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Synthesis and Characterization of Allylic Dinuclear Molybdenum Complexes with Bridging Oxygen and Sulfur Containing Ligands

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Complexes of the type $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}L)_3]$ and $[Na(thf)_x][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}L)_3]$ ($L = OC_2H_5$, SC_2H_5, OPh, SPh, $OC_6H_4CH_3$, and SCH_2Ph) were synthesized using two different methods. The first was by the reaction of the starting material $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)Cl]$ with NaSR or NaOR and $[NEt_4]^+$, using 2:3 (metal:ligand) mole ratio in thf at room temperature. The second was by the in situ reactions of the ligands with the intermediate $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)(thf)]^+$, which was generated by reacting the starting material $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)Cl]$ with $Ag[BF_4]$. The complexes were characterized by means of IR, NMR, and elemental analysis. The X-ray structure of the complex $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$ was determined, and cyclic voltammetery measurements for the complexes $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$ and $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}OC_6H_4CH_3)_3]$ were carried out. The $OC_6H_4CH_3$ complex exhibited a reversible oxidation wave at ca. 0.1 V whereas the SC_6H_5 complex did not.

There is an extensive chemistry of molybdenum compounds containing sulfur and oxygen ligands.[1–12] Those compounds are important in some industrial processes such as hydrodesulfurization and polymerization of certain dienes,[2] and in the biological reduction of dinitrogen to ammonia using the active site of molybdenum in nitrogenase enzyme.[3–5] Although, many thiolato-bridged complexes with a variety of CO-ligands have been reported, the use of the allyl moiety as supporting ligand remains relatively unexploited.[6] Examples of molybdenum allyl complexes, where the bridging ligands are –SR or –OR, are those complexes of the general formula $[Mo_2(CO)_4(\eta^3\text{-}C_3H_5)_2L_3]$ in which L is either a thiol or an alkoxide. These complexes are produced from the reaction of the corresponding ligands with the starting material $[Mo(CO)_2(\eta^3\text{-}C_3H_5)Y_2X]$ in which X is a halide or pseudohalide and Y is a monodentate ligand.[4,5b,5c]

These complexes found to act as catalysts for the polymerization of certain dienes[7] and the organic synthesis for allylic alkylation.[8] Molybdenum complexes of the formula $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)X]$ have been extensively used for the synthesis of many allylic derivatives. These derivatives can be obtained by the replacement of the weakly bonded nitriles by nitrogen,[9,10] phosphorus,[11] arsenic,[12] or carboxylic[13] ligands. However, examples reported with sulfur ligands are much rarer and involve (S, S) anionic donors.[14,15]

1,2-Dithiolate ligands are examples where the (S, S) ligands may be bonded to molybdenum. During the past decades the coordination chemistry of unsaturated 1,2-dithiolate ligands has been thoroughly investigated and reviewed regularly.[16–18] All molybdenum oxotransferase and hydroxylase enzymes which catalyze the overall reaction

$$X + H_2O \rightleftharpoons XO + 2H^+ + 2e^- \tag{1}$$

are now recognized to contain a molybdenum cofactor, Moco. In these compounds, a molybdenum atom is coordinated to one or two pterin dithiolene ligands Figure 1.[19]

DuBois and co-workers reported the synthesis of a series of complexes in which sulfur ligands bonded to the molybdenum atom in a bridging form.[20,21] They were interested in investigating the effect of the electron-withdrawing substituents on the sulfide ligand reactivity toward olefins and hydrogen. They found that the electron-withdrawing cyclopentadiene (Cp) substituent leads to an enhancement of the acceptor properties of the bridging sulfur ligands.

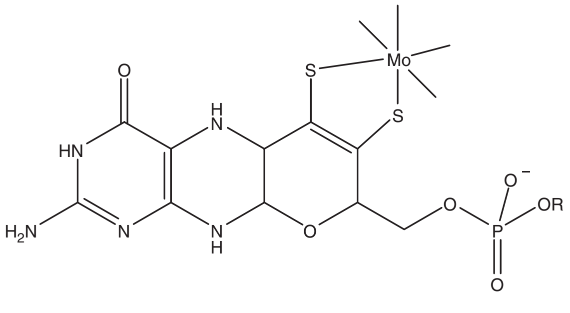

Figure 1. Molybdenum oxotransferase and hydroxylase enzyme cofactor.

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Green and Ng reported the synthesis of a series of binuclear thiolato-bridged Mo complexes $[(\eta\text{-}C_7H_3R^1{}_4)Mo(\mu\text{-}SR^2)_3Mo(\eta\text{-}C_7H_3R^1{}_4)][BF_4]$ ($R^1 = H$ or Me; $R^2 = Et$, Pr, Bu, Ph, or CH_2Ph).[22] Cyclic voltammetry measurements of these compounds exhibited two reversible reduction waves due to the cleavage of the Mo–Mo bond to give the anion $[(\eta\text{-}C_7H_3R_4)Mo(\mu\text{-}SR)_3Mo(\eta\text{-}C_7H_3R_4)]^-$.

Borgmann and co-workers reported the synthesis of several complexes with (η^3-allyl)Mo-units in oxygen-rich coordination spheres containing RO^- ligands.[4] These compounds are important as models for catalytic intermediates in industrial processes. They started with the neutral complex $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)Cl]$ and reacted it with $Ag[BF_4]$, to produce the cationic complex $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)(thf)]^+$.

In this paper we report the synthesis and characterization of some anionic complexes of the type $[\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}L)_3]^-$ ($L = OC_2H_5$, SC_2H_5, OPh, SPh, $OC_6H_4CH_3$, and SCH_2Ph). These complexes were synthesized using two different methods. The first was by the reaction of the starting material $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)Cl]$ with sulfur or oxygen containing ligands and $[NEt_4]^+$ using 2:3 (metal:ligand) mole ratio in thf at room temperature. The second was by the in situ reactions of the ligands with the intermediate $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)(thf)]^+$, which was generated by reacting the starting material $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)Cl]$ with $Ag[BF_4]$.

Experimental

Materials and Methods. All reactions were carried out using standard Schlenk and vacuum line techniques under an inert atmosphere of dinitrogen (N_2). Tetrahydrofuran (thf) was purchased from Scharlau. Toluene and hexane were obtained from Avonchem. Toluene, thf, and hexane were distilled over sodium with benzophenone. Acetonitrile was purchased from Gainland Chemical Co., dried over phosphorus pentaoxide and distilled before use. Allyl chloride was freshly distilled before use. Molybdenum hexacarbonyl, ethanol, *p*-cresol, phenol, sodium, ethanethiol, thiophenol, and allyl chloride were purchased from Aldrich. Silver tetrafluoroborate was obtained from Acros Co.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AC-200 MHz spectrometer and tetramethylsilane (TMS) was used as internal reference. Infrared (IR) spectra were carried out with a Nicolet-impact 410 FT-IR spectrophotometer. Elemental analysis was performed by Laboratoire D'Analyze Elementaire Universite de Montreal, Montreal, Canada. Cyclic voltammetery measurements were performed using a BAS CV-50W. X-ray crystallographic single crystal structural determination was carried out on a Syntex $P2_1$ four circle diffractometer (graphite monochromator, scintillation counter, low-temperature device LT-1).

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-720896 for the $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of Complexes. General Procedure for the Preparation of the Complex $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)Cl]$ (I): This complex was used as a starting material and prepared as reported in the literature.[8] The following procedure was used for the preparation: Under nitrogen atmosphere, 5.28 g (20 mmol) of $[Mo(CO)_6]$ were placed in a 250-mL three-neck flask fitted with a condenser, vacuum adapter and a septum. At room temperature and with continuous stirring, two aliquots (40 mL each) of toluene and acetonitrile were then added to the flask through the septum. To the resulting mixture, 2.5 mL of allyl chloride (2.3 g, 30 mmol) were then added. The mixture was heated to reflux under nitrogen. After about 30 min, the color became yellow, and then changed to orange. Upon cooling to room temperature and vacuum reduction of the mixture's volume to 2/3 of its original volume, a yellow solid was obtained. The solid was filtered under nitrogen and washed with hexane to afford 5.8 g of a yellow powder, yield 93%, and melting point 168 °C.

General Procedure for the Preparation of $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}L)_3]$ ($L = OC_2H_5$, OC_6H_5, SC_6H_5, OC_7H_7, SC_2H_5, and $SCH_2C_6H_5$): The sodium salts of the respective anionic ligands (NaL) were prepared by the reaction of sodium metal (3.0 mmol) with the ligand (L) (3.0 mmol) in 15 mL of thf. The suspension was stirred for 7 h at room temperature. A solution of **I** (2 mmol) in 70 mL of thf was placed in a 250-mL Schlenk flask. With stirring, 3 mmols of the ligand and 1 mmol of NEt_4Cl were then added. The reaction mixture was stirred at room temperature for 2 h. An orange solution formed and NaCl precipitated. The solution was filtered over celite. The solvent was removed under vacuum at 25 °C and the resulting yellow solid was washed three times with 15 mL aliquots of hexane. The solid product was recrystallized from thf/hexane (ca. 1:5 ratio) at ca. 0 °C. All products were yellow solids and found as follows.

$[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}OC_2H_5)_3]$ (1a); Yield 72%. Mp 75–77 °C (decomp.). IR (thf solution, cm^{-1}) $\nu_{(co)}$: 1922(s), 1823(s). ^{1}H NMR (DMSO-d_6): allyl protons {δ 0.85 (dd, 4H, CH_2 anti), 2.9 (dd, 4H, CH_2 syn), and 3.4 (m, 2H, CH)}; NEt_4^+ protons {1.2 (t, 12H, CH_3) and 3.1 (q, 8H, CH_2)}; ethoxide ligand protons {1.3 (t, 9H, CH_3) and 5.1 (q, 6H, CH_2)}. Anal. Calcd for $C_{24}H_{45}Mo_2NO_7$: C, 44.3; H, 7.0%. Found: C, 44.0; H, 6.8%.

$[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}OC_6H_5)_3]$ (2a); Yield 84%. Mp 157–160 °C (decomp.). IR (thf solution, cm^{-1}) $\nu_{(co)}$: 1922(s), 1820(s). ^{1}H NMR (DMSO-d_6): allyl protons {δ 0.9 (dd, 4H, CH_2 anti), 2.8 (dd, 4H, CH_2 syn), and 3.6 (m, 2H, CH)}; NEt_4^+ protons {1.15 (t, 12H, CH_3) and 3.2 (q, 8H, CH_2)}; phenoxide ligand protons {6.7 and 7.2 (m, 15H)}. Anal. Calcd for $C_{36}H_{45}Mo_2NO_7$: C, 54.4; H, 5.7%. Found: C, 54.0; H, 5.5%.

$[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$ (3a); Yield 85%. Mp 145–147 °C (decomp.). IR (thf solution, cm^{-1}) $\nu_{(co)}$: 1933(s), 1838(s). ^{1}H NMR (DMSO-d_6): allyl protons {δ 0.75 (dd, 4H, CH_2 anti), 2.8 (dd, 4H, CH_2 syn), and 3.6 (m, 2H, CH)}; NEt_4^+ protons {1.15 (q, 12H, CH_3) and 3.2 (q, 8H, CH_2)}; thiophenolate ligand {7.2, 7.7 (m, 15H)}. Anal. Calcd for $C_{36}H_{45}Mo_2NO_4S_3$: C, 51.2; H, 5.4; S, 11.4%. Found: C, 51.6; H, 6.0; S, 11.0%.

$[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}OC_7H_7)_3]$ (4a); Yield 85%. Mp 93–95 °C (decomp.). IR (thf solution, cm^{-1}) $\nu_{(co)}$: 1919(s), 1822(s). ^{1}H NMR (DMSO-d_6): allyl protons {δ 0.75 (dd, 4H, CH_2 anti), 2.9 (dd, 4H, CH_2 syn), and 3.6 (m, 2H, CH)}; NEt_4^+ protons {1.15 (t, 12H, CH_3) and 3.2 (q, 8H, CH_2)}; cresolate ligand {2.2 (s, 9H, CH_3) and 6.6, 7.0 (dd, 12h, Ph)}. Anal. Calcd for $C_{39}H_{51}Mo_2NO_7$: C, 55.9; H, 6.1%. Found: C, 55.4; H, 5.9%.

$[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_2H_5)_3]$ (5a); Yield 76%. Mp 76–78 °C (decomp.). IR (thf solution, cm^{-1}) $\nu_{(co)}$: 1924(s), 1821(s). ^{1}H NMR (DMSO-d_6): allyl protons {δ 0.85 (dd, 4H, CH_2 anti), 2.9 (dd, 4H, CH_2 syn), and 3.4 (m, 2H, CH)}; NEt_4^+ protons {1.2 (t, 12H, CH_3) and 3.1 (q, 8H, CH_2)}; ethanethiolate ligand

{1.4 (t, 9H, CH_3) and 5.3 (q, 6H, CH_2)}. Anal. Calcd for $C_{24}H_{45}Mo_2NO_4S_3$: C, 41.2; H, 6.5; S, 13.8%. Found: C, 41.6; H, 6.7; S, 13.9%.

$[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SCH_2C_6H_5)_3]$ (6a); Yield 87%. Mp 135–138 °C (decomp.). IR (thf solution, cm^{-1}) $\nu_{(co)}$: 1916(s), 1824(s). ^1H NMR (DMSO-d_6): allyl protons {δ 0.75 (dd, 4H, CH_2 anti), 2.8 (dd, 4H, CH_2 syn), and 3.6 (m, 2H, CH)}; $NEt_4{}^+$ protons {1.15 (q, 12H, CH_3) and 3.2 (q, 8H, CH_2)}; ligand {3.8 (m, 6H, CH_2), 7.4, 7.3 (m, 15H, Ph)}. Anal. Calcd for $C_{39}H_{51}Mo_2NO_4S_3$: C, 53.0; H, 5.8; S, 10.9%. Found: C, 52.8; H, 5.4; S, 10.7%.

General Procedure for the Preparation of $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)(thf)][BF_4]$ (II): To a stirred solution of **I** (0.487 g, 1.5 mmol) in thf, a solution of 0.292 g (1.5 mmol) $Ag[BF_4]$ in 5 mL of thf was added using a cannula. Immediately, AgCl precipitated as a grayish solid. After 5 min of stirring, the suspension was filtered and the orange filtrate stored for 14 h at −20 °C. The resulting yellow solid was separated by filtration in the cold and dried at high vacuum.[1] Yield 61%, Mp 127 °C decomposition.

General Procedure for the Preparation of $[Na(thf)_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}L)_3]$ (L = OC_6H_5, SC_6H_5, OC_7H_7, OC_2H_5, $SCH_2C_6H_5$, and SC_2H_5): The sodium salts of the respective anionic ligands NaL were prepared by the reaction of sodium metal (3.0 mmol) with the ligand (L) (3.0 mmol) in 15 mL of thf. The suspension was stirred for 7 h at room temperature. A solution of the cation of **II** (prepared in situ, **I** (1.5 mmol) and $Ag[BF_4]$ (1.5 mmol) in 5 mL of thf, as reported in Ref. 1) was added to the above suspension via a cannula. A fine white precipitate formed and the color of the solution brightened-up. After 2 h of stirring the solution was filtered over celite. The filtrate was overlaid with 100 mL of light petroleum ether and stored at −20 °C for 14 h. The yellow product was dried at high vacuum that resulted in a loss of some of the thf coordinated to the cation. The following yellow compounds were obtained and found to be as follows:

$[Na(thf)_x][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}OC_2H_5)_3]$ (1b); Yield 68%. Mp 74–76 °C (decomp.). IR (thf solution, cm^{-1}) $\nu_{(co)}$: 1923(s), 1822(s). ^1H NMR (DMSO-d_6): allyl {δ 0.85 (dd, 4H, CH_2 anti), 2.9 (dd, 4H, CH_2 syn), and 3.4 (m, 2H, CH)}; thf {1.8 and 3.6}; ethoxide ligand {1.3 (t, 9H, CH_3) and 3.2 (q, 6H, CH_2)}. Anal. Calcd for $C_{20}H_{33}Mo_2NaO_8$, $(x-1)$thf molecules lost on drying: C, 39.0; H, 5.4%. Found: C, 38.5; H, 5.2%.

$[Na(thf)_x][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}OC_6H_5)_3]$ (2b); Yield 83% Mp 156–158 °C (decomp.). IR (thf solution, cm^{-1}) $\nu_{(co)}$: 1921(s), 1827(s). ^1H NMR (DMSO-d_6): allyl {δ 0.8 (dd, 4H, CH_2 anti), 2.7 (dd, 4H, CH_2 syn), and 3.2 (m, 2H, CH)}; thf {1.8 (4H, t, CH_2) and 3.6 (m, 4H, CH_2)}; phenolate ligand {6.8, 7.3 (m, 15H)}. Anal. Calcd for $C_{32}H_{33}Mo_2NaO_8$, $(x-1)$thf molecules lost on drying: C, 50.5; H, 4.4%. Found: C, 50.0; H, 4.7%.

$[Na(thf)_x][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$ (3b); Yield 87%. Mp 148–150 °C (decomp.). IR (thf solution, cm^{-1}) $\nu_{(co)}$: 1924(s), 1836(s). ^1H NMR (DMSO-d_6): allyl {δ 0.9 (dd, 4H, CH_2 anti), 2.9 (dd, 4H, CH_2 syn), and 3.4 (m, 2H, CH)}; thf {1.6 (4H, t, CH_2) and 3.5 (m, 4H, CH_2)}; thiophenolate ligand {7.3, 7.7 (m, 15H)}. Anal. Calcd for $C_{32}H_{33}Mo_2NaO_5S_3$, $(x-1)$thf molecules lost on drying: C, 47.5; H, 4.1; S, 11.9%. Found: C, 47.1; H, 3.9; S, 11.5%.

$[Na(thf)_x][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}OC_7H_7)_3]$ (4b); Yield 85% Mp 92–95 °C (decomp.). IR (thf solution, cm^{-1}) $\nu_{(co)}$: 1917(s), 1823(s). ^1H NMR (DMSO-d_6): allyl {δ 0.8 (dd, 4H, CH_2 anti), 2.9 (dd, 4H, CH_2 syn), and 3.2 (m, 2H, CH); thf {2.0 (t, 4H, CH_2) and 3.6 (m, 4H, CH_2)}; cresolate ligand {6.6, 6.9 (m, 12H)}. Anal. Calcd for $C_{35}H_{39}Mo_2NaO_8$, $(x-1)$thf molecules lost on drying: C, 52.4; H, 4.9%. Found: C, 52.5; H, 5.0%.

$[Na(thf)_x][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_2H_5)_3]$ (5b); Yield 78%. Mp 74–76 °C (decomp.). IR (thf solution, cm^{-1}) $\nu_{(co)}$: 1924(s), 1824(s). (DMSO-d_6): allyl {δ 0.85 (dd, 4H, CH_2 anti), 2.9 (dd, 4H, CH_2 syn), and 3.4 (m, 2H, CH)}; thf {3.1 (q, 8H, CH_2)}; ethanethiolate ligand {1.2 (t, 9H, CH_3) and 1.5 (q, 6H, CH_2)}. Anal. Calcd for $C_{20}H_{33}Mo_2NaO_5S_3$, $(x-1)$thf molecules lost on drying: C, 36.2; H, 5.0; S, 14.5%. Found: C, 36.8; H, 5.2; S, 14.6%.

$[Na(thf)_x][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SCH_2C_6H_5)_3]$ (6b); Yield 87%. Mp 135–138 °C (decomp.). IR (thf solution, cm^{-1}) $\nu_{(co)}$: 1918(s), 1826(s). ^1H NMR (DMSO-d_6): allyl {δ 0.9 (dd, 4H, CH_2 anti), 2.9 (dd, 4H, CH_2 syn), and 3.4 (m, 2H, CH)}; thf {1.6 (t, 4H, CH_2) and 3.5 (m, 4H, CH_2)}; ligand {3.8 (m, 6H, CH_2) and 7.3, 7.5 (m, 15H)}, 1.7, 3.7 (thf). Anal. Calcd for $C_{35}H_{39}Mo_2NaO_5S_3$, $(x-1)$thf molecules lost on drying: C, 49.4; H, 4.6; S, 11.3%. Found: C, 49.1; H, 4.5; S, 11.3%.

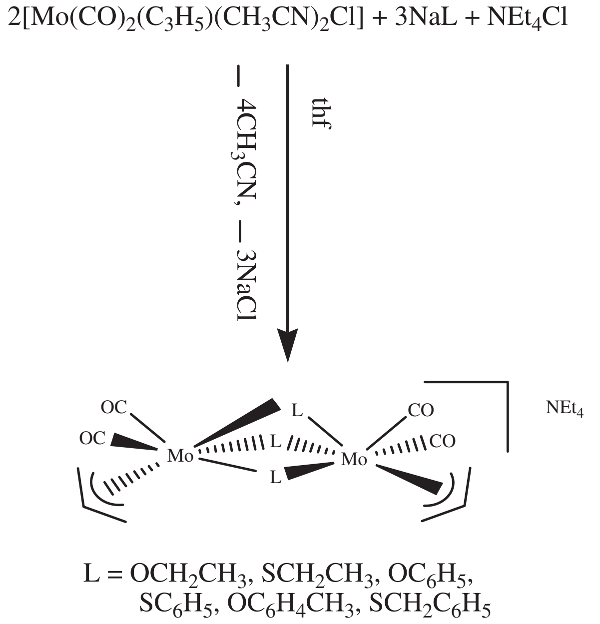
Cyclic Voltammetry Measurements. Cyclic voltammetry measurements were carried out for the complexes $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$ and $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}OC_6H_4CH_3)_3]$ in CH_3CN solvent with Glassy Carbon working electrode and Ag/Ag^+ as reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP).

X-ray Crystallographic Structure Determination. X-ray crystallographic structure determination of the complex $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$ was performed. The cell constants and reflections were measured at a temperature of 150 K on a Syntex $P2_1$ four circle diffractometer with graphite monochromator, $\lambda = 0.71069$ Å, μ (Mo Kα) $= 0.87\ mm^{-1}$ and an ω scan with scan range $4° < 2\theta < 54°$ $(+h,+k,\pm l)$ and a scan speed of 3–29° min^{-1}, intensity dependent. Structure solution and refinement were done using direct methods in combination with Fourier procedures (SHELXTL PLUS); full-matrix least squares on F^2, non-hydrogen atoms with anisotropic temperature factors, $[NEt_4]^+$-counter ions disordered.

Results and Discussion

Characterization of the Complexes. The complexes of the type $[\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}L)_3]^-$ (L = ethoxide, ethanethiolate, phenolate, thiophenolate, cresolate, and benzylthiolate) were synthesized in good yields by the displacement of the labile ligands thf and CH_3CN from the starting materials $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)Cl]$ and the intermediate $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)(thf)]^+$ (the intermediate was generated in situ by the reaction of $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)Cl]$ with $Ag[BF_4]$ in thf) by the sodium thiolate or sodium alkoxide salts of the forms [Na][SR] (RSH = ethanethiol, thiophenol, and benzylthiol) and [Na][OR] (ROH = ethanol, phenol, and 4-methylphenol). The reactions were carried out at room temperature as shown in Schemes 1 and 2. The mole ratio employed for the preparation of these complexes was 2:3 (metal:ligand).

Complexes **1a** to **6a** and **1b** to **6b** are soluble in highly polar solvents such as DMSO and slightly soluble in less polar solvents such as thf and chlorinated solvents. The color of these complexes is yellow. They are air sensitive in both solution and solid states. Complexes containing thiol ligands are of very high sensitivity to air.



L = OCH_2CH_3, SCH_2CH_3, OC_6H_5, SC_6H_5, $OC_6H_4CH_3$, $SCH_2C_6H_5$

Scheme 1.

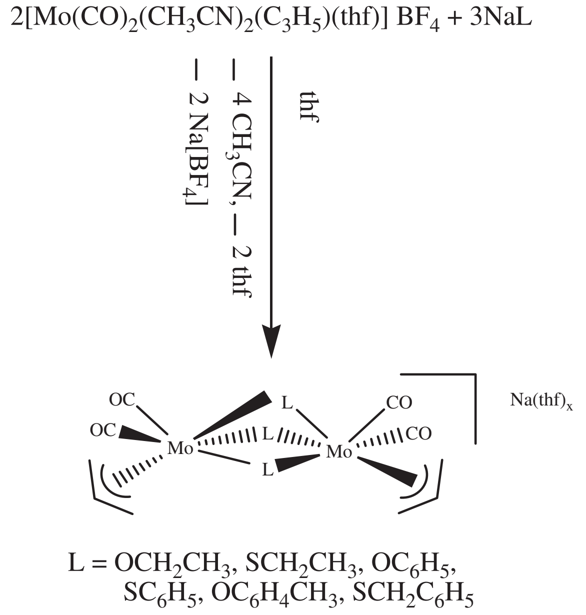
The IR spectra of these complexes show strong bands in the range 1915–1925 and 1815–1830 cm^{-1} which are assigned to the stretching frequencies of the terminal carbonyl groups. The terminal CO bands in all these complexes are shifted to lower values compared to those of the starting complex $[Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)Cl]$ (1955 and 1867 cm^{-1}).[1] This is due to the strong π-back donation from the metal to the CO ligands. This π-bonding is a result of the increased electron density around the metal atom due to the strong ability of the RS$^-$ and RO$^-$ ligands to donate electrons.

The ^{1}H NMR spectroscopic data of the synthesized complexes includes the characteristic protons in their expected chemical shift regions. The protons of the allyl ligands in all complexes appear as a doublet in the range 0.75–0.90 ppm for anti, 2.7–2.9 ppm for syn protons and multiplet in the range 3.2–3.6 ppm for CH protons of the allyl groups.

X-ray Structure Analysis for $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$ (3a). The new complexes are of special interest to inorganic chemists and biochemists. Complexes of molybdenum with sulfur containing ligands are important due to the presence of the Mo–S and Mo–SR bonds in several enzymes and co-enzymes (such as Nitrogenase).

In order to prove the structure, we were successful in obtaining single crystals of the SC_6H_5-containing complex. Crystals suitable for the X-ray study was obtained by recrystallization from thf. The complex **3a** ($Mo_2C_{36}H_{45}O_4NS_3$), relative formula mass 843.82 g mol^{-1}; crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 10.946(2)$ Å, $b = 20.613(3)$ Å, $c = 16.227(3)$ Å, and $\beta = 90.48(1)°$; $V = 3667.2$ Å^3; $d_{\text{calcd}} = 1.528$ g cm^{-3}, $Z = 4$, $\mu = 0.87$ mm^{-1}.

The cell constants and reflections were measured at a temperature of 150 K on a Syntex $P2_1$ Four Circle Diffractometer with graphite monochromator, $\lambda = 0.71069$ Å, μ(Mo Kα) = 0.87 mm^{-1} and an ω scan with scan range $4° < 2\theta < 54°$ $(+h,+k,\pm l)$. There were 8037 unique reflections (7288 with $I > 1.96\sigma(I)$).



L = OCH_2CH_3, SCH_2CH_3, OC_6H_5, SC_6H_5, $OC_6H_4CH_3$, $SCH_2C_6H_5$

Scheme 2.

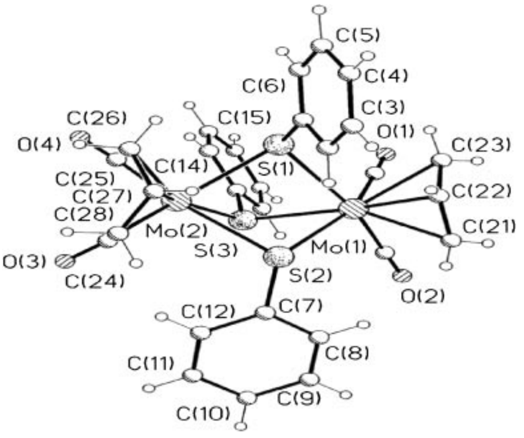


Figure 2. X-ray structure of the $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$ (**3a**) complex.

The structure was solved by the use of direct methods in combination with Fourier procedures (SHELXTL PLUS program); full-matrix least squares on F^2, 454 variables, anisotropic temperature factors for all non-H atoms, hydrogen atoms riding at idealized positions with common isotropic temperature factors. The refinement converged at $R1 = 0.0372$ for all reflections. The values for $wR2$ and GOF are 0.1003 and 1.060, respectively.

Description of the Crystal Structure of Complex $[NEt_4]$-$[\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$. The complex consists of a monoclinic crystal containing arrays of Mo dimers that have three (SC_6H_5) ligands bonded to two Mo atoms in a bridging form, Figure 2. The distance between the Mo atom and the S atom ranges between 2.507 and 2.654 Å. The angle between Mo–S–Mo is ca. 90°. Each Mo atom is bonded to two carbonyl moieties and one allyl moiety. The allyl moiety is bonded to Mo in an η^3-fashion with Mo–C bond distance ranging between 2.222 and 2.340 Å. The angle S–Mo–S ranges

Table 1. Crystal Date of $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$ (**3a**)

Bond distances/Å		Bond angles/°	
Mo(1)–S(1)	2.615(1)	S(1)–Mo(1)–S(2)	78.2(1)
Mo(1)–S(2)	2.634(1)	S(1)–Mo(1)–S(3)	74.9(1)
Mo(1)–S(3)	2.507(1)	S(1)–Mo(1)–C(19)	93.2(1)
Mo(1)–C(19)	1.951(3)	S(1)–Mo(1)–C(20)	161.9(1)
Mo(1)–C(20)	1.942(3)	S(1)–Mo(1)–C(21)	125.3(1)
Mo(1)–C(21)	2.340(4)	S(1)–Mo(1)–C(22)	91.9(1)
Mo(1)–C(22)	2.222(4)	S(1)–Mo(1)–C(23)	83.7(1)
Mo(1)–C(23)	2.316(3)	S(2)–Mo(1)–S(3)	70.7(1)
		S(2)–Mo(1)–C(19)	159.6(1)
		S(2)–Mo(1)–C(20)	103.3(1)
		S(2)–Mo(1)–C(21)	88.9(1)
		S(2)–Mo(1)–C(22)	94.5(1)
		S(2)–Mo(1)–C(23)	126.2(1)
		S(3)–Mo(1)–C(19)	89.3(1)
		S(3)–Mo(1)–C(20)	88.5(1)
		S(3)–Mo(1)–C(21)	148.5(1)
		S(3)–Mo(1)–C(22)	161.7(1)
		S(3)–Mo(1)–C(23)	149.5(1)
Mo(2)–S(1)	2.603(1)	S(1)–Mo(2)–S(2)	78.1(1)
Mo(2)–S(2)	2.654(1)	S(1)–Mo(2)–S(3)	74.9(1)
Mo(2)–S(3)	2.520(1)	S(1)–Mo(2)–C(24)	161.4(1)
Mo(2)–C(24)	1.934(3)	S(1)–Mo(2)–C(25)	95.4(1)
Mo(2)–C(25)	1.942(3)	S(1)–Mo(2)–C(26)	83.6(1)
Mo(2)–C(26)	2.333(4)	S(1)–Mo(2)–C(27)	92.8(1)
Mo(2)–C(27)	2.225(4)	S(1)–Mo(2)–C(28)	126.6(1)
Mo(2)–C(28)	2.331(4)	S(2)–Mo(2)–S(3)	70.1(1)
		S(2)–Mo(2)–C(24)	104.7(1)
		S(2)–Mo(2)–C(25)	166.3(1)
		S(2)–Mo(2)–C(26)	119.0(1)
		S(2)–Mo(2)–C(27)	87.6(1)
		S(2)–Mo(2)–C(28)	85.0(1)
		S(3)–Mo(2)–C(24)	88.7(1)
		S(3)–Mo(2)–C(25)	96.7(1)
		S(3)–Mo(2)–C(26)	154.5(1)
		S(3)–Mo(2)–C(27)	156.2(1)
		S(3)–Mo(2)–C(28)	143.5(1)
		Mo(1)–S(1)–Mo(2)	90.3(1)
		Mo(1)–S(2)–Mo(2)	88.8(1)
		Mo(1)–S(3)–Mo(2)	94.8(1)

from 70.1–78.2 according to the position of phenyl group. Table 1 shows selected bond distances and angles for the complex above.

Cyclic Voltammetry Measurements for the Complexes $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}OC_6H_4CH_3)_3]$ (4a) and $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$ (3a). To study the electrochemical behavior of these complexes, cyclic voltammetry (CV) for the $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}OC_6H_4CH_3)_3]$ (**4a**) and $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$ (**3a**) complexes were carried out. As shown in Figures 3 and 4 the **4a** complex exhibits reversible oxidation around +0.1 V. On the other hand, the **3a** complex displays an irreversible oxidation wave in CV. This might be due to the cleavage of the S–Mo bond upon oxidation of the SPh-complex (S atom oxidizes). While in the OPh-complex the oxidation takes place on the metal atom.

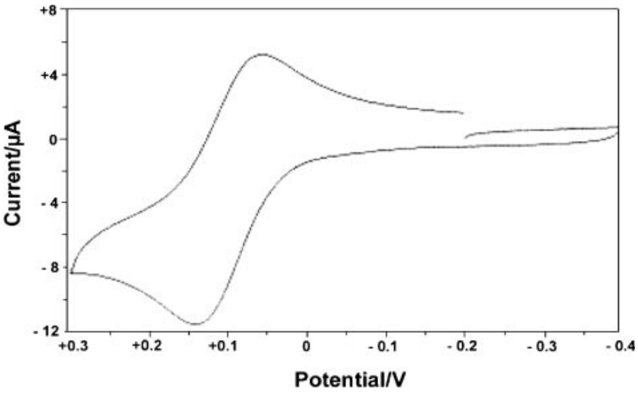


Figure 3. Cyclic voltammogram for the $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}OC_6H_4CH_3)_3]$ (**4a**) complex.

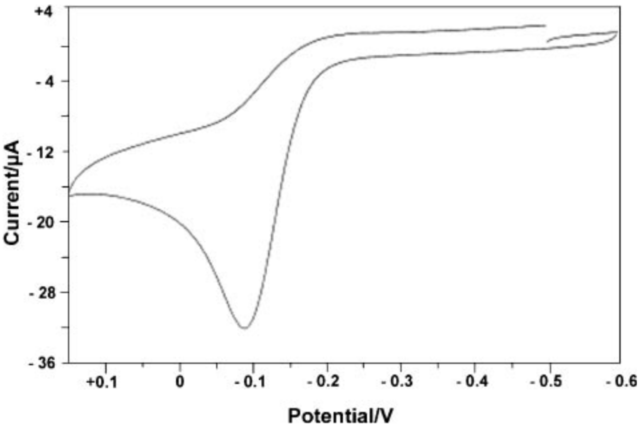


Figure 4. Cyclic voltammogram for the $[NEt_4][\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}SC_6H_5)_3]$ (**3a**) complex.

Conclusion

We prepared complexes of the general formula $[\{Mo(CO)_2(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}L)_3]^-$ ($L = OC_2H_5$, SC_2H_5, OC_6H_5, SC_6H_5, OC_7H_7, and $SCH_2C_6H_4$) in good yields using two reaction paths. Except for the difference of the counter cation, the two methods used gave the same dinuclear anions and almost the same yields. The X-ray crystal structural determination confirms the presence of the three ligands in bridging modes between the two Mo atoms. Cyclic voltammetry measurements indicated that the OPh complexes exhibit reversible oxidation while the SPh has irreversible oxidation modes.

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