂P)₂C₂(PPh₂)₂S₂]₂·Et₂O (**6**·Et₂O).

5^a					
C(1)-I(1)	2.147(3)	P(1)-S(1)	1.997(1)	Li(1)-S(2)	2.512(5)
C(1)-P(1)	1.750(3)	P(2)-S(2)	2.022(1)	Li(2)-S(2)	2.461(5)
C(1)-P(2)	1.745(3)	Li(1)-S(1)	2.466(4)	Li(2)···I(1)	3.167(1)
P(1)-C(1)-P(2)	123.8(2)	P(1)-S(1)-Li(1)	106.2(1)	S(1)-Li(1)-S(2A)	99.8(1)
P(1)-C(1)-I(1)	111.8(2)	P(2)-S(2)-Li(1)	100.9(1)	S(2)-Li(1)-S(2A)	102.5(3)
P(2)-C(1)-I(1)	107.3(2)	P(2)-S(2)-Li(2)	111.5(1)	S(2)-Li(2)-S(2A)	105.5(3)
C(1)-P(1)-S(1)	120.6(1)	S(1)-Li(1)-S(2)	117.4(1)	O(1)-Li(2)-	127.2(1)
C(1)-P(2)-S(2)	118.6(1)	S(1)-Li(1)-S(1A)	119.5(3)	S(2)/S(2A)	
6·Et₂O					
C(1)-P(1)	1.762(3)	C(2)-P(4)	1.692(3)	P(2)-S(4)	2.133(1)
C(1)-P(2)	1.692(3)	C(2)-S(2)	1.769(3)	P(3)-S(3)	1.969(1)
C(1)-S(2)	1.775(3)	P(1)-S(1)	1.975(1)	P(4)-S(4)	2.137(1)
C(2)-P(3)	1.766(3)				
C(1)-S(2)-C(2)	109.1(1)	C(2)-P(4)-S(4)	114.7(1)	P(2)-C(1)-S(2)	109.0(2)
C(1)-P(1)-S(1)	114.6(1)	P(2)-S(4)-P(4)	102.8(1)	P(3)-C(2)-P(4)	124.9(2)
C(1)-P(2)-S(4)	111.5(1)	P(1)-C(1)-P(2)	123.9(2)	P(3)-C(2)-S(2)	122.2(2)
C(2)-P(3)-S(3)	119.2(1)	P(1)-C(1)-S(2)	123.3(2)	P(4)-C(2)-S(2)	111.4(2)

^a Symmetry operation (A): -x, y, 0.5z.

References

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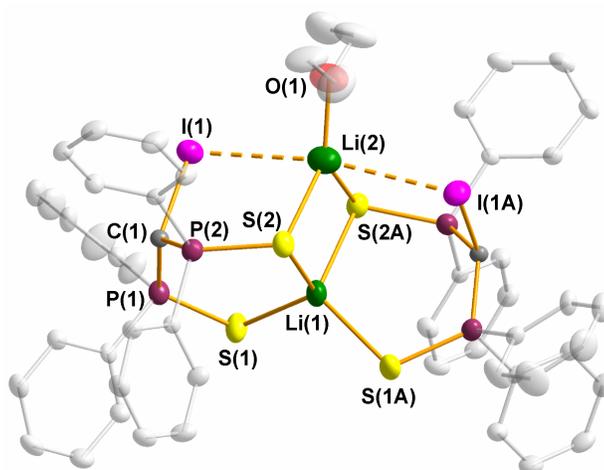


Figure S1. Crystal structure of **5** with 50 % thermal ellipsoid. Hydrogen atoms have been omitted for clarity.

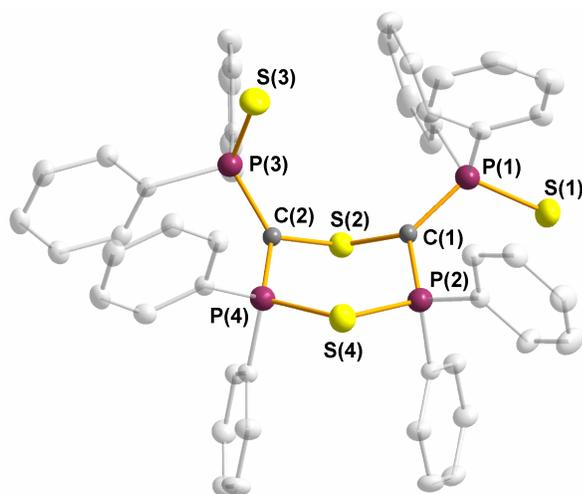


Figure S2. Molecular structure of **6**·Et₂O with 50% thermal ellipsoids. Hydrogen atoms and Et₂O solvate have been omitted for clarity.