Supplementary Information

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

Chalcogenidobis(ene–1,2–dithiolate)molybdenum(IV) Complexes (Chalcogenide E = S, Se): Probing Mo≡E and Ene–1,2–dithiolate Substituent Effects on Geometric and Electronic Structure

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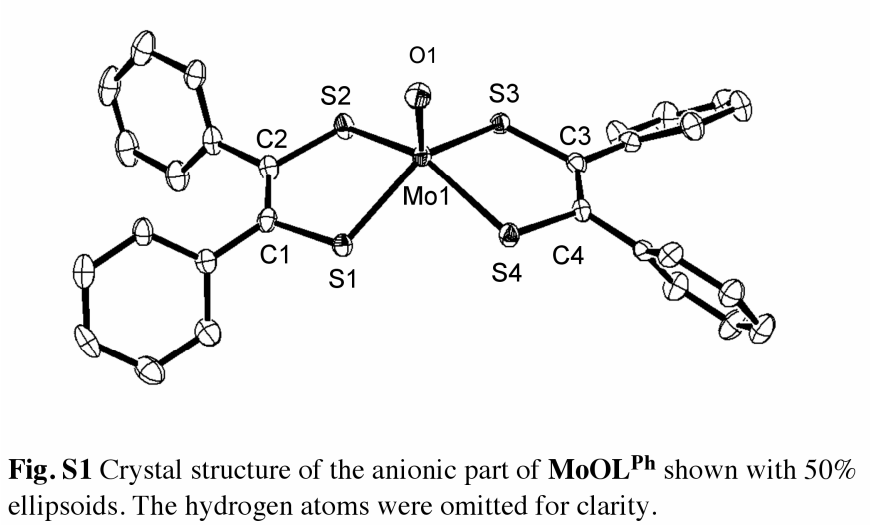

Fig. S1 Crystal structure of the anionic part of **MoOL^{Ph}** shown with 50% ellipsoids. The hydrogen atoms were omitted for clarity.

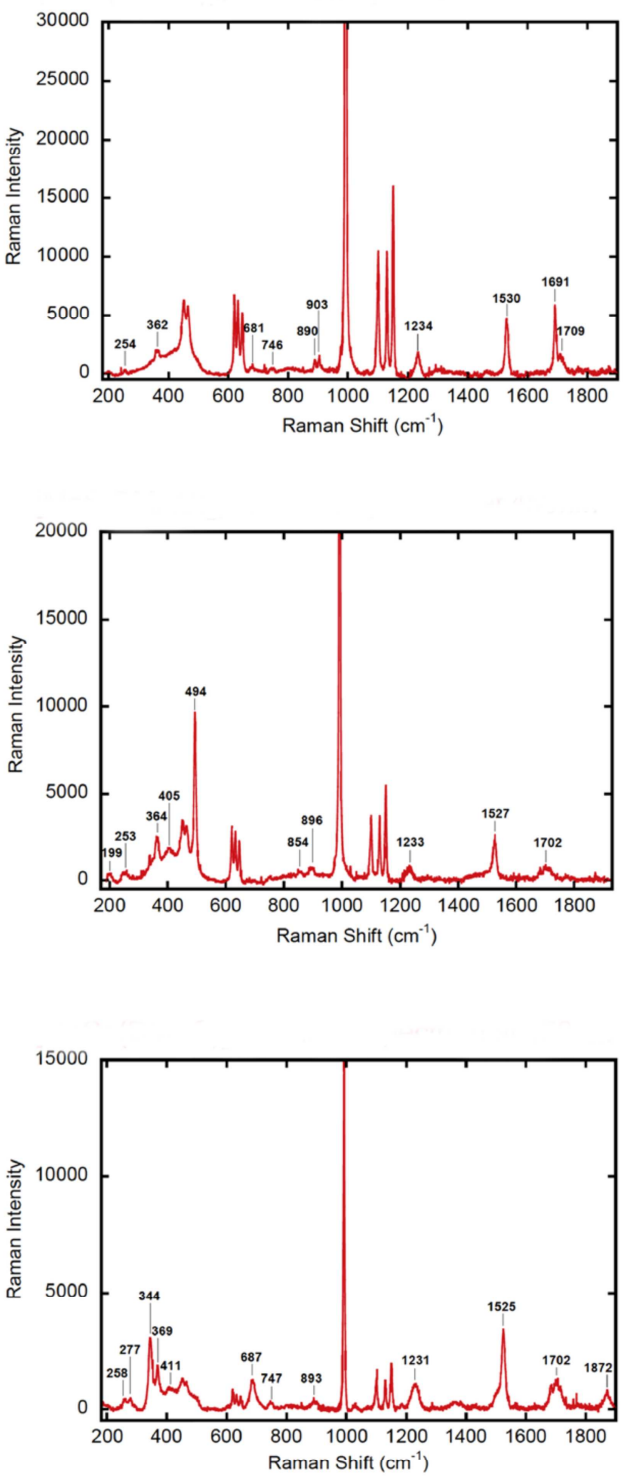

Fig. S2 Solid State resonance Raman spectra collected at 458nm for **MoOL**$^{\mathbf{COOMe}}$ (above), **MoSL**$^{\mathbf{COOMe}}$ (middle), and **MoSeL**$^{\mathbf{COOMe}}$ (bottom).

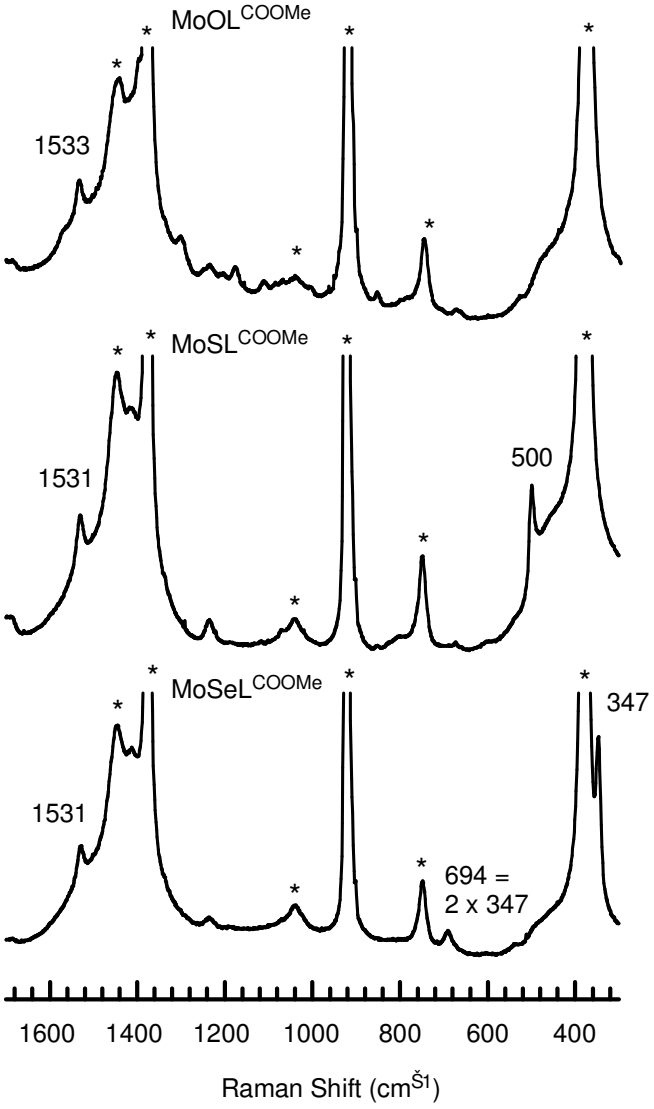

Fig. S3 resonance Raman spectra of **MoOL^{COOMe}** (above), **MoSL^{COOMe}** (middle), and **MoSeL^{COOMe}** (bottom) in CH_3CN using Ar ion laser with excitation at 488 nm (asterisks indicate solvent peaks).

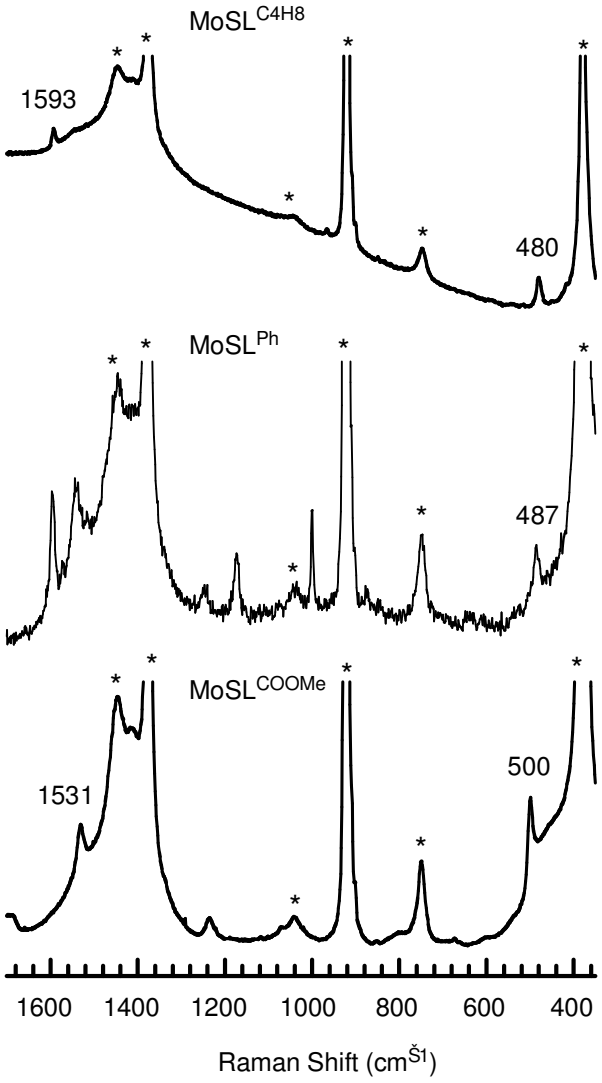

Fig. S4 resonance Raman spectra of **MoSL^{C4H8}** (above), **MoSL^{Ph}** (middle), and **MoSL^{COOMe}** (bottom) in CH_3CN using Ar ion laser with excitation at 488 nm (asterisks indicate solvent peaks).

Table S1 Crystallographic Data for **MoOL^{Ph}**

	MoOL^{Ph}
formula	$C_{44}H_{60}MoN_2OS_4$
fw	857.15
cryst system	monoclinic
space group	$P2_1$
a, Å	14.733(9)
b, Å	8.778(5)
c, Å	17.409(11)
β, deg	104.966(10)
V, Å^3	2175.0(23)
Z	2
ρ, g cm^{-3}	1.309
μ, mm^{-1}	0.528
data	21205
unique data	9877
*R*1[a]	0.0443
*wR*2 (F^2)[b]	0.1097
GOF	1.028

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = \{\Sigma(w(Fo^2 - Fc^2)^2)/\Sigma w(F_o^2)^2\}^{1/2}$.

Table S2. Selected Bond Distances (Å) and Angles (deg) of **MoOL^{Ph}**

	MoOL^{Ph}
Mo1–O1	1.709(2)
Mo1–S1	2.3874(7)
Mo1–S2	2.3761(7)
Mo1–S3	2.3824(8)
Mo1–S4	2.3778(7)
S1–C1	1.792(2)
S2–C2	1.782(3)
S3–C3	1.785(2)
S4–C4	1.786(3)
C1–C2	1.345(4)
C3–C4	1.369(5)
Mo1–4S plane	0.7871(5)
O1–Mo1–S1	110.45(8)
O1–Mo1–S2	108.37(7)
O1–Mo1–S3	110.64(8)
O1–Mo1–S4	107.04(7)
S1-Mo1-S2	82.20(2)
S1-Mo1-S3	138.89(2)
S1-Mo1-S4	86.70(2)
S2-Mo1-S3	83.92(2)
S2-Mo1-S4	144.57(3)
S3-Mo1-S4	82.67(2)

Gaussian Reference

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