Supporting Information

Kinetics and Mechanism of Oxygen Atom Transfer from Methyl Phenyl Sulfoxide to Triarylphosphines Catalyzed by an Oxorhenium(V) Dimer

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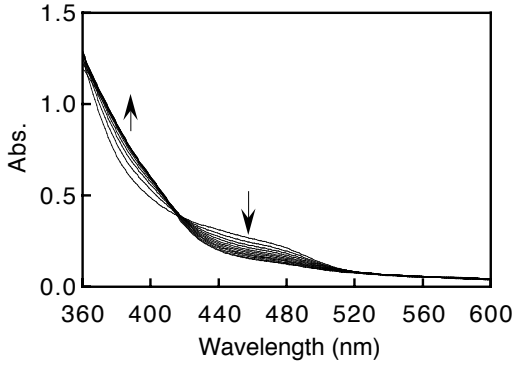

Figure S1. UV/Vis spectral changes accompanying the formation of **D**–L (L = methyl phenyl sulfoxide). Arrows indicate the direction of the absorbance change.
[{MeReO(mtp)}$_2$] = 0.49 mmol L^{-1} and [MeS(O)Ph]$_T$ = 0-0.244 M in benzene at 23.0 ˚C.

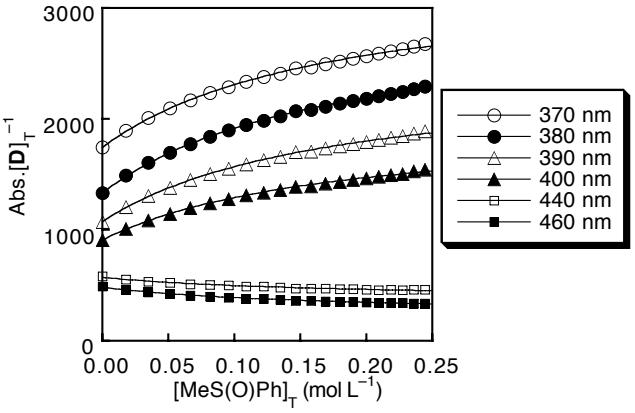

Figure S2. Plots of absorbance at selected wavelengths against the total concentrations of MeS(O)Ph. The solid lines represent the best fit based on the **D** + L = **D**–L model.

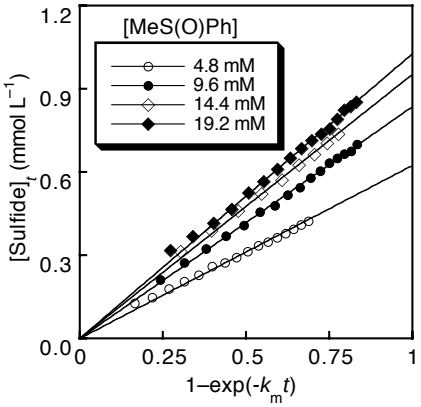

Figure S3. Plots of [Sulfide]$_t$ against {1–exp(–$k_m t$)} at different concentrations of MeS(O)Ph.

[{MeReO(mtp)}$_2$] = 0.49 mM and [PPh_3] = 21.7 mM in C_6D_6 at 23 ˚C.

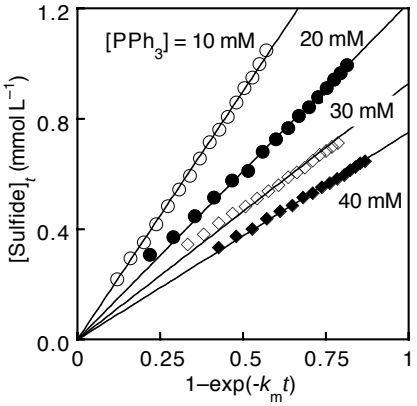

Figure S4. Plots of [Sulfide]$_t$ against {1–exp(–$k_m t$)} at different concentrations of PPh_3. [{MeReO(mtp)}$_2$] = 0.49 mM and [MeS(O)Ph] = 9.9 mM in C_6D_6 at 23 ˚C.

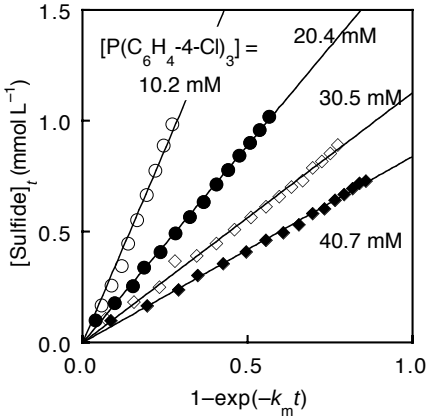

Figure S5. Plots of [Sulfide]$_t$ against {1–exp(–$k_m t$)} at different concentrations of $P(C_6H_4\text{-}4\text{-}Cl)_3$. [{MeReO(mtp)}$_2$] = 0.50 mM and [MeS(O)Ph] = 10.2 mM in C_6D_6 at 23 ˚C.

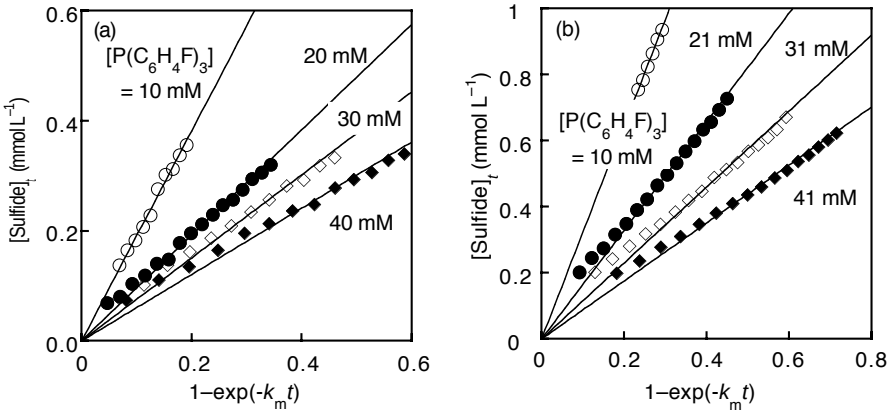

Figure S6. Plots of [Sulfide]$_t$ against {1 – exp(–$k_m t$)} at different concentrations of $P(C_6H_4\text{-}4\text{-}F)_3$ for the oxygen atom transfer reaction from MeS(O)Ph to $P(C_6H_4F)_3$. (a) [{MeReO(mtp)}$_2$] = 0.83 mM and [MeS(O)Ph] = 3.6 mM, (b) [{MeReO(mtp)}$_2$] = 0.76 mM and [MeS(O)Ph] = 9.4 mM in C_6D_6 at 23 ˚C.

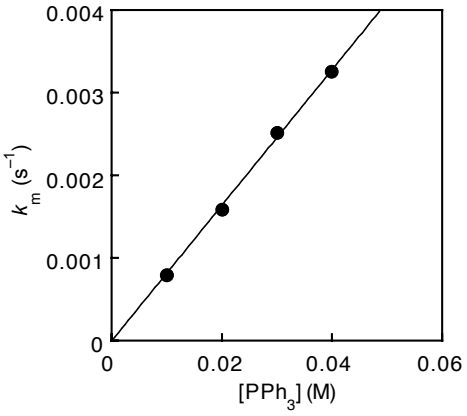

Figure S7. Dependence of k_m on [PPh_3] in the monomerization reaction of **D**. [{MeReO(mtp)}$_2$] = 0.49 mM and [MeS(O)Ph] = 9.9 mM in C_6D_6 at 23 ˚C.

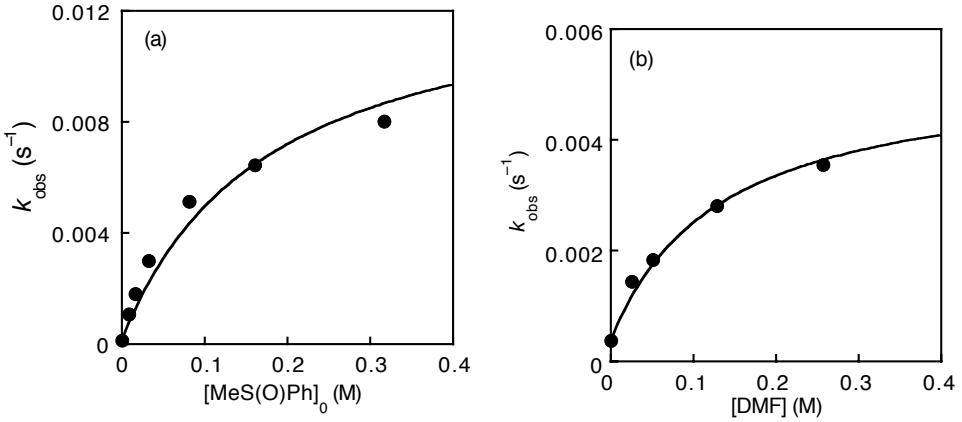

Figure S8. Dependence of k_{obs} for monomerization of **D** by PPh_3 in the presence of (a) [MeS(O)Ph] and (b) [DMF]. (a) [**D**] = 0.4 mM and [PPh_3] = 10.8 mM, (b) [**D**] = 0.2 mM and [PPh_3] = 17.3 mM.

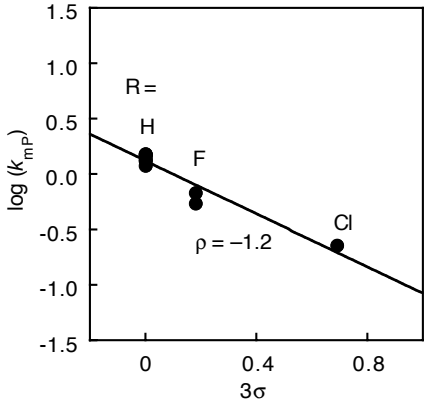

Figure S9. Hammett plot for the monomerization rate constant, k_{mp} for P(C_6H_4-4-R)$_3$ in C_6D_6 at 23 ˚C.