Supporting Information for
On the Reactivity of P-Chloro Dithieno[3,2-*b*:2',3'-*d*]phosphole Oxide

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Figure S1. Structure of compound **4** in the solid state (50% probability).

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacements parameters ($\text{\AA}^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Label	x	y	z	U(eq)
C1	5605(4)	6481(4)	5437(5)	34.1(1.0)
C10	1345(4)	5142(3)	3850(4)	27.5(9)
C11	1140(4)	4070(4)	3871(5)	33.2(1.0)
C12	1067(4)	3495(4)	2702(5)	37.8(1.1)
C13	1188(4)	4019(4)	1497(5)	36.3(1.0)
C14	1393(4)	5085(3)	1464(5)	32(1)
C2	4338(4)	6300(3)	5179(4)	28.2(9)
C3	3725(4)	7138(3)	4471(4)	23.3(8)
C4	4552(4)	7934(3)	4213(4)	27.2(9)
C5	3947(4)	8836(3)	3556(4)	25.8(9)
C6	2648(4)	8727(3)	3234(4)	24.0(8)
C7	2089(4)	9651(3)	2687(4)	29.1(9)
C8	2974(5)	10433(3)	2594(4)	33.2(1.0)
C9	1485(4)	5663(3)	2648(4)	24.6(8)
N1	1684(3)	6744(3)	2581(3)	24.6(7)
O1	1204(3)	7523(2)	4934(3)	25.3(7)
P1	2124.9(9)	7490.5(7)	3874.3(9)	20.1(3)
S1	6086.3(1.0)	7665.0(9)	4818.7(1.2)	34.0(4)
S2	4487.8(1.1)	10059.5(8)	3189.3(1.1)	34.2(4)

Table S2: Bond lengths (Ångstrom).

Bond	Length (Å)		
C1 - C2	1.354(6)	C3 - P1	1.800(4)
C1 - H1	0.9500	C4 - C5	1.454(6)
C1 - S1	1.722(5)	C4 - S1	1.716(4)
C10 - C11	1.386(6)	C5 - C6	1.384(6)
C10 - H10	0.9500	C5 - S2	1.708(4)
C11 - C12	1.385(7)	C6 - C7	1.414(6)
C11 - H11	0.9500	C6 - P1	1.803(4)
C12 - C13	1.399(7)	C7 - C8	1.368(6)
C12 - H12	0.9500	C7 - H7	0.9500
C13 - C14	1.379(6)	C8 - H8	0.9500
C13 - H13	0.9500	C8 - S2	1.725(5)
C14 - H14	0.9500	C9 - C10	1.396(6)
C2 - C3	1.417(6)	C9 - C14	1.400(6)
C2 - H2	0.9500	C9 - N1	1.399(5)
C3 - C4	1.369(6)	N1 - H1N	0.95(2)
		N1 - P1	1.656(3)
		O1 - P1	1.479(3)

Table S3: Bond angles (°).

Atoms	Angle (°)		
C1 - C2 - C3	112.1(4)	C3 - C4 - S1	111.7(3)
C1 - C2 - H2	123.9	C3 - P1 - C6	92.48(19)
C10 - C11 - H11	119.6	C4 - C3 - C2	112.6(4)
C10 - C9 - C14	118.8(4)	C4 - C3 - P1	109.6(3)
C10 - C9 - N1	122.4(4)	C4 - C5 - S2	133.0(3)
C11 - C10 - C9	120.5(4)	C4 - S1 - C1	91.0(2)
C11 - C10 - H10	119.8	C5 - C4 - S1	133.8(3)
C11 - C12 - C13	118.8(4)	C5 - C6 - C7	112.6(4)
C11 - C12 - H12	120.6	C5 - C6 - P1	108.6(3)
C12 - C11 - C10	120.8(4)	C5 - S2 - C8	91.2(2)
C12 - C11 - H11	119.6	C6 - C5 - C4	114.9(4)
C12 - C13 - H13	119.5	C6 - C5 - S2	111.9(3)
C13 - C12 - H12	120.6	C6 - C7 - H7	124.1
C13 - C14 - C9	120.2(4)	C7 - C6 - P1	138.0(3)
C13 - C14 - H14	119.9	C7 - C8 - H8	123.7
C14 - C13 - C12	121.0(4)	C7 - C8 - S2	112.6(3)
C14 - C13 - H13	119.5	C8 - C7 - C6	111.7(4)
C2 - C1 - H1	123.7	C8 - C7 - H7	124.1
C2 - C1 - S1	112.5(3)	C9 - C10 - H10	119.8
C2 - C3 - P1	137.7(3)	C9 - C14 - H14	119.9
C3 - C2 - H2	123.9	C9 - N1 - H1N	123(5)
C3 - C4 - C5	114.3(4)	C9 - N1 - P1	124.4(3)

N1 - C9 - C14	118.8(4)	O1 - P1 - N1	114.89(18)
N1 - P1 - C3	109.14(18)	P1 - N1 - H1N	111(5)
N1 - P1 - C6	107.39(17)	S1 - C1 - H1	123.7
O1 - P1 - C3	113.40(17)	S2 - C8 - H8	123.7
O1 - P1 - C6	117.21(17)		

Table S4: Hydrogen coordinates ($\times 10^4$) and isotropic displacements parameters ($\text{\AA}^2 \times 10^3$).

Label	x	y	z	U(eq)
H1	6167.0	6006.0	5907.0	41.0
H10	1389.0	5526.0	4660.0	33.0
H11	1050.0	3725.0	4696.0	40.0
H12	936.0	2759.0	2720.0	45.0
H13	1129.0	3635.0	688.0	44.0
H14	1471.0	5429.0	636.0	38.0
H1N	1750(80)	7120(60)	1770(50)	90(30)
H2	3910.0	5685.0	5442.0	34.0
H7	1207.0	9720.0	2416.0	35.0
H8	2777.0	11108.0	2240.0	40.0

Figure S2. Frontier orbitals for compounds **3a,b,c**; (B3LYP/6-31G(d) level of theory).

Table S5. Cartesian Coordinates of Optimized Species **3a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.615910	1.073985	0.004383
2	6	0	-0.349923	1.047212	0.563139
3	6	0	0.212172	2.341367	0.731072
4	6	0	-0.631518	3.328444	0.291117
5	16	0	-2.132618	2.690529	-0.328279
6	1	0	1.189649	2.538599	1.155732
7	1	0	-0.469274	4.397841	0.291777
8	6	0	-2.241383	-0.229028	-0.164765
9	6	0	-1.478307	-1.304227	0.255639
10	16	0	-3.769723	-0.740958	-0.790430
11	6	0	-2.125953	-2.555487	0.076077
12	6	0	-3.370468	-2.411503	-0.479971
13	1	0	-1.698409	-3.514642	0.344054
14	1	0	-4.086956	-3.182925	-0.727854
15	15	0	0.088444	-0.683102	0.921088
16	8	0	0.507758	-1.030853	2.307496
17	8	0	1.134030	-1.148080	-0.261515
18	6	0	2.442729	-0.696992	-0.358372
19	6	0	3.257210	-0.556671	0.773489
20	6	0	4.565396	-0.128280	0.564402
21	1	0	2.872317	-0.787201	1.760098
22	6	0	4.103999	-0.070463	-1.779913
23	6	0	5.006619	0.122855	-0.736298
24	1	0	5.234577	-0.003604	1.411410
25	1	0	4.402543	0.103581	-2.812104
26	1	0	6.021124	0.451866	-0.937676
27	7	0	2.837565	-0.469418	-1.601464

Table S6. Cartesian Coordinates of Optimized Species **3b**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.395044	-2.385731	-0.546874
2	6	0	2.143340	-2.557011	-0.015138
3	6	0	1.487080	-1.316521	0.204350
4	6	0	2.251473	-0.221963	-0.161061
5	16	0	3.791159	-0.702373	-0.783768
6	1	0	4.119016	-3.143535	-0.814281
7	1	0	1.717203	-3.527941	0.209239
8	6	0	1.618621	1.071052	0.053597
9	6	0	0.346268	1.016501	0.596279
10	16	0	2.130703	2.701830	-0.208590
11	6	0	-0.225076	2.300162	0.808003
12	6	0	0.619008	3.307559	0.417342
13	1	0	-1.208030	2.475926	1.229295
14	1	0	0.451484	4.375355	0.458473
15	15	0	-0.090678	-0.728048	0.874048
16	8	0	-0.539754	-1.138673	2.232863
17	8	0	-1.120590	-1.144086	-0.345687
18	6	0	-2.434659	-0.692031	-0.383591
19	6	0	-2.881348	-0.105573	-1.570974
20	6	0	-3.321992	-0.853017	0.680663
21	1	0	-2.189844	0.010849	-2.403152
22	6	0	-4.628634	-0.399650	0.500445
23	1	0	-2.990036	-1.311234	1.605693
24	6	0	-4.986131	0.174889	-0.719713
25	1	0	-5.360600	-0.498161	1.296743
26	1	0	-6.000339	0.532924	-0.886009
27	7	0	-4.134815	0.320757	-1.743766

Table S7. Cartesian Coordinates of Optimized Species **3c**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.610869	1.079405	-0.012615
2	6	0	-0.349958	1.048326	0.558276
3	6	0	0.226382	2.338491	0.708587
4	6	0	-0.602795	3.326891	0.244483
5	16	0	-2.106114	2.695656	-0.376404
6	1	0	1.202820	2.531586	1.137302
7	1	0	-0.428877	4.394347	0.229027
8	6	0	-2.247873	-0.220041	-0.168368
9	6	0	-1.498255	-1.296860	0.272833
10	16	0	-3.778399	-0.725995	-0.792969
11	6	0	-2.158449	-2.544081	0.110866
12	6	0	-3.398333	-2.395568	-0.454393
13	1	0	-1.743559	-3.503121	0.398480
14	1	0	-4.122384	-3.162973	-0.692604
15	15	0	0.067236	-0.680390	0.944339
16	8	0	0.481330	-1.022588	2.332081
17	8	0	1.117780	-1.161569	-0.237833
18	6	0	2.425533	-0.719628	-0.328102
19	6	0	3.226552	-0.440654	0.781260
20	6	0	4.537029	-0.024411	0.536487
21	1	0	2.850325	-0.562832	1.790459
22	6	0	4.285976	-0.173444	-1.723053
23	1	0	5.190077	0.202824	1.377542
24	1	0	4.733761	-0.061439	-2.709098
25	6	0	2.961474	-0.589984	-1.609202
26	1	0	2.354146	-0.808063	-2.481062
27	7	0	5.076571	0.114790	-0.680216

Table S8. Cartesian Coordinates of Optimized Species 4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.339172	-2.505265	-0.391508
2	6	0	2.087597	-2.581556	0.162321
3	6	0	1.482653	-1.301182	0.293246
4	6	0	2.290324	-0.270602	-0.158413
5	1	0	4.029454	-3.310571	-0.603715
6	1	0	1.626531	-3.513884	0.468418
7	6	0	0.450854	1.094414	0.525813
8	6	0	-0.071936	2.411943	0.629005
9	6	0	0.800505	3.352202	0.143833
10	6	0	1.714893	1.059114	-0.036446
11	1	0	-1.042424	2.657541	1.044455
12	1	0	0.671965	4.425367	0.099265
13	7	0	-1.197353	-1.153365	-0.213774
14	1	0	-0.783098	-1.452760	-1.090288
15	15	0	-0.072828	-0.609440	0.943384
16	8	0	-0.489485	-0.843313	2.356927
17	6	0	-2.536471	-0.704264	-0.325228
18	6	0	-3.130312	-0.624698	-1.593553
19	6	0	-3.289231	-0.363379	0.810212
20	6	0	-4.454934	-0.213059	-1.726311
21	1	0	-2.549928	-0.884925	-2.476607
22	6	0	-4.607967	0.064352	0.660061
23	1	0	-2.844205	-0.456284	1.795115
24	6	0	-5.201346	0.141289	-0.601406
25	1	0	-4.899683	-0.162173	-2.716744
26	1	0	-5.180487	0.325446	1.546357
27	1	0	-6.232243	0.466818	-0.706183
28	16	0	3.802587	-0.861314	-0.755715
29	16	0	2.281856	2.643266	-0.445510

Figure S5: $^{13}\text{C}\{^1\text{H}\}$ NMR of **3a** in CDCl_3 .

Figure S6: ^1H NMR of **3b** in CDCl_3 .

Figure S7: $^{31}\text{P}\{^1\text{H}\}$ NMR of **3b** in CDCl_3 .

Figure S8: $^{13}\text{C}\{^1\text{H}\}$ NMR of **4b** in CDCl_3 .

Figure S9: ^1H NMR of **4** in CDCl_3 .

Figure S10: ^1H NMR (aromatic region) of **4** in CDCl_3 .

Figure S11: $^{31}\text{P}\{^1\text{H}\}$ NMR of **4** in CDCl_3 .

Figure S8: $^{13}\text{C}\{^1\text{H}\}$ NMR of **4b** in CDCl_3 .