

Supporting Information
(Experimental detail, Chart S1, Table S1, and Figures S1 – S5)

Monooxo Molybdenum(VI) Complexes Possessing Olefinic Dithiolene Ligands: Probing Mo–S Covalency Contributions to Electron Transfer in DMSO Reductase Family Molybdoenzymes

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Experimental Section

General. All reagents and solvents were used as received unless otherwise noted. All reactions were carried out under argon in a Schlenk tube or a Miwa DB0-1KP glovebox. $(\text{Et}_4\text{N})_2[\text{MoO}(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ was prepared according to the literature.¹

Synthesis and Characterization of Complexes.

$(\text{Et}_4\text{N})[\text{Mo}^{\text{IV}}(\text{OSiBuPh}_2)(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ ($\mathbf{1}^{\text{OSiBuPh}_2}$). To 8 mL of an acetonitrile solution containing $(\text{Et}_4\text{N})_2[\text{MoO}(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ (200.0 mg, 0.255 mmol), ${}^t\text{BuPh}_2\text{SiCl}$ (144.8 mL, 0.566 mmol) was added to give an orange solution. The solvent was removed under reduced pressure to provide a yellow powder. The powder was collected by filtration and dried in vacuo. Yield 221.3 mg (97%). Anal. Calcd. for $\text{C}_{36}\text{H}_{51}\text{MoNO}_9\text{S}_4\text{Si}$ (MW = 894.09): C 48.36; H 5.75; N 1.57. Found: C 48.33; H 5.72; N 1.61%. ${}^1\text{H}$ NMR (CD_3CN , anionic part): δ 0.80 (s, 9H), 3.82 (s, 12H), 7.28-7.43 (m, 10H). UV-vis spectrum (CH_3CN): $\lambda_{\text{max}} = 331$ nm ($\epsilon = 17600 \text{ M}^{-1} \text{ cm}^{-1}$), 416 (sh), 517 (550), 659 (360). ESI-MS (CH_3CN): 765 $[\text{M}]^-$. Cyclic voltammogram (CV, CH_3CN): +0.76 V vs. SCE (irreversible), -1.44 V (reversible). IR (KBr): ν 505 (w), 710 (w), 915 (s, ν_{SiO}), 1014 (w), 1075 (w), 1112 (w), 1237 (vs), 1393 (w), 1431 (m), 1543 (m), 1705 (s), 1726 (s) cm^{-1} .

$(\text{Et}_4\text{N})[\text{Mo}^{\text{IV}}(\text{OSiPr}_3)(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ ($\mathbf{1}^{\text{OSiPr}_3}$). This complex was prepared by a similar method as for the preparation of $\mathbf{1}^{\text{OSiBuPh}_2}$ except that ${}^i\text{Pr}_3\text{SiCl}$ was used instead of ${}^t\text{BuPh}_2\text{SiCl}$. ${}^1\text{H}$ NMR (CD_3CN , anionic part): δ 0.82 (d, 18H), 1.098 (hep, 3H), 73.791 (s, 12H). UV-vis spectrum (CH_3CN): $\lambda_{\text{max}} = 362$ nm ($\epsilon = 20269 \text{ M}^{-1} \text{ cm}^{-1}$), 412 (1634), 507 (363). ESI-MS (CH_3CN): 683 $[\text{M}]^-$. This complex was very hygroscopic for characterization by elemental analysis, IR, and CV.

$(\text{Et}_4\text{N})[\text{Mo}^{\text{VI}}\text{O}(\text{OSiBuPh}_2)(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ ($\mathbf{2}^{\text{OSiBuPh}_2}$). An acetone solution (1 mL) of Me_3NO (5.2 mg, 0.069 mmol) was added to a THF solution (6 mL) of $\mathbf{1}^{\text{OSiBuPh}_2}$ (50.7 mg, 0.057 mmol). The resultant purple solution was concentrated to ~ 3 mL. After any undissolved solid was removed by filtration, the solution was concentrated again to ~ 1

mL. An addition of 6 mL of hexane to the solution obtained yielded a purple powder, which was collected by filtration and dried in vacuo. Yield 44.6 mg (86%). Anal. Calcd. for $C_{36}H_{51}MoNO_{10}S_4Si$ (MW = 910.09): C 47.51; H 5.65; N 1.54. Found: C 47.17; H 5.79; N 1.68%. 1H NMR (CD_3CN , anionic part): δ 1.03 (s, 9H), 3.71 (s, 12H), 7.32-7.42 (m, 6H), 7.77 (m, 4H). UV-vis spectrum (CH_3CN): λ_{max} = 320 nm (sh), 426 (ϵ = 2800 $M^{-1} cm^{-1}$), 563 (3140), 729 (1310). ESI-MS (CH_3CN): 781 $[M]^-$. Cyclic voltammogram (CV, CH_3CN): -0.46 V vs. SCE (reversible). IR (KBr): ν 505 (m), 613 (w), 706 (w), 876 (s, ν_{MoO}), 916 (s, ν_{SiO}), 1027 (m), 1240 (vs), 1393 (w), 1429 (m), 1460 (m), 1543 (w), 1702 (s), 1727 (s) cm^{-1} .

(Et₄N)[Mo^{VI}O(OSiPr₃)(S₂C₂(COOMe)₂)₂] (2^{OSiPr₃}). This complex was prepared by a similar method as for the preparation of 2^{OSiBuPh₂} except that 1^{OSiPr₃} (0.059 mmol) was used instead of 1^{OSiBuPh₂}. Yield 31.4 mg (64%). Anal. Calcd. for $C_{29}H_{53}MoNO_{10}S_4Si$ (MW = 910.09): C 42.06; H 6.45; N 1.69. Found: C 42.12; H 5.79; N 1.80%. 1H NMR (CD_3CN , anionic part): δ 1.08 (d, 18H), 1.12-1.17 (m, 3H), 3.72 (s, 12H). UV-vis spectrum (CH_3CN): λ_{max} = 350 nm (sh), 430 (sh), 559 (ϵ = 2828 $M^{-1} cm^{-1}$), 742 (948). IR (KBr): ν 681 (w), 767 (w), 868 (s, ν_{MoO}), 909 (vs, ν_{SiO}), 1000 (w), 1024 (m), 1241 (vs), 1394 (w), 1432 (m), 1463 (m), 1538 (w), 1699 (s), 1727 (s) cm^{-1} .

Physical Measurements. FT-IR spectra were recorded with a Perkin Elmer Spectrum One. Resonance Raman (rR) scattering was excited at 632.8 nm with a He-Ne ion laser (Jasco NRS-1000). Raman shifts were calibrated with inden. UV-vis spectra were recorded on a Hewlett Packard 8453 photo diode array spectrophotometer. ESI-MS (electrospray ionization mass spectra) measurements were performed on a PE SCIEX API 150EX

X-ray Crystallography. Single crystals of 1^{OSiBuPh₂} and 2^{OSiPr₃} were obtained by recrystallization from their acetonitrile/ether solutions. Each single crystal was mounted on a glass fiber with traces of viscous oil. The X-ray data were collected

with graphite-monochromated Mo-K α radiation on a Rigaku/MSM Mercury CCD diffractometer at -160 or -150 °C. The structures were solved by direct methods (SIR-97)² and expanded using DIRDIF 99.³ The atoms except hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 . The hydrogen atoms in all structures were attached at idealized positions on carbon atoms and were not refined. All structures converted in the final stages of refinement showed no movement in atom positions. Calculations were performed using Single Crystal Structure Analysis Software, Ver. 3.6.0.⁴ Crystallographic parameters of the three complexes are summarized in Table S1.

References

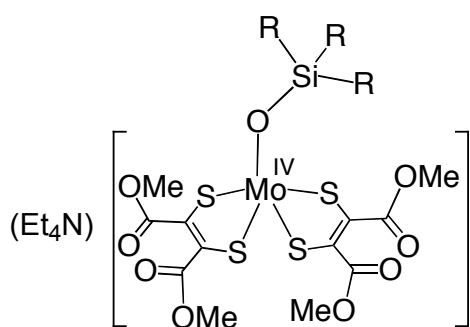
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Complete Gaussian Reference.

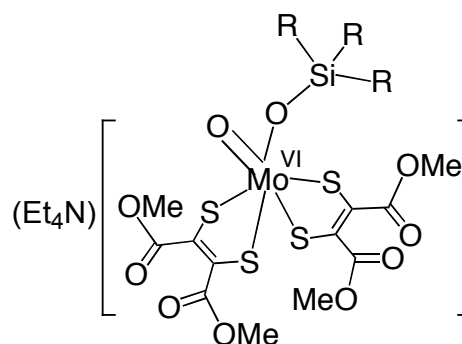
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Chart S1. Designation and Abbreviation of Complex Structures



R = ⁱPrⁱPrⁱPr **1^{OSiPr3}**
 R = ^tBuPhPh **1^{OSiBuPh2}**



R = ⁱPrⁱPrⁱPr **2^{OSiPr3}**
 R = ^tBuPhPh **2^{OSiBuPh2}**

Table S1. Crystallographic data of $(\text{Et}_4\text{N})[\text{Mo}^{\text{IV}}(\text{OSi}^i\text{BuPh}_2)(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ (**1**^{OSiBuPh2}) and $(\text{Et}_4\text{N})[\text{Mo}^{\text{VI}}\text{O}(\text{OSi}^i\text{Pr}_3)(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ (**2**^{OSiPr3})

	1 ^{OSiBuPh2}	2 ^{OSiPr3}
formula	$\text{C}_{36}\text{H}_{51}\text{MoNO}_9\text{S}_4\text{Si}$	$\text{C}_{29}\text{H}_{53}\text{MoNO}_{10}\text{S}_4\text{Si}$
fw	894.07	828.00
size (mm)	$0.30 \times 0.20 \times 0.20$	$0.38 \times 0.10 \times 0.05$
temperature (K)	100	110
crystal system	orthorhombic	triclinic
space group	$P2_12_12_1$ (no. 19)	$P-1$
<i>Z</i>	4	2
<i>a</i> , Å	10.4641(16)	9.394
<i>b</i> , Å	18.324(3)	11.937(6)
<i>c</i> , Å	22.244(4)	18.151(10)
α , deg	90	97.052(4)
β , deg	90	95.998(7)
γ , deg	90	100.549(6)
<i>V</i> , Å ³	4265.2(12)	1969.0(18)
μ , cm ⁻¹	5.80	6.21
GOF	0.864	1.225
<i>R</i> ₁ % (<i>I</i> > 2.0 σ <i>I</i>)	3.16	5.27
<i>wR</i> ₂ % (all data)	8.71	13.40

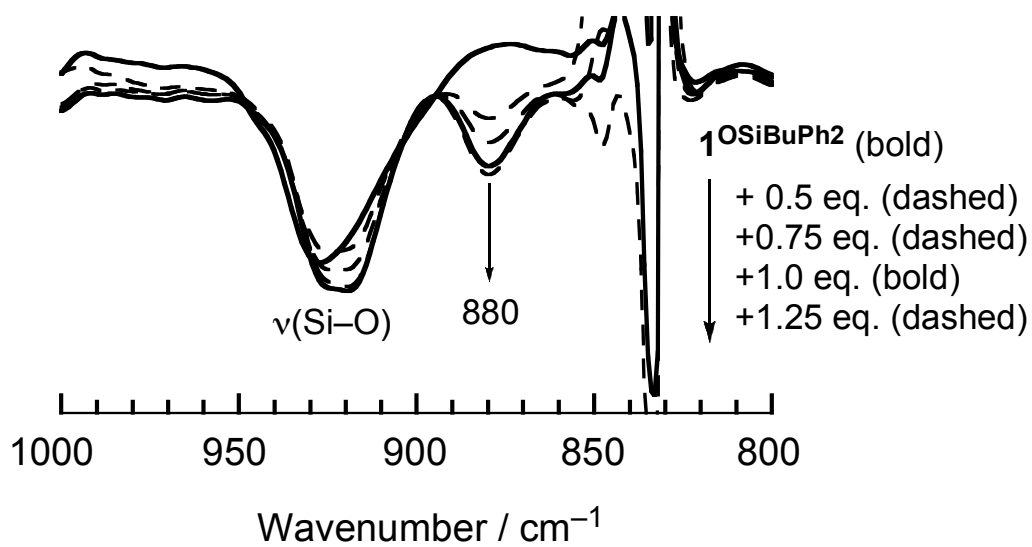


Figure S1. Titration of $(\text{Et}_4\text{N})[\text{MoO}(\text{OSi}^t\text{BuPh}_2)(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ (**1 OSiBuPh₂**) with Me_3NO in CD_3CN .

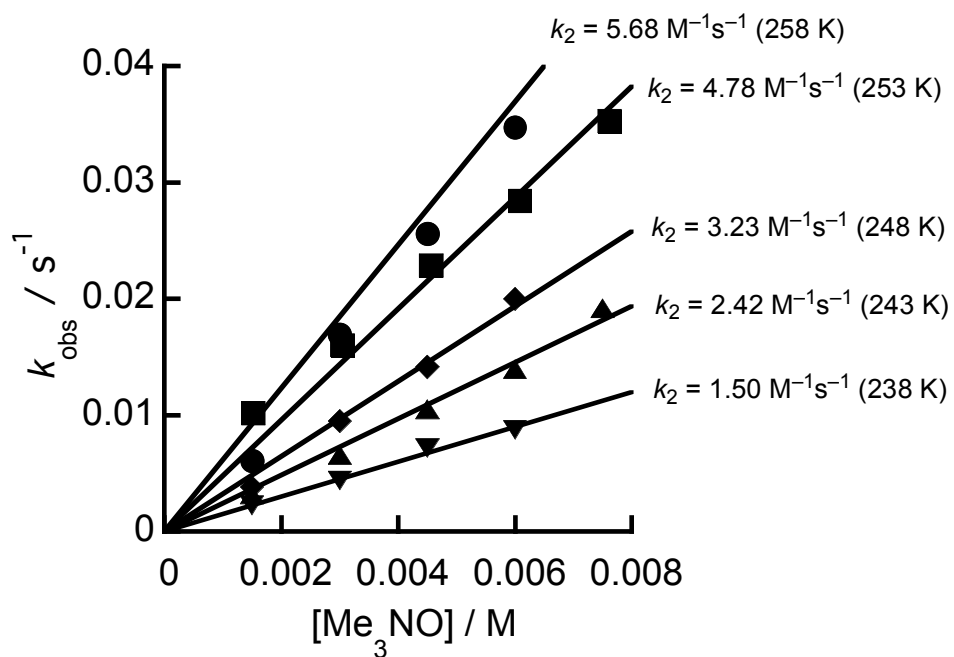


Figure S2. Temperature dependent plots of k_{obs} vs. $[\text{Me}_3\text{NO}]$ in the reaction of $(\text{Et}_4\text{N})[\text{Mo}^{\text{VI}}\text{O}(\text{OSi}^t\text{BuPh}_2)(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ with Me_3NO in CH_3CN .

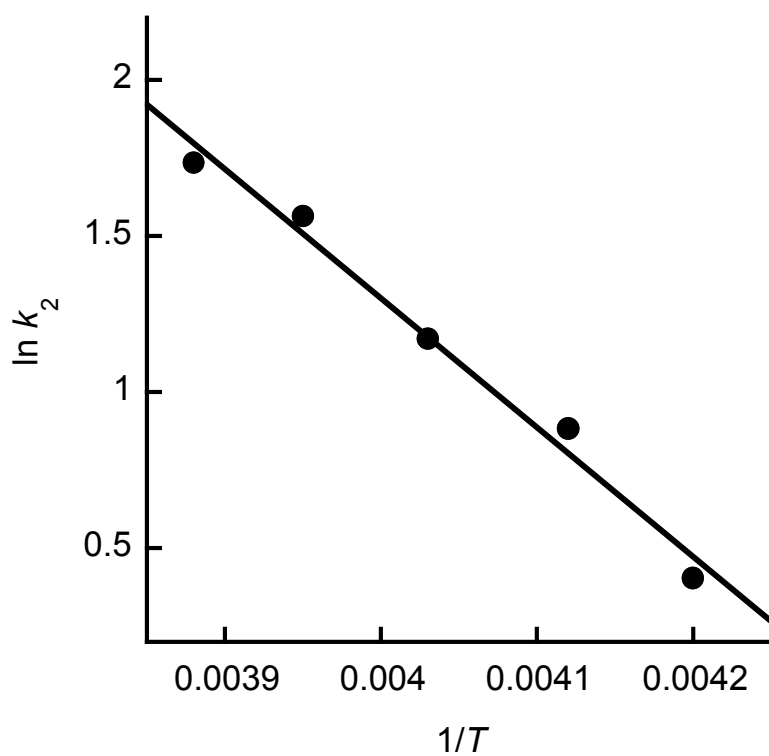


Figure S3. Arrhenius plot for the reaction of $(\text{Et}_4\text{N})[\text{Mo}^{\text{VI}}\text{O}(\text{OSi}^t\text{BuPh}_2)(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ with Me_3NO in CH_3CN .

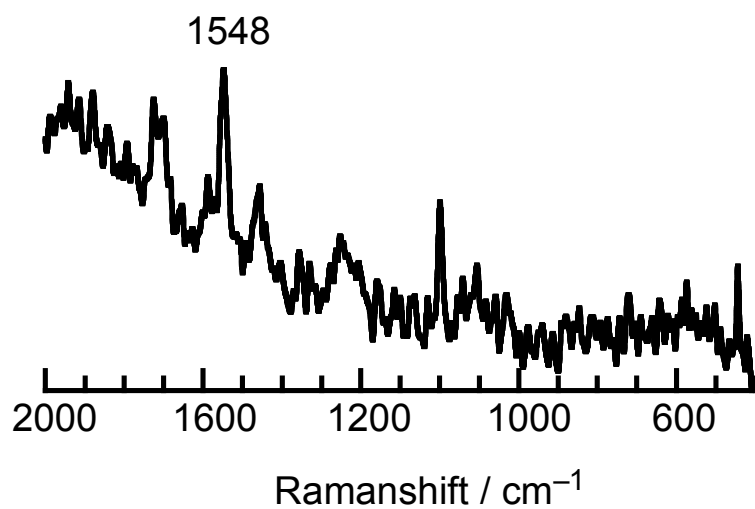


Figure S4. FT Raman spectrum of
(Et₄N)[Mo^{IV}(OSi^tBuPh₂)(S₂C₂(COOMe)₂)₂] (**1^{OSiBuPh2}**)

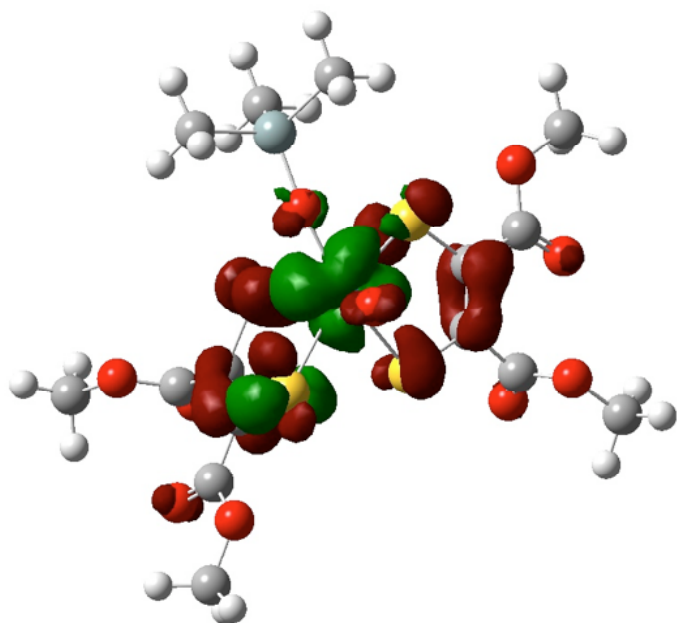


Figure S5. EDDM for Band 2 in Figure 4.