Synthesis of $(\eta^5\text{-}R^1C_5H_4)(CO)_2Mo(\eta^2\text{-}S_2R)$ *via* Reaction of $(\mu\text{-}RS)(\mu\text{-}p\text{-}MeC_6H_4SO_2S)Fe_2(CO)_6$ with Nucleophiles $(\eta^5\text{-}R^1C_5H_4)(CO)_3MoSeNa$. Crystal Structure of $(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2Mo(\eta^2\text{-}S_2Bu^t)$

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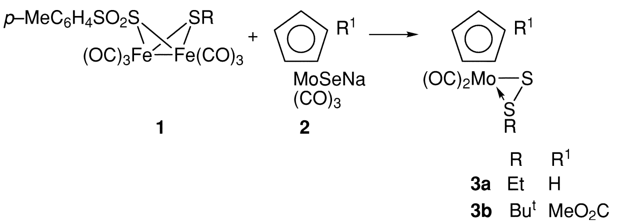
The reaction of $(\mu\text{-}RS)(\mu\text{-}p\text{-}MeC_6H_4SO_2S)Fe_2(CO)_6$ with $(\eta^5\text{-}R^1C_5H_4)(CO)_3MoSeNa$ gave organomolybdenum complexes $(\eta^5\text{-}R^1C_5H_4)(CO)_2Mo(\eta^2\text{-}S_2R)$ (**3a** R = Et, R^1 = H; **3b** R = Bu^t, R^1 = MeO_2C), the structure of **3b** being determined by X-ray diffraction analysis.

We previously reported[1] that the $[Et_3NH^+]$ salts of sulfur-centered anions $[(\mu\text{-}RS)(\mu\text{-}S^-)Fe_2(CO)_6]$ reacted with toluene-*p*-sulfonyl chloride $p\text{-}MeC_6H_4SO_2Cl$ to give the expected toluene-*p*-sulfonyl substituted Fe_2S_2 butterfly-shaped clusters of the type $(\mu\text{-}RS)(\mu\text{-}p\text{-}MeC_6H_4SO_2S)Fe_2(CO)_6$ (**1**). In order to study the chemical reactivities of this new type of cluster and to further discover applications in the synthesis of transition metal cluster complexes, we recently studied the reaction of clusters **1** with some molybdenum sodium selenides of the type $(\eta^5\text{-}R^1C_5H_4)(CO)_3MoSeNa$ (**2**) prepared by an insertion reaction of the Mo–Na bond in $(\eta^5\text{-}R^1C_5H_4)(CO)_3MoNa$ with selenium powder.[2] We found that the reaction of an equivalent of clusters **1** (R = Et, Bu^t) with $(\eta^5\text{-}R^1C_5H_4)(CO)_3MoSeNa$ (R^1 = H, MeO_2C) in THF at room temperature afforded two organic monomolybdenum complexes **3a**,**b**, as shown in Scheme 1.



Scheme 1

Complexes **3a**,**b** are new, and represent, to our knowledge, the first examples of organomolybdenum complexes with an $\eta^2\text{-}S_2R$ alkylperthio ligand. The IR spectrum of **3a** exhibits two absorption bands at 1940 and 1847 cm^{-1} for its terminal carbonyls, whereas that of **3b** displays one absorption band at 1713 cm^{-1} for its ester carbonyl and two absorption bands at 1975 and 1868 cm^{-1} for its terminal carbonyls. The ^1H NMR spectra of **3a**,**b** show their respective resonance signals. For example, the parent cyclopentadienyl ring of **3a** exhibits one singlet at δ 6.08, whereas the substituted cyclopentadienyl ring of **3b** displays two sets of signals, one at δ 5.48 assigned to two β-H remote from the substituent and the other at δ 5.93–6.15 attributed to two α-H close to the substituent due to the electron-withdrawing effect of the MeO_2C substituent.[3–5]

Table 1 Crystal data collection and refinement for **3b**

Formula	$C_{13}H_{16}MoO_4S_2$
M_r	396.34
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	13.965(3)
b/Å	11.842(2)
c/Å	19.417(2)
V/Å^3	3211(2)
Z	8
D_c/g cm^{-3}	1.640
$F(000)$	1600
μ/mm^{-1}	1.085
T/°C	26
Independent reflections	2540
Observed data with $I \geqslant 3\sigma(I)$	803
Radiation (λ/Å)	Mo-Kα (0.710 73)
Scan type	$\omega/2\theta$
$2\theta_{max}$/°	46
R	0.064
R_w	0.061
Goodness of fit indicator	0.86
Max. shift in final cycle	0.48
Largest peak in final diff. map/e Å^{-3}	1.96

In order to confirm the structures of **3a**,**b**, an X-ray diffraction analysis for **3b** was undertaken. The crystal structure of **3b** was obtained by data collection on a CAD4 diffractometer using Mo-Kα radiation (λ = 0.71073 Å), solved by direct methods and refined by full-matrix least squares. The crystallographic data and data collection

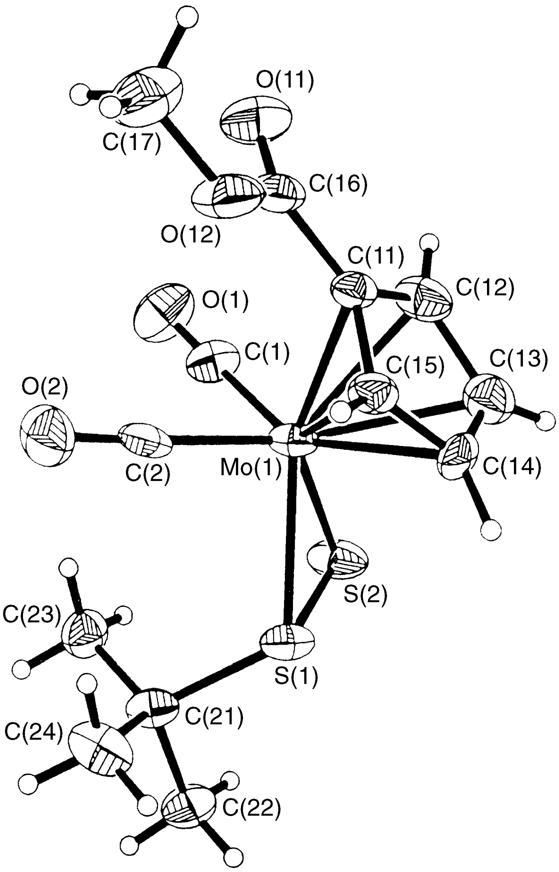


Fig. 1 ORTEP view of **3b** with atom-labeling scheme

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*To receive any correspondence.

parameters are listed in Table 1. An ORTEP view of the molecular structure is shown in Fig. 1.

Fig. 1 shows that the organomolybdenum complex **3b** consists of one molybdenum atom coordinated with one η^5-$MeO_2CC_5H_4$, two terminal CO and one η^2-S_2Bu^t ligands. That is, **3b** contains the same structural unit of $(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2Mo$ as the complex $(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2Mo[(\mu\text{-}Ph_2C_2)Co(CO)_3]$ **4**.[6] The η^2-S_2Bu^t in **3b** and $[(\mu\text{-}Ph_2C_2)Co(CO)_3]$ in **4** are isoelectronic (3e) ligands, which have little influence upon the $(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2Mo$ structural unit. For instance, the C(11)–C(16) bond length in **3b** and the corresponding one in **4** are 1.456(26) and 1.480(26) Å,[6] respectively, which lie in between a normal C–C single and normal C=C double bond. This implies that there exists some conjugative interactions between the π-system of the substituent MeO_2C and the cyclopentadienyl ring in both **3b** and **4**. The η^2-S_2Bu^t ligand of **3b** is coordinated to the Mo(1) atom through its S(1) and S(2) atoms. The Mo(1)–S(1), Mo(1)–S(2) and S(1)–S(2) bond lengths are 2.446(4), 2.506(5) and 2.015(8) Å, respectively. Thus, the three atoms Mo(1), S(1) and S(2) constitute an approximate isosceles triangle. In fact, this coordination geometry resembles those formed from other transition metal and alkylperthio ligands found in some mononuclear transition metal complexes, such as $(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)(\eta^2\text{-}S_2CH_2SiMe_3)$ [S–S 2.027(4) Å][7] and $[Os(CO)_2(PPh_3)_2(\eta^2\text{-}S_2Me)]ClO_4\cdot0.5C_6H_6$ [S–S 2.022(7) Å].[9]

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Techniques used: X-Ray diffraction, IR, ^1H NMR

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Tables 2 and 3: Atomic coordinates and thermal parameters, selected bond lengths and bond angles

Appendix: Tables of anisotropic thermal parameters and complete bond lengths and bond angles

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