Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

Synthesis of a Stable Radical Anion via the One Electron Reduction of a 1,1-Bis-phosphinosulfide Alkene Derivative

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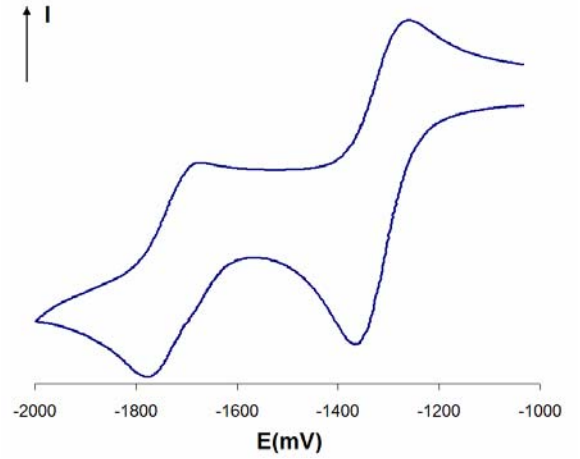
Detailed experimental procedures for electrochemical and EPR measurements.
Computational details and references.
Theoretical structure of **1** and **1**$^{\bullet-}$.

Detailed experimental procedure for electrochemical and EPR measurements

1. Cyclic Voltammetry.

Cyclic voltammetry of **1** was carried out at room temperature at 50 mV/s, in dried CH_3CN, with a BAS electrochemical station (Model CV-50W). nBu_4NBF_4 (0.3 mol/L) was used as a supporting electrolyte. All measurements were performed under dry argon atmosphere. A standard three-electrode cell was used; this cell was equipped with a platinum working electrode (diameter: 1.6mm), a platinum wire counter-electrode and a SCE reference electrode (with 1M LiCl salt-bridge solution). SCE reference electrode was checked against the ferrocenium/ferrocene couple (Fc^+/Fc) for each experiment.



2. Computational details and references

Geometry optimizations of **1** and $\mathbf{1}^{-}$ were performed with the Turbomole [1] program package (ver. 5.8) using the B-P86 exchange-correlation functional [2] and SV (P) **Erreur ! Signet non défini.** standard basis sets. This basis set consists of the contractions: (4s,1p)/[2s,1p] for H, (7s,4p,1d)/[3s,2p,1d] for C, (10s,7p,1d) / [4s,3p,1d] for P and S. Minima were characterized with harmonic frequency calculations (no imaginary frequencies). The electronic properties and hyperfine coupling constants were obtained with the Gaussian 03 package [3] by running single-point calculations at the optimized geometries. Theses single-point calculations were carried out at the B3PW91 level of theory [4]. H, C, P and S were represented by TZVP [5] basis set and Na was represented by 6-31+g* [6] basis set. It consists of the following contractions. (5s,1p)/[3s,1p] for H, (10s,6p,1d)/[4s,3p,1d] for C, (13s,9p,1d)/[5s,4p,1d] for P and S.

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3. Theoretical structure of 1 (x,y,z coordinates)

C	-0.6451623	1.4945477	0.0322951
C	-0.0981174	0.2193447	0.0180016
P	1.6621271	-0.0607786	-0.5403991
S	1.9324814	-0.2798420	-2.5009979
P	-1.1263077	-1.2587284	0.5326368
S	-1.2392122	-1.6145278	2.4881745
H	1.0043922	3.8076501	-3.7183856
H	0.0912778	-3.9843674	-3.5303398
H	-4.2773575	-0.0577745	-3.2108706
C	0.7700488	3.8354142	-2.6414663
H	1.3401987	5.9240276	-2.4020822
C	-0.0130553	-3.9742218	-2.4329666
H	0.1644386	1.7487720	-2.5907041
H	0.5095203	-6.0755787	-2.1994187
H	-0.5433828	-1.8789798	-2.3901262
C	-4.1828170	-0.4348001	-2.1788855
C	0.9547044	5.0171190	-1.9070067
H	3.8052122	1.5433660	-1.6435701
C	0.2901242	2.6748633	-2.0109358
H	-2.0282847	-0.1819070	-2.1470768
C	0.2248380	-5.1411793	-1.6871275
H	-6.3222518	-0.7662713	-1.9343055
C	-0.3800538	-2.7827588	-1.7868097
H	5.3401372	3.2954084	-0.6792130
C	-2.9147763	-0.5136789	-1.5817115
H	3.1756651	-2.3591226	-1.4038336
C	-5.3273100	-0.8294823	-1.4628280
C	3.6843528	1.8896590	-0.6029672
H	-2.7864782	2.7693928	-1.0734012
C	4.5355975	2.8666959	-0.0588009
C	0.6353689	5.0424328	-0.5361413
C	-0.0262994	2.6857884	-0.6329898
H	4.3067069	-4.2579965	-0.1952440
C	3.0907076	-2.4620994	-0.3089483
C	0.0979789	-5.1134249	-0.2877190
C	-0.5030846	-2.7515874	-0.3812263
H	0.7731381	5.9674122	0.0477888
C	-2.7846588	-0.9928867	-0.2605505
H	-4.8936622	3.4873126	0.0553586
C	-5.1995160	-1.2981636	-0.1447350
C	2.6536019	1.3370574	0.1793380
H	0.2831595	-6.0243328	0.3053073
C	-2.9358329	2.5540426	-0.0034221
C	3.7185096	-3.5174153	0.3716501
C	0.1302249	3.8956208	0.0891370
C	2.3339746	-1.5109670	0.4036610
C	-0.2656072	-3.9241464	0.3634882
H	-6.0937290	-1.6017543	0.4246143
C	4.3618301	3.2959000	1.2673033
C	-4.1149067	2.9622043	0.6326615
C	-3.9317848	-1.3806603	0.4565048
H	5.0309770	4.0615594	1.6941027
C	-1.9339291	1.8495990	0.7102185
H	-0.1379971	3.9256200	1.1572029
H	-0.3759229	-3.8861226	1.4602321
C	2.4752456	1.7739740	1.5093739
C	3.5944630	-3.6302154	1.7670204
H	-3.8142961	-1.7420739	1.4922819
C	3.3277537	2.7498465	2.0489838
C	2.2133861	-1.6228817	1.8053394

H	4.0867960	-4.4598167	2.3017627
C	-4.2991321	2.7128427	2.0059132
H	1.6598046	1.3658979	2.1287108
C	-2.1261249	1.6130840	2.0906111
H	-5.2223267	3.0450376	2.5094873
C	2.8387735	-2.6837953	2.4800167
H	1.6067095	-0.9092155	2.3810691
H	3.1809786	3.0881771	3.0882414
C	-3.2980943	2.0492043	2.7320377
H	-1.3526505	1.0823690	2.6639303
H	2.7268158	-2.7707635	3.5732815
H	-3.4261528	1.8601337	3.8105572

mode	7	8	9	10	11	12
frequency	13.66	19.22	29.22	29.80	36.46	40.86

Theoretical structure of $1^{\cdot-}$ (x,y,z coordinates)

C	0.0000000	0.0000000	1.6243107
C	0.0000000	0.0000000	0.1642845
P	-0.4431670	1.4956288	-0.7595612
S	-2.3360481	1.8706213	-1.3385253
P	0.4431670	-1.4956288	-0.7595612
S	2.3360481	-1.8706213	-1.3385253
H	-4.3938395	1.5436533	2.2596721
H	-3.9663338	-1.5322975	-3.2082229
H	-2.8267426	-3.8649522	2.2711995
C	-3.3685491	1.4850442	2.6644479
H	-3.8410777	2.5962988	4.4879828
C	-2.8732321	-1.6488291	-3.2995671
H	-2.6420999	0.3934833	0.9432267
H	-2.9339392	-2.0858823	-5.4340387
H	-2.5272314	-1.2079526	-1.2046717
C	-1.8899197	-3.9494363	1.6943347
C	-3.0636215	2.0716635	3.9063661
H	-1.4602752	4.1733603	-0.3110855
C	-2.3808260	0.8243881	1.9211531
H	-1.9524952	-1.8778639	1.0416311
C	-2.2944189	-1.9516757	-4.5441114
H	-1.5676421	-6.0415106	2.2167538
C	-2.0624163	-1.4689073	-2.1666905
H	-0.5845397	6.2018099	0.9242711
C	-1.4021195	-2.8303639	0.9977022
H	-1.0114663	2.0061442	-3.5686736
C	-1.1837229	-5.1651443	1.6660888
C	-0.5097239	4.1350695	0.2497022
H	-0.2799471	-1.3022798	4.0297264
C	-0.0183838	5.2544279	0.9434268
C	-1.7397736	1.9909162	4.3863177
C	-1.0393799	0.7120759	2.3901153
H	0.4334132	2.3040796	-5.6255627
C	0.0869329	1.9046774	-3.5164130
C	-0.8977605	-2.0743354	-4.6508786
C	-0.6619368	-1.6055548	-2.2661681
H	-1.4707288	2.4652409	5.3467785
C	-0.2000086	-2.9199780	0.2647000
H	1.4707288	-2.4652409	5.3467785
C	0.0183838	-5.2544279	0.9434268
C	0.2000086	2.9199780	0.2647000
H	-0.4334132	-2.3040796	-5.6255627
C	0.7527712	-1.3303445	3.6472580
C	0.8977605	2.0743354	-4.6508786
C	-0.7527712	1.3303445	3.6472580
C	0.6619368	1.6055548	-2.2661681
C	-0.0869329	-1.9046774	-3.5164130
H	0.5845397	-6.2018099	0.9242711
C	1.1837229	5.1651443	1.6660888
C	1.7397736	-1.9909162	4.3863177
C	0.5097239	-4.1350695	0.2497022
H	1.5676421	6.0415106	2.2167538
C	1.0393799	-0.7120759	2.3901153
H	0.2799471	1.3022798	4.0297264
H	1.0114663	-2.0061442	-3.5686736
C	1.4021195	2.8303639	0.9977022
C	2.2944189	1.9516757	-4.5441114
H	1.4602752	-4.1733603	-0.3110855
C	1.8899197	3.9494363	1.6943347
C	2.0624163	1.4689073	-2.1666905

H	2.9339392	2.0858823	-5.4340387
C	3.0636215	-2.0716635	3.9063661
H	1.9524952	1.8778639	1.0416311
C	2.3808260	-0.8243881	1.9211531
H	3.8410777	-2.5962988	4.4879828
C	2.8732321	1.6488291	-3.2995671
H	2.5272314	1.2079526	-1.2046717
H	2.8267426	3.8649522	2.2711995
C	3.3685491	-1.4850442	2.6644479
H	2.6420999	-0.3934833	0.9432267
H	3.9663338	1.5322975	-3.2082229
H	4.3938395	-1.5436533	2.2596721

mode	7	8	9	10	11	12
frequency	18.27	18.38	26.81	30.31	30.85	36.44