Supplementary Information

(Complete Gaussian Reference, Tables S1 and S2 and Figures S1-S4)

A new series of bis(ene-1,2-dithiolato)tungsten(IV), -(V), -(VI) complexes as reaction centre models of tungsten enzymes: preparation, crystal structures and spectroscopic properties.

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Complete Gaussian Reference.

Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Table S1. The optimized Cartesian coordinates and converged SCF energy of $\mathbf{W^{VI}O_2L^{COOMe}}$.

Charge = -2 Multiplicity = 1

O	-0.0203909037	0.0266560859	-0.0037868569
O	-0.0070160407	-0.0026809096	2.2552133185
C	0.6369819762	0.0044998434	1.0377514375
C	-1.4268123337	0.0022160422	2.1823495948
H	-1.8029215648	0.9015163338	1.6682625810
H	-1.7763808826	-0.0094949797	3.2247601826
H	-1.8075299736	-0.8821318036	1.6465171821
S	7.6286290123	-0.0813441105	1.9202842550
S	5.4531352581	-2.4723033450	2.5495364745
S	2.8192896069	-0.0470913493	2.7866596993
S	4.5910356147	-0.0471017660	0.0106388113
O	5.5684106251	1.9590201438	2.3242428575
O	5.2578261636	0.1528534590	4.3942357735
O	9.9324282550	-3.3286274979	1.8613724769
O	10.2873982730	-1.1177798238	1.5609306980
O	7.3561708927	-5.0422928995	1.4257339929
O	7.8877372970	-4.6137712821	3.5793848121
O	2.0883807652	-1.0283674564	-2.0540826766
O	2.0080230954	1.2160222982	-1.8077742933
C	8.0717452674	-1.8089140398	2.0303711718
C	7.1261533559	-2.7818612161	2.2829777440
C	9.4635427428	-2.1901931319	1.8220636898
C	11.6519172481	-1.4500111324	1.3398756361
C	7.4832633614	-4.2429989872	2.3303710236
C	2.0901298615	-0.0134580797	1.1556584723
C	2.8689807167	-0.0279564115	0.0164667367
C	2.2618453021	-0.0475136256	-1.3603785473
C	1.3962428344	1.2773866884	-3.0952292821
H	12.0969374640	-1.9413303741	2.2202428989

H	12.1607383807	-0.4951389814	1.1442346150
H	11.7694320779	-2.1242867901	0.4763495983
H	2.0491959907	0.8427268626	-3.8684607242
H	1.2309102412	2.3453902660	-3.2961787339
H	0.4380045357	0.7359068379	-3.0949667088
C	8.2789718322	-5.9809903192	3.6943971162
H	8.6023713287	-6.1118997766	4.7368088521
H	7.4385371119	-6.6567652692	3.4704324041
H	9.1079096950	-6.2059083004	3.0061404946
W	5.2792341057	0.2631099802	2.6473733924

E(RB3LYP) = -2877.13354776

Table S2. The optimized Cartesian coordinates and converged SCF energy of $\mathbf{W^{VI}O(S)L^{COOMe}}$.

Charge = -2 Multiplicity = 1

O	0.0490955880	-0.0518907540	0.0006029244
O	-0.0034874948	-0.0108253468	2.2583868115
C	0.6737669616	-0.0196166425	1.0612445164
C	-1.4204362673	-0.0581704711	2.1467682264
H	-1.8120350024	0.8121235461	1.5957710172
H	-1.7983845279	-0.0519951741	3.1790785457
H	-1.7540759081	-0.9706091824	1.6271787266
S	7.5983244292	0.0357758926	2.0223133331
S	5.4563938585	-2.3564043711	2.6930979024
S	2.8140202322	0.0500545041	2.8722842567
S	4.6588040361	0.0210754982	0.1768749940
O	5.5466733532	2.0593928916	2.4131170837
O	9.9221439257	-3.1904167618	1.9114960901
O	10.2541202087	-0.9783524853	1.5894870910
O	7.3449986000	-4.9260471520	1.5487782006
O	7.9249004305	-4.4784422504	3.6860552247
O	2.2756144163	-1.0665121647	-1.9722024508
O	2.0944788130	1.1757786677	-1.7616881800
C	8.0570043547	-1.6833284368	2.1213609223
C	7.1196918500	-2.6616683151	2.3972512846
C	9.4451842228	-2.0553577464	1.8775885093
C	11.6159140289	-1.3015301853	1.3391947182
C	7.4878213553	-4.1205893872	2.4454364441
C	2.1242611056	0.0148689276	1.2210262578
C	2.9354754149	-0.0056890656	0.1096791555
C	2.3835443115	-0.0700460522	-1.2880328923
C	1.5223239461	1.1961791746	-3.0690273633
H	12.0843421952	-1.7840748114	2.2121720007
H	12.1126209837	-0.3439520557	1.1266531019

H	11.7190129865	-1.9799219897	0.4770670977
H	2.2149681302	0.7747491612	-3.8144128145
H	1.3249064684	2.2543794080	-3.2912097477
H	0.5847706877	0.6200503784	-3.0901252656
C	8.3293766552	-5.8419834732	3.8029802369
H	8.6728508709	-5.9628192986	4.8400348844
H	7.4904596230	-6.5257717309	3.5989106821
H	9.1473254992	-6.0644052461	3.1008941956
W	5.2695697907	0.3767248489	2.7657695854
S	5.2273464516	0.3034064640	4.9886740801

E(RB3LYP) = -3200.11265482

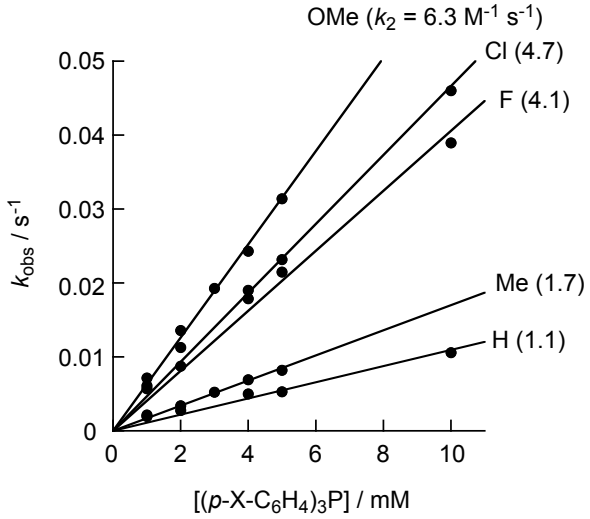

Fig. S1 Plots of k_{obs} vs. [(*p*-X-C_6H_4)$_3$P] in the sulfur atom transfer from $\mathbf{W^{VI}O(S)L^{COOMe}}$ to (*p*-X-C_6H_4)$_3$P

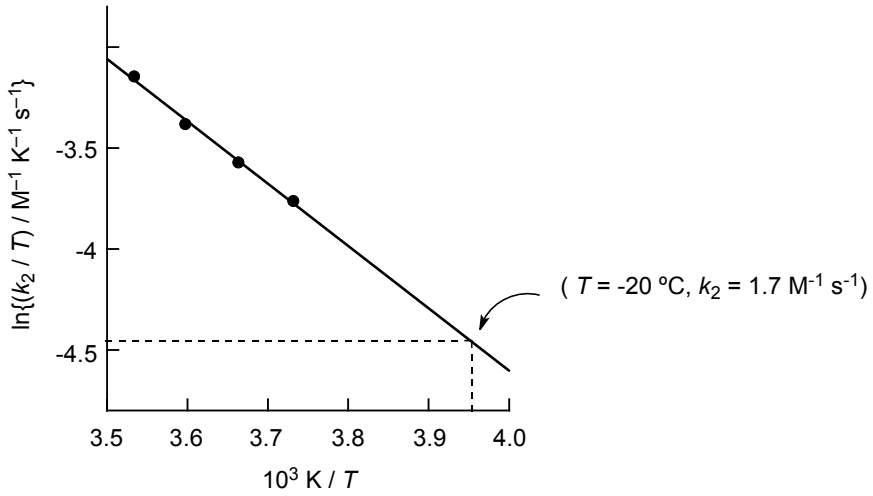

Fig. S2 The Eyring plot for the sulfur atom transfer from $\mathbf{W^{VI}O(S)L^{COOMe}}$ to P(*p*-Cl-C_6H_4)$_3$.

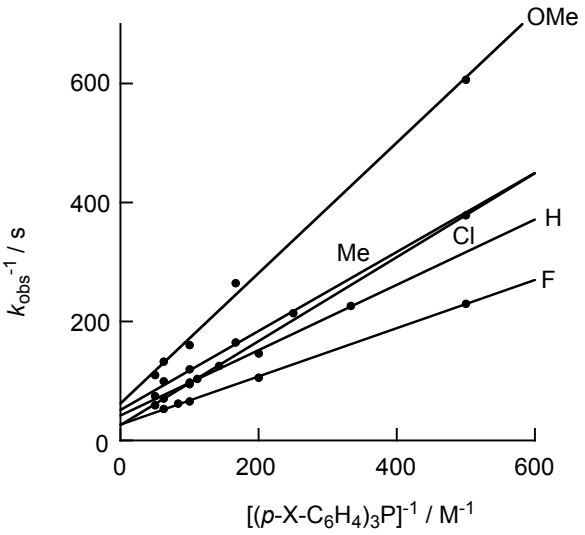

Fig. S3 The double reciprocal plots of k_{obs}^{-1} against $[(p\text{-X-C}_6\text{H}_4)_3\text{P}]^{-1}$.

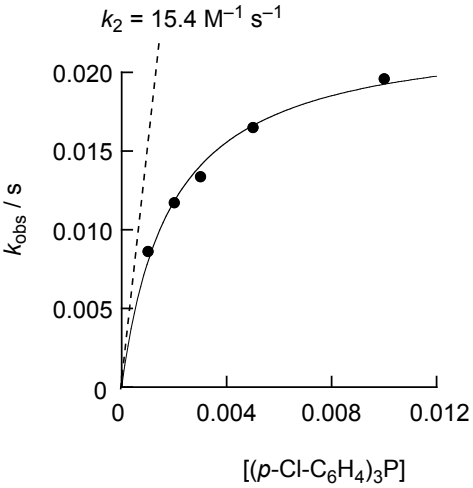

Fig. S4 Plot of k_{obs} vs. $[(p\text{-Cl-C}_6\text{H}_4)_3\text{P}]$. The k_2 (M^{-1} s^{-1}) was obtained as an initial slop (dotted line) of the curvature.