Table I. Rate Constant Data for Reactions 1 and 2 (Acetone-d_6)[a]

X^-	*T*, °C 0	10	20	30	40
			a. k_{obsd}, L mol^{-1} s^{-1}		
Cl^-			$1.1\ (0.1) \times 10^{-2}$	$3.5\ (0.15) \times 10^{-2}$	$5.7\ (0.5) \times 10^{-2}$
Br^-		$1.6\ (0.05) \times 10^{-1}$	$2.4\ (0.3) \times 10^{-1}$	$1.6\ (0.1)$	
I^-	$7.2\ (0.6) \times 10^{-2}$	$6.3\ (0.3) \times 10^{-1}$	$7.6\ (0.3) \times 10^{-1}$		
			b. k_2, L mol^{-1} s^{-1}		
Cl^-			$9.2\ (0.9)$	$3.2\ (0.3) \times 10$	$1.8\ (0.2) \times 10^2$
Br^-		$1.9\ (0.2)$	$8.7\ (1)$	$3.0\ (0.4) \times 10$	
I^-	$9.9\ (1) \times 10^{-1}$	$1.75\ (0.15)$	$5.9\ (0.5)$		

[a] Parenthetical numbers are errors estimated from the standard deviation.

Table II. Activation State Parameters for k_2[a]

X^-	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu
Cl^-	27 (4)	36 (8)
Br^-	24 (4)	26 (7)
I^-	14 (4)	−8 (4)

[a] Parenthetical numbers are estimated errors.

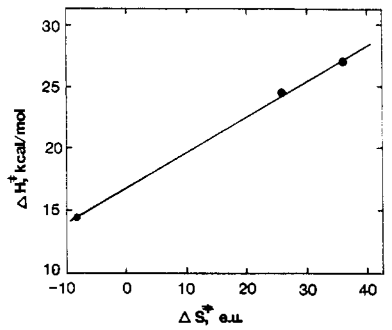

Figure 1. Correlation of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the dealkylation step of the Arbuzov reaction, k_2.

require reconsideration in light of computational errors that were present in the rate constant and Arrhenius calculations. The mechanistic sequence described by reactions 1 and 2 is not affected.

$$[CpCo(dppe)X]^+ + P(OR)_3 \xrightarrow{K_{eq}} [CpCo(dppe)P(OR)_3]^{2+} + X^- \quad (1)$$

$$[CpCo(dppe)P(OR)_3]^{2+} + X^- \xrightarrow{k_2} [CpCo(dppe)P(O)(OR)_2]^+ + RX \quad (2)$$

However, the relative roles of $\Delta S^\ddagger$ and $\Delta H^\ddagger$ in the dealkylation step, k_2, need further comment.

Table I contains the revised data for the rate constants K_{obsd} ($=K_{eq}k_2$) and k_2 in which three of the original values were found to be incorrect. The error estimates for K_{eq}[1] should be approximately doubled, owing to the practical difficutly of measuring small differences in the integrated intensities of the associated species. Table II contains the revised values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ calculated for the dealkylation step, k_2.

It is apparent that the nucleophilicity of X^-, which contributes to the value of $\Delta H^\ddagger$, plays a greater role in the rate of the reaction than previously suggested. This result is in line with the established trend[2] in the nucleophilic strength of Cl^-, Br^-, and I^-. $\Delta S^\ddagger$ is also quite sensitive to X^-, suggesting that the concert of bond breaking, bond formation, and charge redistribution occurring in the transition state of the k_2 step is sharply influenced by the choice of the nucleophile. As before,[1] a direct correlation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ exists (Figure 1), suggesting that, despite the differences in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for this series, the mechanism of the dealkylation step among these compounds is the same.

Acknowledgment. We are indebted to Professor James H. Espenson (Iowa State University) for calling our attention to the likelihood of errors in the original paper.

Registry No. [CpCo(dppe)Cl], 97391-44-1; [CpCo(dppe)Br], 97391-45-2; [CpCo(dppe)I], 97391-46-3; P(OMe)$_3$, 121-45-9.

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(2) Edwards, J. O. *J. Am. Chem. Soc.* **1954**, *76*, 1540.

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Simplified Procedure for the Preparation of Metal Diselenolenes[†]

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Received February 6, 1985

While metal dithiolenes are relatively easy to prepare, particularly the mnt (maleonitriledithiolato) complexes, the selenium analogues are rarer because the precursor diselenolato ligands are unknown and the diselete ("1,2-diselenetene", precursor for the neutral diselenolene complexes) requires extreme conditions for its preparation;[2] in fact, only the bis(trifluoromethyl)diselete is known so that only the trifluoromethyl derivatives of metal diselenolenes ("*cis*-1,2-bis(trifluoromethyl)ethene-1,2-diselenolato–metal" complexes) are known to date.

In this publication we present a new, simplified method for the preparation of metal diselenolenes containing both methyl and trifluoromethyl groups as substituents. While the procedure appears to be general, in this report we deal only with the nickel complexes.

Results and Discussion

Bis[1,2-bis(trifluoromethyl)ethenediselenolato]nickel (**1**) is usually prepared according to Scheme I.[2]

The main difficulty with this procedure rests with the preparation of the heterocycle **2**. The latter is prepared by the reaction of hexafluorobut-2-yne with refluxing selenium (bp 688)! The crude product is formed as an impure (purified by distillation) red oil containing foul-smelling organoselenium contaminants. Furthermore, it would appear that this procedure is limited to the preparation of analogues of **2** that contain electron-withdrawing functional groups and a functionality that can survive the drastic conditions involved.

Our approach to a more general preparation of nickel diselenolenes is shown in Schemes II and III.

The conditions for the preparation of heterocycle **4** are essentially those developed by Cava[3] for the preparation of the carboxymethyl analogue of **4**. Compound **4** is an easily purifiable amber solid, soluble in most organic solvents. In the reaction

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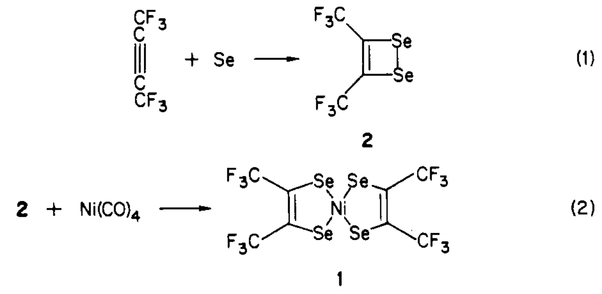
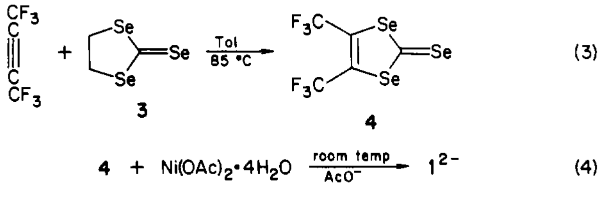
[†] Work mostly performed at Bell Laboratories.

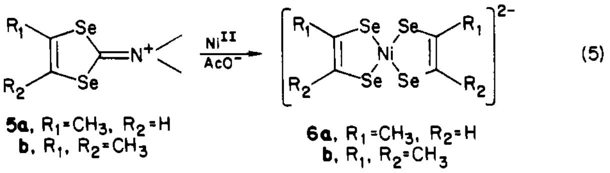
Scheme I



Scheme II



Scheme III



5a, $R_1 = CH_3$, $R_2 = H$
b, $R_1, R_2 = CH_3$

6a, $R_1 = CH_3$, $R_2 = H$
b, $R_1, R_2 = CH_3$

leading from **4** to **1**, the transition metal acts both as "stabilizing trap" for the unstable diselenolate dianion and as catalyst for the hydrolysis of **4**. Since the complex is formed as an ionic species, it is easily separated from the byproduct nickel selenide.

The hydrolytic formation of **1** is rather slow, but the unreacted selone can be recovered readily by hexane extraction from the reaction mixture as described in the Experimental Section. The diselenolene **1** was obtained as the monoanion with tetraphenylarsonium as counterion. All spectroscopic data for the tetraphenylarsonium salt derived from **1** were in accord with those of other diselenolenates obtained in this study and published results for this specific complex.[2]

Heterocycles **5** are available from the various tetraselenafulvalene (TMTSF) syntheses.[4] Hydrolysis of heterocycles **5** (reaction 5) involves a series of steps, the last of which, the probable hydrolysis of a diselenocarbonate, is also catalyzed by the transition-metal acetate. The driving force for this reaction is expected to result from the chelation of the transition metal by the two selenium atoms of the heterocycle.

In principle, chelates **6** should be produced as the doubly charged species; however, the dianion is a very powerful reducing agent such that its isolation was expected to be difficult. Therefore, exposure of the reaction mixture to the atmosphere allowed us to isolate the monoanions as their tetrabutylammonium or tetraphenylarsonium salts (see Experimental Section) in the form of paramagnetic, bright green solids. Acidic hydrogen peroxide oxidized the green monoanions to black, neutral species. Spectroscopic as well as electrochemical properties of these complexes are given in Table I as well as in the Experimental Section.

Table I

	E_1,[a] V	E_2,[a] V
$[NiSe_4C_4H_2(CH_3)_2]Bu_4N$	-0.04	-0.74
$[NiSe_4C_4(CH_3)_4]Bu_4N$	-0.02	-0.88
$[NiSe_4C_4(CF_3)_4]AsPh_4$	0.90[b]	-0.06[b]

[a] E peak vs. SCE in CH_2Cl_2 with Bu_4NBF_4 as electrolyte. [b] Lit.[2] $E_1 = 0.89$, $E_2 = -0.17$ (same conditions).

Experimental Section

Bis(trifluoromethyl)-1,3-diselenole-2-selone. In a three-neck flask equipped with a magnetic stirring bar, dry ice–acetone condenser, and nitrogen inlet were placed 2.34 g (8.4 mmol) of 1,3-selenolane-2-selone (Strem Chemical) and 10 mL of dry toluene. Hexafluoro-2-butyne (3 g, 18.5 mmol) was condensed into the flask, and the mixture was heated gradually to 85 °C and kept at this temperature for 15 min. Additional hexafluoro-2-butyne[5] (1 g, 6.2 mmol) was added in small portions over 15 min until no more starting material was detected by TLC. The mixture was allowed to cool to room temperature and filtered, yielding 3.5 g of amber solid. Recrystallization from ethanol afforded red-orange crystals (mp 42.5–43.5 °C). IR (neat film on NaCl, cm^{-1}): 1580 (w), 1250 (s), 1155 (s), 925 (w), 870 (w), 695 (m). UV-Vis (CH_2Cl_2, λ_{max}, nm (ϵ)): 547 (134), 402 (11976), 345 (2371). Anal. Calcd for $C_5F_6Se_3$: C, 14.6; F, 27.75. Found: C, 14.68; F, 27.71.

$NiSe_4C_4(CF_3)_6$. In a three-neck flask equipped with a magnetic stirring bar and nitrogen inlet and outlet were placed 478 mg of $Ni(OAc)_2 \cdot 4H_2O$, 200 mg of anhydrous NaOAc, and 10 mL of methanol. To this stirred solution, at ambient temperature, was added the above selone (411 mg, 1 mmol) all at once. An immediate reaction was noted by the formation of a salmon-colored precipitate and a purple-red solution. This mixture was heated to reflux for 4 h, cooled, evaporated under nitrogen, and extracted with petroleum ether to remove any unreacted selone. The green residue was extracted with ether and acetonitrile. The solvent was evaporated, and the residue was treated with a freshly prepared and filtered aqueous solution of tetraphenylarsonium chloride hydrate and ether with constant stirring overnight. Separation of the ether layer and drying afforded 90 mg of a green, crystalline solid whose spectroscopic properties were in good accord with published values.[2]

$[NiSe_4C_4H_2(CH_3)_2](C_4H_9)_4N$. To 250 mg (1 mmol) of $Ni(OAc)_2 \cdot 4H_2O$, 800 mg (2 mmol) of **5a**, and 1 g (12 mmol) of sodium acetate was added 35 mL of methanol, and the mixture was heated to reflux for $^1/_2$ h. When the mixture was cooled, the green crystals that had formed were isolated by filtration, washed with methanol, and dried under a fast stream of dry nitrogen. The solid was suspended in methylene chloride and treated with 560 mg (2 mmol) of tetrabutylammonium chloride. After it was stirred for several minutes, the mixture was filtered to remove a brown residue. The filtrate was evaporated to dryness and redissolved in a minimum of methylene chloride. Ether was added to the cloud point, and the sample was set aside overnight. The resulting crystalline mass was filtered, washed with ether, and dried under a stream of nitrogen to afford 280 mg (40% yield) of green crystals, which melted at 122–122.7 °C. IR (neat film, cm^{-1}): 2980 (s), 1515 (m), 1465 (s), 1379 (m), 1262 (m), 1168 (w), 882 (w), 759 (m), 739 (s). UV-vis (CH_2Cl_2, λ_{max}, nm (ϵ)): 900 (2680), 660 (770). Anal. Calcd for $C_{22}H_{44}NNiSe_4$: C, 37.89; H, 6.31; N, 2.00; Ni, 8.43; Se, 45.35. Found: C, 37.90; H, 6.35; N, 1.95; Ni, 8.46; Se, 44.82. EPR ($CDCl_3$): $g = 2.1078$.

$[NiSe_4C_4(CH_3)_4](C_4H_9)_4N$. To a degassed, cooled (0 °C) solution of 498 mg (2 mmol) of $Ni(OAc)_2 \cdot 4H_2O$, 656 mg (8 mmol) of NaOAc, and 576 mg (8 mmol) of $NaHCO_3$ was added 1.65 g (4 mmol) of **5b**. The resulting mixture was heated to reflux for 15 min and allowed to cool. The resulting green precipitate was isolated by filtration, washed copiously with methanol, and dried under a dry nitrogen stream. The resulting solid was combined with 1.11 g (4 mmol) of $Bu_4N^+Cl^-$ in 70 mL of degassed acetonitrile and heated to reflux for 40 min. After the mixture was cooled and filtered, the green filtrate was evaporated down to a green oil contaminated with a white solid. The oil was dissolved in a minimum amount of benzene, filtered, and evaporated. This purification was repeated four times until no more white solid was present. The resulting green gum was dissolved in a minimum of benzene and treated with several drops of dichloromethane. Slow evaporation afforded dark green crystals of mp 138.2–138.3 °C. IR (neat film on NaCl, cm^{-1}): 2980 (s), 1528 (s), 1465 (s), 1380 (s), 1360 (m), 1160 (w), 1100 (w), 1055 (w), 1025 (w), 910 (m), 875 (m), 738 (m). UV-vis (CH_2Cl_2, λ_{max}, nm (ϵ)): 920 (7558), 735 (1715), 678 (1889). Anal. Calcd for $C_{24}H_{48}NNiSe_4$: C, 39.74; H, 6.62; N, 1.93; Ni, 8.10; Se, 43.60. Found: C, 40.05; H, 6.77; N, 2.01; Ni, 9.08. EPR ($CHCl_3$): $g = 2.1064$.

$NiSe_4C_4(CH_3)_4$. To a solution of 260 mg (0.36 mmol) of the above tetrabutylammonium salt in 20 mL of acetonitrile was added 1 mL of

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(5) Commercial hexafluoro-2-butyne is sometimes contaminated with a volatile impurity (not characterized by us). The outcome of this preparation may depend strongly on the purity of the acetylene.

an acetonitrile solution containing 0.03 mL (0.36 mmol) of concentrated hydrochloric acid and 20.4 mg (0.18 mmol) of 30% hydrogen peroxide. The mixture was stirred for 10 min at room temperature and filtered. The resulting black solid was washed with acetonitrile and dried under a nitrogen stream. Soxhlet extraction of the solid overnight with carbon disulfide afford a deeply colored solution that deposited black crystals upon slow evaporation. IR (KBr, cm^{-1}): 2320 (m), 1435 (s), 1365 (s), 912 (s). UV-vis (CH_2Cl_2, λ_{max}, nm (ϵ)): 830 (1374), 710 (3531), 485 (2045).

Anal. Calcd for $C_8H_{12}NiSe_4$: C, 19.89; H, 2.49; Ni, 17.16; Se, 65.47. Found: C, 19.75; H, 2.53; Ni, 16.84; Se, 61.38.

Registry No. III, 17107-91-4; IV, 66251-92-1; VIa·Bu_4N, 97316-36-4; VIb·Bu_4N, 97316-38-6; $[NiSe_4C_4(CF_3)_4]AsPh_4$, 20413-89-2; $NiSe_4C_4(CH_3)_4$, 97316-39-7; $Ni(OAc)_2$, 373-02-4; hexafluoro-2-butyne, 692-50-2.

Contribution from the AFRC Unit of Nitrogen Fixation,
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A Convenient One-Step Synthesis of Thiolato Complexes with Molybdenum–Molybdenum Triple Bonds. X-ray Crystal Structure of $[Mo_2(SC_6H_2\text{-}i\text{-}Pr_3)_6]$

P. J. Blower,[1a] J. R. Dilworth,*[1a,c] and Jon Zubieta*[1b]

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There is considerable current interest in the chemistry of dinuclear complexes with metal–metal multiple bonds,[2a,b] particularly involving alkoxide ligands. The recent reports of the multistage synthesis of $[Mo_2(SC_6H_2Me_3)_6]$[2c] and related species in low yield prompts us to report a very convenient one-step route into the same series of complexes.

The sodium salt of the bulky thiolate 2,4,6-triisopropylthiophenolate (TIPTNa) reacts with $[MoCl_4(thf)_2]$ (thf = tetrahydrofuran) in the presence of CO to give $[Mo(CO)_2(TIPT)_3]^-$,[3] and in the absence of CO no characterizable species were obtained. However, in 1,2-dimethoxyethane as solvent $MoCl_4$ gives a mixture of $[Mo_2(TIPT)_6]$ (I) and $[MoO(TIPT)_4]^-$ (II) in yields of 20–25% and 45–50%, respectively.

Experimental Section

All reactions were carried out under an atmosphere of dinitrogen with use of conventional Schlenk-tube techniques. The solvents were dried over appropriate drying agents and freshly distilled under dinitrogen prior to use. ^1H NMR spectra were recorded on a JEOL FX90Q instrument in deuteriodichloromethane with tetramethylsilane as internal standard. Infrared spectra were recorded on a Unicam SP 2000 spectrophotometer. Microanalyses were performed by Mrs. A. Olney at the University of Sussex or C. J. Macdonald at the Unit of Nitrogen Fixation. 2,4,6-Triisopropylthiophenol and 2,4,6-trimethylthiophenol were prepared by $LiAlH_4$ reduction of the commercially available sulfonyl chlorides. $MoCl_4$[4] was prepared by literature methods.

Preparation of $[Mo_2(SC_6H_2Me_3)_6]$. 2,4,6-Trimethylthiophenol (TMTH) (0.72 mL, 4.7 mmol) in 1,2-dimethoxyethane (40 mL) was treated with sodium metal (0.5 g in small pieces) and stirred at 50 °C for 1 h. It was then cooled to room temperature and filtered to remove excess sodium. $MoCl_4$ (0.28 g, 0.12 mmol) was then added to the solution of the sodium salt. The solution became dark purple and after stirring for 0.5 h was orange-brown. It was then filtered through Celite filter aid and evaporated to dryness. Extraction with hexane gave orange-red $[Mo_2(SC_6H_2Me_3)_6]$, which was recrystallized from thf–hexane; yield 28%. Anal. Calcd for $Mo_2C_{54}H_{66}S_6$: C, 59.0; H, 6.0. Found: C, 58.7; H, 6.4.

Table I. Summary of Crystal Data and Experimental Details for the Structural Study of $[Mo_2(SC_6H_2\text{-}i\text{-}Pr_3)_6]$

(A) Crystal Parameters[a] at 23 °C

a = 17.679 (3) Å
b = 21.019 (4) Å
c = 24.215 (5) Å
V = 8998.3 (14) Å^3
space group: *Pban*
Z = 4
D_{calcd} = 1.18 g/cm^3

(B) Measurement of Intensity Data

cryst dimens: 0.20 × 0.24 × 0.17 mm
instrument: Nicolet R3m
radiation: Mo Kα (λ = 0.71069 Å)
scan mode: coupled θ(cryst)–2θ(counter)
scan rate: variable, 3–30°/min
scan range: $2 \le 2\theta \le 45°$
scan length: from $[2\theta(K\alpha_1) - 1.0]°$ to $[2\theta(K\alpha_2) + 1.0]°$
bkgd measmt: stationary counter, stationary cryst at beginning and end of each 2θ scan, each taken for 0.5 the time of the scan
stds: 3 collected every 197 reflcns; no signif dev over the 70 h of data collecn
no. of reflcns collected: 6631
no. of indep reflcns used in soln: 2525 with $I_o \ge 3\sigma(I_o)$

(C) Reduction of Intensity Data and Summary of Structure and Refinement[b]

data redn: data corrected for bkgd, attenuation, Lorentz, and polarization effects in the usual fashion
abs coeff: 8.5 cm^{-1}
abs cor: none (T_{max}/T_{min} = 1.05)
structure soln: Mo atom position located from a sharpened Patterson map all non-H atoms located on subsequent difference Fourier maps; H atoms included as fixed contributors in the final refinement cycles
atomic scattering factors: neutral atomic scattering factors used throughout anal.
anamalous dispersion: applied to all non-H atoms
final discrepancy factor:[c] R = 0.070; R_w = 0.073
goodness of fit:[d] 1.69

[a] From a least-squares fitting of the setting angle of 25 reflections. [b] All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using local versions of the Nicolet SHELXTL interactive crystallographic software package as described in: Sheldrick, G. M. "Nicolet SHELXTL Operations Manual"; Nicolet XRD Corp.: Cupertino, CA, 1979. [c] $R = \sum[|F_o| - |F_c|/\sum|F_o|]$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\delta^2(F_o) + g^*(F_o)^2$; g = 0.001. [d] GOF $= [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

Preparation of $[Mo_2(SC_6H_2\text{-}i\text{-}Pr_3)_6]$ (I). A 1,2-dimethoxyethane (40 mL) solution of the sodium salt of 2,4,6-triisopropylthiophenol (2.1 mL, 9.8 mmol) was prepared as above and a solution of $MoCl_4$ (0.38 g, 2.0 mmol) in 1,2-dimethoxyethane (20 mL) added. The resulting mixture was stirred at room temperature for 16 h and filtered through Celite filter aid. Washing of the resulting filtered solid with methanol and addition of $[Ph_4P]Br$ gave $[Ph_4P][MoO(SC_6H_2\text{-}i\text{-}Pr_3)_4]$ as a blue crystalline solid (30% yield). The filtrate was evaporated to dryness and the residue triturated with pentane (30 mL). The resulting pink-brown solid was filtered off, washed with methanol until the washings were no longer blue, and recrystallized as red prisms from dichloromethane–acetonitrile; yield 25%. Anal. Calcd for $Mo_2C_{90}H_{138}S_6$: C, 67.4; H, 8.6. Found: C, 67.2; H, 8.9.

X-ray Data Collection and Structure Solution. Red prisms of I suitable for a structure determination were obtained by slow diffusion of acetonitrile into a dichloromethane solution. The details of data collection and structure solution are summarized in Table I. Atomic positional and isotropic thermal parameters are listed in Table II.

Results and Discussion

The orange-red derivatives $[Mo_2(SAr)_6]$ (Ar = TIPT, TMT) are isolated as dark-red crystals that are indefinitely stable in air as solids and can be recrystallized in reagent grade solvents in air. The other products, the blue complexes $[MoO(SAr)_4]^-$, are

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