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Electronic Supplementary Information

Nucleophilic Behaviour of Dioxo- and Thiooxophosphorane Complexes

$[MoCp(CO)_2\{E,P\text{-}EP(O)(2,4,6\text{-}C_6H_2{}^tBu_3)\}]^-$ (E = O, S).

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Computational Details

All DFT calculations were carried out using the GAUSSIAN03 package,[1] in which the hybrid method B3LYP was used with the Becke three-parameter exchange functional,[2] and the Lee-Yang-Parr correlation functional.[3] An accurate numerical integration grid (99,590) was used for all the calculations *via* the keyword Int=Ultrafine. Effective core potentials and their associated double-ζ LANL2DZ basis set were used for the metal atoms.[4] The light elements (P, O, S, C and H) were described with the 6-31G* basis.[5] Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from the X-ray data of compounds **5** and **6**, and frequency analysis were performed to ensure that a minimum structure with no imaginary frequencies was achieved in each case. Molecular orbitals and vibrational modes were visualized using the MOLEKEL program.[6] The topological analysis of the electron density was carried out with the *Xaim* routine.[7]

(1) Gaussian 03, Revision B.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004

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(6) Portmann, S.; Lüthi, H. P.; MOLEKEL: An Interactive Molecular Graphics Tool. *CHIMIA* **2000**, *54*, 766.

(7) Ortiz, *J*. C.; Bo, C. *Xaim*; Departamento de Química Física e Inorgánica, Universidad Rovira i Virgili: Tarragona, Spain, 1998.

Table S1. Cartesian Coordinates for the Optimized Structure of the Anion in 2

Mo	4.2538200	1.2771860	0.5532080
P	2.3075260	0.9722570	2.0459830
O	2.1200830	2.1185520	-1.5722660
O	4.2979380	-1.2882900	-1.2341780
O	0.9255460	0.4192630	1.7983180
C	2.9051600	1.7876820	-0.7655710
C	4.2397900	-0.3476920	-0.5390650
C	6.6756250	1.4037150	0.7108610
H	7.2759890	0.5168760	0.5530280
C	6.2093900	2.2961090	-0.3062140
H	6.4325870	2.2333270	-1.3631230
C	5.4532620	3.3230660	0.3386070
H	4.9926780	4.1707720	-0.1521970
C	5.4632840	3.0727130	1.7437270
H	4.9712310	3.6625240	2.5046570
C	6.2147850	1.8886860	1.9624030
H	6.3485690	1.3987620	2.9184040
C	2.3907580	2.0963330	3.5633840
C	2.1889350	3.5063320	3.4488250
C	2.8200760	4.3470180	4.3784570
H	2.7151880	5.4199700	4.2555130
C	3.5917860	3.8766040	5.4424460
C	3.5871700	2.4987390	5.6445650
H	4.0998500	2.0993120	6.5095930
C	2.9522170	1.5933460	4.7763470
C	1.2747560	4.2630180	2.4274580
C	2.1207920	5.1976050	1.5301430
H	2.8061690	4.6117630	0.9102910
H	2.7116350	5.9145040	2.1121300
H	1.4660770	5.7700820	0.8598060
C	0.4012620	3.3923570	1.5041130
H	-0.3158850	4.0490250	0.9929960
H	-0.1549330	2.6290360	2.0508070
H	0.9729150	2.8851470	0.7285110
C	0.2711640	5.1214340	3.2497860
H	-0.3932010	5.6652210	2.5661130
H	0.7564780	5.8607220	3.8941390
H	-0.3508710	4.4805340	3.8856000
C	4.3393710	4.8635520	6.3581590
C	3.3240270	5.7924800	7.0658890
H	2.7298480	6.3650550	6.3458880
H	3.8426490	6.5082390	7.7181000
H	2.6287490	5.2106510	7.6822820
C	5.3080650	5.7221070	5.5103370
H	6.0465100	5.0904660	5.0032950
H	5.8479310	6.4374980	6.1453720
H	4.7766680	6.2920980	4.7411690
C	5.1672590	4.1480550	7.4431990
H	4.5339240	3.5650560	8.1216290
H	5.7061100	4.8882180	8.0477910
H	5.9084900	3.4704330	7.0046450
C	2.8952870	0.1193400	5.2988460
C	2.4495210	0.1479240	6.7902170
H	2.3507050	-0.8817130	7.1557320
H	1.4747830	0.6387540	6.8992550
H	3.1566050	0.6556640	7.4531150
C	4.2913860	-0.5393680	5.2084680
H	4.2594160	-1.5553210	5.6261090
H	5.0415040	0.0297430	5.7730390
H	4.5993510	-0.5992850	4.1619610
C	1.8641420	-0.7898100	4.5929760
H	2.1885330	-1.1012410	3.6022530
H	0.8906690	-0.3008040	4.4917090
H	1.7282060	-1.6973540	5.1964300
O	3.5342220	-0.0081090	2.2239260

G (a.u.): -1682.577536

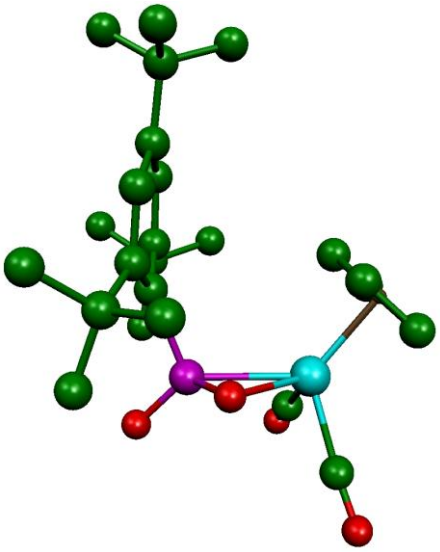

Table S2. Cartesian Coordinates for the Optimized Structure of the Anion in 3

Mo	4.3805460	1.3859060	0.3938060
P	2.5346100	0.8623070	2.0521860
S	4.2005200	-0.3865840	2.2761920
O	1.9870450	1.8722110	-1.5638540
O	4.6419980	-1.1358960	-1.4351060
O	1.1778190	0.2436820	1.7805120
C	2.8600670	1.6777620	-0.8077380
C	4.5089690	-0.2139070	-0.7297800
C	6.7375860	1.8497530	0.2709050
H	7.4295680	1.0522110	0.0332210
C	6.0444060	2.6727350	-0.6705100
H	6.1448150	2.6381910	-1.7473640
C	5.2383940	3.5892660	0.0721290
H	4.6174600	4.3665860	-0.3530530
C	5.4477440	3.3464640	1.4621030
H	4.9674140	3.8608000	2.2829440
C	6.3664170	2.2727090	1.5777000
H	6.6781840	1.8083890	2.5034850
C	2.5160960	1.9940720	3.5886680
C	2.3363570	3.4061000	3.4406900
C	2.9733030	4.2571640	4.3566590
H	2.8917840	5.3291530	4.2048610
C	3.6981870	3.7940990	5.4579850
C	3.6037530	2.4295900	5.7211970
H	4.0317150	2.0423060	6.6376570
C	2.9649550	1.5211410	4.8580310
C	1.3640990	4.1340700	2.4533270
C	2.1099230	5.1453850	1.5541140
H	2.7867190	4.6210190	0.8751910
H	2.6941650	5.8719370	2.1304320
H	1.3899610	5.7071190	0.9444260
C	0.5151340	3.2297900	1.5411270
H	-0.2531080	3.8500770	1.0597910
H	0.0185290	2.4281050	2.0908160
H	1.0929750	2.7660810	0.7437310
C	0.3427080	4.9077670	3.3369610
H	-0.3809550	5.4270760	2.6953230
H	0.8140450	5.6562170	3.9814090
H	-0.2119720	4.2143620	3.9797010
C	4.4661280	4.7789300	6.3579900
C	3.4779050	5.7753090	7.0103080
H	2.9280520	6.3506490	6.2579430
H	4.0131820	6.4878310	7.6525260
H	2.7423410	5.2457180	7.6270440
C	5.4892640	5.5648930	5.5039870
H	6.2125120	4.8853660	5.0388190
H	6.0432350	6.2810710	6.1258300
H	4.9996070	6.1264030	4.7015670
C	5.2379700	4.0650770	7.4846540
H	4.5644200	3.5439580	8.1746490
H	5.8058860	4.7992990	8.0695730
H	5.9477040	3.3319830	7.0851550
C	2.6839600	0.1184560	5.4926650
C	1.8797670	0.3885490	6.7995070
H	1.6469190	-0.5652280	7.2904490
H	0.9322660	0.8920410	6.5733930
H	2.4238920	1.0077650	7.5190890
C	3.9936020	-0.6155890	5.8620310
H	3.7618870	-1.5771110	6.3396160
H	4.6066990	-0.0380680	6.5644900
H	4.5887350	-0.8080610	4.9654880
C	1.7944390	-0.8348620	4.6668350
H	2.3180030	-1.2877820	3.8258680
H	0.9108770	-0.3323180	4.2662060
H	1.4608420	-1.6504030	5.3226830

G (a.u.): -2005.548898

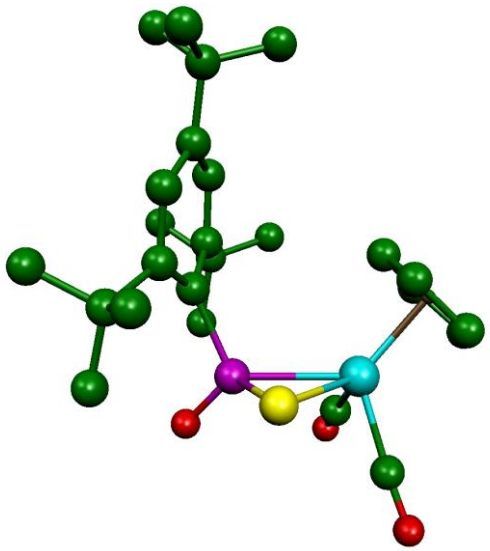

Table S3. Cartesian Coordinates for the Optimized Structure of 5

Mo	4.4812530	1.3902020	0.4825560
P	2.5789710	0.9204840	2.0570960
O	2.1051580	1.8805720	-1.5177950
O	4.8651120	-1.0522390	-1.4425200
O	1.3895340	0.0453540	1.7598910
C	2.9596890	1.6861570	-0.7576860
C	4.6838830	-0.1666130	-0.7120340
C	6.7974570	1.8913560	0.3350540
H	7.5223990	1.1203020	0.1106280
C	6.0841300	2.6831050	-0.6190440
H	6.1891320	2.6364890	-1.6946400
C	5.2614030	3.5994780	0.1080950
H	4.6256520	4.3579040	-0.3282070
C	5.4747780	3.3841880	1.5004410
H	4.9904160	3.9106680	2.3113740
C	6.4174280	2.3319320	1.6363350
H	6.7720740	1.9192910	2.5720200
C	2.5265580	1.9685530	3.6155830
C	2.3360380	3.3791640	3.4459570
C	2.9749500	4.2390590	4.3457870
H	2.8651910	5.3085160	4.2004710
C	3.7283690	3.7880750	5.4364610
C	3.6559880	2.4245110	5.7117730
H	4.0932330	2.0545780	6.6302570
C	3.0079100	1.4983750	4.8744190
C	1.3321550	4.0659830	2.4648800
C	2.0365050	5.0708060	1.5266290
H	2.7051950	4.5515730	0.8344240
H	2.6220280	5.8155730	2.0764280
H	1.2920950	5.6106300	0.9291020
C	0.4843340	3.1126710	1.6011750
H	-0.3033300	3.6959730	1.1095720
H	0.0003180	2.3310230	2.1923920
H	1.0487420	2.6339890	0.8001960
C	0.3137010	4.8384940	3.3522540
H	-0.4378230	5.3184900	2.7140430
H	0.7831600	5.6195850	3.9566990
H	-0.2064600	4.1545130	4.0320290
C	4.4917570	4.7878020	6.3226790
C	3.4906300	5.7625740	6.9885210
H	2.9226120	6.3344030	6.2470960
H	4.0234230	6.4795390	7.6251840
H	2.7730220	5.2199110	7.6142850
C	5.4825690	5.5928840	5.4481600
H	6.2175690	4.9307280	4.9754180
H	6.0285430	6.3200120	6.0614270
H	4.9700630	6.1468960	4.6545170
C	5.2961590	4.0890730	7.4358090
H	4.6459680	3.5619820	8.1431900
H	5.8613450	4.8349380	8.0059830
H	6.0137170	3.3679930	7.0277240
C	2.7125620	0.1141410	5.5350470
C	1.8824300	0.4273240	6.8162000
H	1.6181020	-0.5112470	7.3179800
H	0.9526540	0.9476670	6.5603200
H	2.4274000	1.0460480	7.5344630
C	4.0029950	-0.6230800	5.9603760
H	3.7442160	-1.5547930	6.4781000
H	4.6131010	-0.0267160	6.6473790
H	4.6223500	-0.8748520	5.0949720
C	1.8314700	-0.8432070	4.7105460
H	2.3456820	-1.2806040	3.8575450
H	0.9310220	-0.3526800	4.3328340
H	1.5201150	-1.6725320	5.3568760
S	4.4389490	-0.3648490	2.3708320
C	3.8380850	-1.9914170	1.7637380
H	3.8967850	-2.6987450	2.5949350
H	2.7991000	-1.8774310	1.4387930
H	4.4634840	-2.3341660	0.9388000

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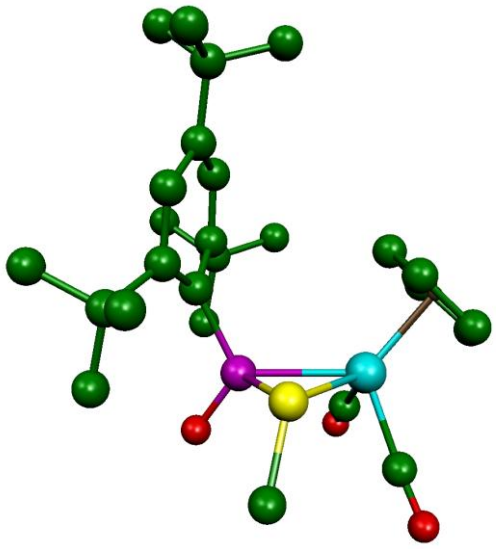

Table S4. Cartesian Coordinates for the Optimized Structure of 6

Mo	4.2743210	1.4018240	0.3207310
P	2.6109950	1.0083230	2.1151670
O	1.9274510	2.1085850	-1.6413320
O	4.3036850	-1.1528650	-1.5020840
O	1.1308440	0.3123060	1.9221960
C	2.7814730	1.8401150	-0.8955310
C	4.2623310	-0.2189050	-0.8140410
C	6.6117680	1.7111520	0.0422590
H	7.2497450	0.8901680	-0.2568160
C	5.9129680	2.5992360	-0.8331890
H	5.9447940	2.5878980	-1.9143330
C	5.2137990	3.5453980	-0.0193260
H	4.6215580	4.3730050	-0.3852180
C	5.5003980	3.2569870	1.3487890
H	5.1150830	3.7879460	2.2089410
C	6.3594220	2.1300150	1.3816640
H	6.7208500	1.6374280	2.2743910
C	2.4527660	2.0364430	3.6499510
C	2.2971590	3.4540990	3.4879670
C	2.9370930	4.2890040	4.4098760
H	2.8655320	5.3612910	4.2655210
C	3.6499830	3.8126230	5.5149300
C	3.5447000	2.4483740	5.7742430
H	3.9631960	2.0608150	6.6934060
C	2.9113280	1.5396520	4.9097510
C	1.3512320	4.1882810	2.4835500
C	2.1343450	5.1411560	1.5539330
H	2.7848570	4.5751680	0.8821960
H	2.7518210	5.8526650	2.1126770
H	1.4370200	5.7202630	0.9365260
C	0.4672260	3.2782710	1.6107420
H	-0.2654650	3.9032970	1.0868860
H	-0.0815580	2.5450240	2.2069680
H	1.0268930	2.7488680	0.8400440
C	0.3572510	5.0257800	3.3397140
H	-0.3567940	5.5309400	2.6784340
H	0.8513960	5.7947290	3.9395610
H	-0.2095380	4.3810840	4.0207290
C	4.4187020	4.7869270	6.4239540
C	3.4296920	5.7901050	7.0653480
H	2.8982740	6.3798000	6.3108800
H	3.9673140	6.4899120	7.7167610
H	2.6804770	5.2685310	7.6717520
C	5.4553120	5.5624750	5.5759910
H	6.1815340	4.8784980	5.1214570
H	6.0064580	6.2724140	6.2045270
H	4.9800590	6.1317330	4.7701300
C	5.1723100	4.0627230	7.5560800
H	4.4884670	3.5503690	8.2423120
H	5.7404180	4.7914290	8.1451760
H	5.8822860	3.3249330	7.1652500
C	2.6587790	0.1270310	5.5291730
C	1.8840210	0.3679260	6.8599080
H	1.6597970	-0.5979970	7.3275370
H	0.9339360	0.8809370	6.6715980
H	2.4476000	0.9607390	7.5850450
C	3.9846870	-0.5991620	5.8537720
H	3.7731410	-1.5601580	6.3383500
H	4.6144800	-0.0177890	6.5360720
H	4.5599490	-0.7941480	4.9447470
C	1.7531900	-0.8166000	4.7117890
H	2.2438010	-1.2329730	3.8326720
H	0.8339630	-0.3197680	4.3898780
H	1.4724480	-1.6631750	5.3492860
C	0.8860750	-0.5899650	0.8347520
H	1.6111830	-1.4102390	0.8373620
H	-0.1193510	-0.9853450	0.9946020
H	0.9273480	-0.0652000	-0.1246470
S	4.1078190	-0.3878880	2.2224370

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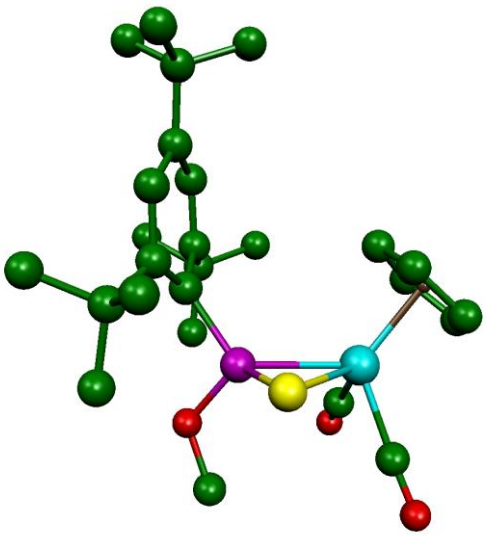

Table S5. Cartesian Coordinates for the Optimized Structure of 8-S

Mo	4.4249860	1.3757470	0.4452010
P	2.5294730	0.9717370	2.0369530
O	2.0321400	1.7357790	-1.5656850
O	4.7672960	-1.2092260	-1.2963700
O	1.3310010	0.1078230	1.7728320
C	2.8935420	1.5903020	-0.8038070
C	4.6077520	-0.2642490	-0.6417130
C	6.7285510	1.8928310	0.1990640
H	7.4550560	1.1217350	-0.0199920
C	5.9718110	2.6369460	-0.7589350
H	6.0410120	2.5503580	-1.8349200
C	5.1607050	3.5707020	-0.0384430
H	4.5013940	4.3044220	-0.4820600
C	5.4275090	3.4142390	1.3531750
H	4.9678060	3.9669760	2.1610140
C	6.3894710	2.3810000	1.4948550
H	6.7831580	2.0094280	2.4323010
C	2.5090340	2.0066810	3.6025910
C	2.3505970	3.4229750	3.4472480
C	2.9953110	4.2582810	4.3656230
H	2.9063590	5.3315530	4.2351910
C	3.7245740	3.7781100	5.4598470
C	3.6232180	2.4127920	5.7158640
H	4.0416730	2.0239940	6.6350350
C	2.9701040	1.5082030	4.8585520
C	1.3657770	4.1438160	2.4708490
C	2.0847940	5.1873010	1.5874160
H	2.7725970	4.6982800	0.8919190
H	2.6526750	5.9160690	2.1751210
H	1.3503490	5.7439020	0.9930610
C	0.5409220	3.2268590	1.5484300
H	-0.2321070	3.8302430	1.0578300
H	0.0379510	2.4236320	2.0928620
H	1.1299060	2.7822050	0.7445030
C	0.3276570	4.8766870	3.3686720
H	-0.4105200	5.3855290	2.7370930
H	0.7860600	5.6283580	4.0174270
H	-0.2061860	4.1632000	4.0061060
C	4.4967600	4.7511930	6.3678120
C	3.5084060	5.7417040	7.0294850
H	2.9641680	6.3341100	6.2863580
H	4.0482070	6.4398110	7.6809780
H	2.7698750	5.2093010	7.6394990
C	5.5175270	5.5421430	5.5150370
H	6.2442780	4.8679870	5.0465340
H	6.0705050	6.2514110	6.1427430
H	5.0285060	6.1142620	4.7194110
C	5.2692740	4.0234860	7.4848940
H	4.5974060	3.5032830	8.1769400
H	5.8418940	4.7509240	8.0712240
H	5.9771050	3.2913420	7.0796170
C	2.6487640	0.1194900	5.5020360
C	1.7651590	0.4377140	6.7459350
H	1.4879950	-0.4978820	7.2462520
H	0.8425100	0.9479760	6.4474030
H	2.2768770	1.0689060	7.4779440
C	3.9212790	-0.6156810	5.9832080
H	3.6390320	-1.5487760	6.4855340
H	4.5014070	-0.0238220	6.6990730
H	4.5772520	-0.8683210	5.1455540
C	1.8092240	-0.8514010	4.6491800
H	2.3649130	-1.2949230	3.8236870
H	0.9204850	-0.3748710	4.2299120
H	1.4801810	-1.6767210	5.2917450
S	4.4605200	-0.3000920	2.4151220
H	3.9929310	-1.4365710	1.8542900

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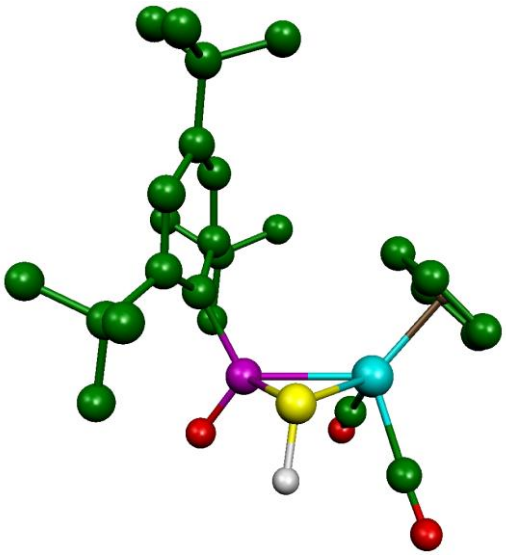


Table S6. Cartesian Coordinates for the Optimized Structure of 8-O

Mo	4.3761560	1.3500440	0.3097850
P	2.7578480	0.9964210	2.1415610
O	1.9244000	1.7515480	-1.6068790
O	4.5375640	-1.3138470	-1.3478510
O	1.3084800	0.2466300	1.8681310
C	2.8244700	1.6011580	-0.8819120
C	4.4482020	-0.3425790	-0.7201420
C	6.6860220	1.7627010	-0.0655260
H	7.3578340	0.9614080	-0.3432920
C	5.9098750	2.5621660	-0.9621980
H	5.9093330	2.4946060	-2.0417130
C	5.1871120	3.5137990	-0.1760170
H	4.5389370	4.2874820	-0.5644670
C	5.5329360	3.3142660	1.1946870
H	5.1492340	3.8708590	2.0392950
C	6.4547100	2.2386030	1.2573400
H	6.8712500	1.8156110	2.1617160
C	2.5277870	2.0234600	3.6640490
C	2.3582210	3.4390270	3.4979400
C	2.9616270	4.2809180	4.4379260
H	2.8805100	5.3523560	4.2919910
C	3.6464920	3.8125880	5.5638250
C	3.5469200	2.4473990	5.8219080
H	3.9388840	2.0648180	6.7547790
C	2.9539390	1.5317320	4.9374170
C	1.4232300	4.1593260	2.4745630
C	2.2045240	5.1478980	1.5816620
H	2.8960350	4.6116780	0.9267130
H	2.7786580	5.8742680	2.1666060
H	1.5090760	5.7098790	0.9466280
C	0.5938790	3.2364940	1.5633750
H	-0.1449410	3.8453830	1.0292240
H	0.0527350	2.4750090	2.1306440
H	1.1929330	2.7399170	0.8006850
C	0.3818430	4.9553490	3.3137650
H	-0.3246420	5.4544590	2.6398380
H	0.8385280	5.7244280	3.9425730
H	-0.1884490	4.2837510	3.9651350
C	4.3812290	4.7946070	6.4921940
C	3.3686460	5.7959000	7.0986840
H	2.8578220	6.3802760	6.3260650
H	3.8832230	6.5008110	7.7630400
H	2.6036800	5.2736230	7.6844600
C	5.4395190	5.5707960	5.6719150
H	6.1817360	4.8876970	5.2427240
H	5.9684130	6.2861930	6.3132390
H	4.9859530	6.1337050	4.8492690
C	5.1034370	4.0789060	7.6499030
H	4.4015110	3.5650910	8.3165140
H	5.6488310	4.8130710	8.2534810
H	5.8294390	3.3439140	7.2841190
C	2.6965750	0.1149810	5.5442360
C	1.8662800	0.3455140	6.8428560
H	1.6366910	-0.6233230	7.3017320
H	0.9175630	0.8455030	6.6166070
H	2.3930480	0.9462630	7.5890010
C	4.0175160	-0.5942350	5.9220780
H	3.7983430	-1.5585060	6.3964510
H	4.6116310	-0.0061480	6.6301070
H	4.6326420	-0.7811540	5.0377870
C	1.8377600	-0.8387100	4.6890520
H	2.3665260	-1.2481050	3.8289500
H	0.9243020	-0.3552030	4.3316440
H	1.5421410	-1.6900210	5.3133360
S	4.3002070	-0.3365150	2.3128000
H	1.3374520	-0.1812010	0.9936390

G (a.u.): -2006.066493

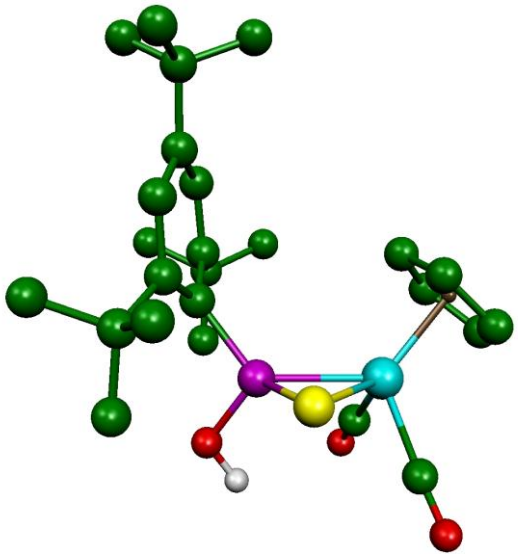


Table S7. Relative energies of DFT-computed isomers.

	5	**6**	**8-S**	**8-O**
G_{gas} (a.u.)	-2045.335898	-2045.343917	-2006.046941	-2006.066493
ΔG_{gas} (Kcal/mol)	5.03	0.00	12.27	0.00

Table S8. Topological properties of the electron density at some bond critical points in the anion of **2**.[a]

Bond	ρ	$\nabla^2(\rho)$
Mo–P	0.488	2.238
Mo–O	0.448	7.495
P–O	1.240	-17.624
P=O	1.428	35.292

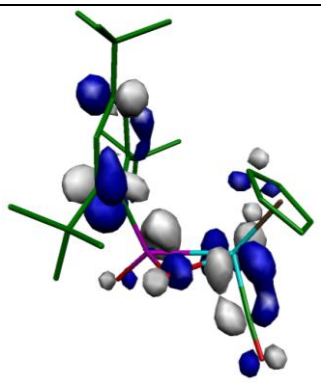
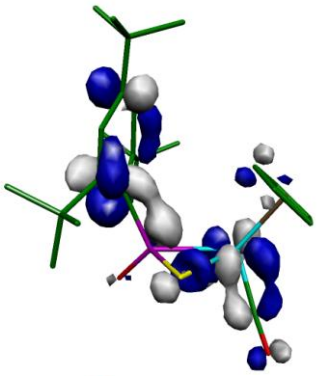
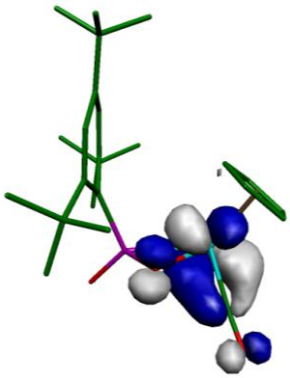
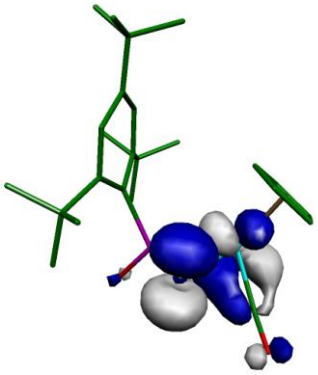
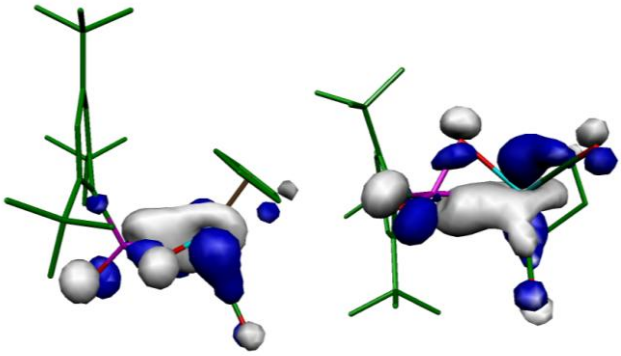
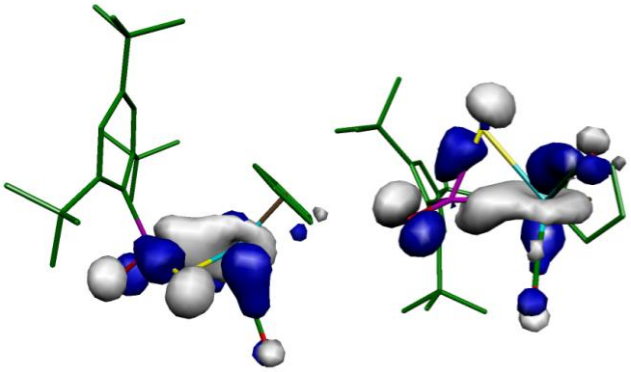
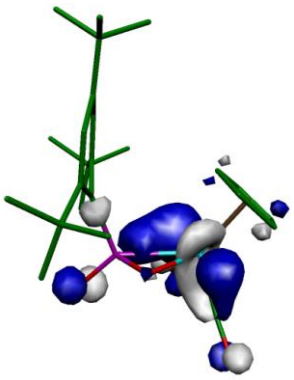
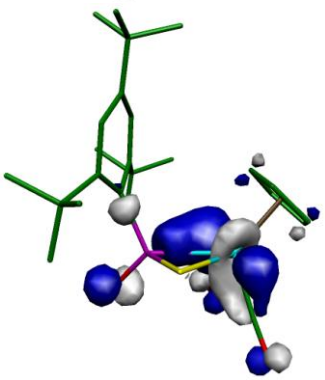
[a] Values of the electron density [ρ] at the bond critical points are given in eÅ^{-3}; values of the Laplacian of the electron density [$\nabla^2(\rho)$] at these points are given in eÅ^{-5}.

Table S9. Topological properties of the electron density at some bond critical points in the anion of **3**.[a]

Bond	ρ	$\nabla^2(\rho)$
Mo–P	0.463	2.368
Mo–S	0.381	2.662
P–S	0.901	-4.496
P=O	1.404	33.996

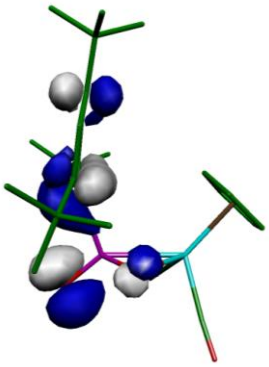
[a] Values of the electron density [ρ] at the bond critical points are given in eÅ^{-3}; values of the Laplacian of the electron density [$\nabla^2(\rho)$] at these points are given in eÅ^{-5}.

Table S10: Selected molecular orbitals of the anions in compounds **2** and **3**.

MO Energy (eV)	**2**	**3**	OM Energy (eV)
LUMO (124) 1.74			LUMO (128) 1.91
HOMO (123) -1.65			HOMO (127) -1.48
MO 122 -1.93			MO 126 -2.02
MO 121 -2.24			MO 125 -2.29

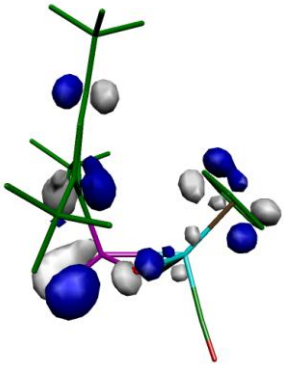
MO 120

-2.82



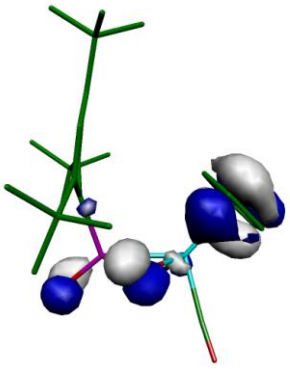
MO 118

-3.56



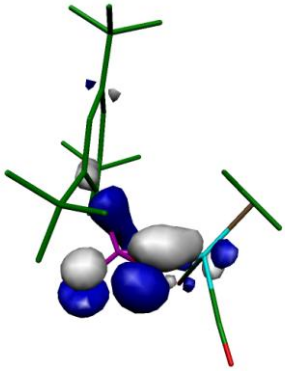
MO 117

-3.61



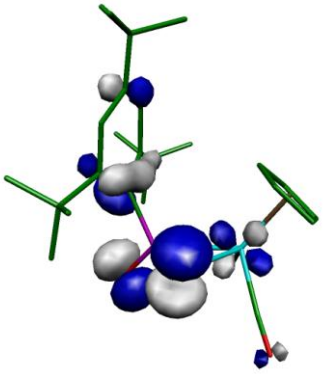
MO 115

-4.15



MO 124

-2.71



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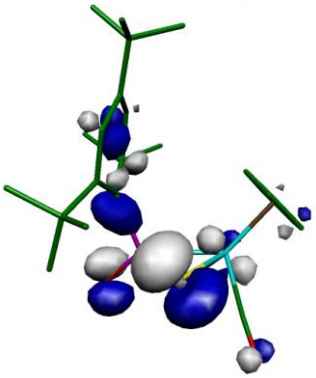
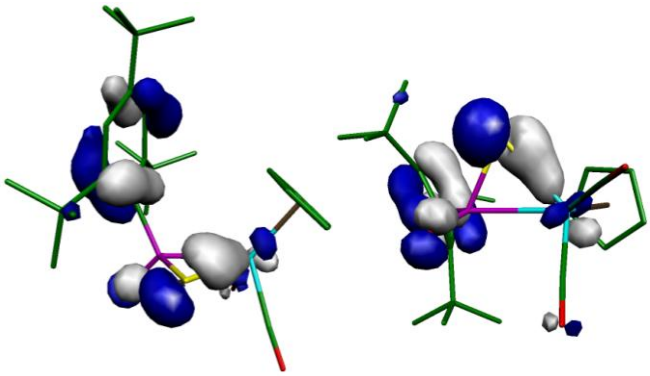


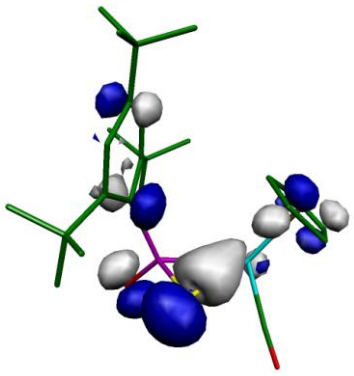
MO 122

-3.48



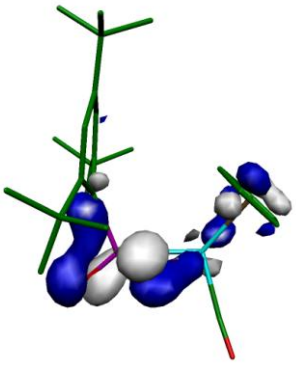
MO 120

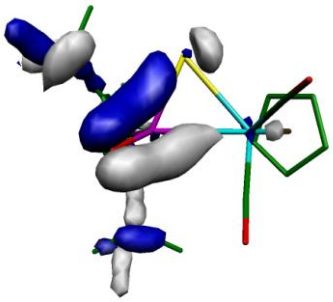
-3.86



MO
114

-4.27





MO
117

-4.98