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Trithio-Chloro Molybdate $[MoClS_3]^-$: A Versatile Precursor for Molybdenum Trisulfido Complexes

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The reaction of trithiomolybdate $[PPh_4]_2[MoOS_3]$ (**1**) with 2 equiv of trimethylchlorosilane generated trithio-chloro molybdate $[PPh_4][MoClS_3]$ (**2**) in high yield, by way of a siloxy complex $[PPh_4][Mo(OSiMe_3)S_3]$ (**3**). This intriguing reaction provided us with a convenient entry into a series of mononuclear molybdenum trisulfido complexes, $[PPh_4][MoS_3X]$ (**4**, X = Cp*; **6a**, X = S^{t}Bu; **6b**, X = SPh; **6c**, X = SMes (Mes = mesityl); **6d**, X = STip (Tip = 2,4,6-triisopropylphenyl); **6e**, X = SDmp (Dmp = 2,6-dimesitylphenyl); **7**, X = NPh_2; **8a**, X = O^{t}Bu; **8b**, X = OPh; **8c**, X = $OC(CH_2)^tBu$; **8d**, X = $OC(CH_2)Ph$), which were obtained by the reactions of **2** with the corresponding potassium salts. In a similar manner, a citrate complex $[PPh_4][MoS_3(Me_3cit)]$ (**9**, $Me_3cit = OC(CH_2CO_2Me)_2(CO_2Me)$) was synthesized, which may model the molybdenum site of the nitrogenase FeMo-cofactor. The molecular structures of **2**, **6c**, **7**, **8a**, **8b**, **8c**, and **9** were determined by X-ray crystallography.

Introduction

Thio/oxo complexes of molybdenum are important constituents in the active sites of molybdo-enzymes, such as the molybdopterin cofactors of oxidoreductases[1] and the FeMo-cofactor of nitrogenase.[2] Thiomolybdate and oxothiomolybdates have also received recent attention as precursors of luminescent[3] and nonlinear optical materials,[4] and they have been used in organic synthesis as sulfur transfer reagents[5] and in medical applications such as anticopper therapy against Wilson's desease.[6] Although mononuclear molybdenum complexes carrying Mo═S bond(s) provide an important basis for the development of this area of chemistry, those with two or more terminal sulfides remain scarce. We have reported the synthesis of the first organometallic trisulfido complexes $[Cp^*MS_3]$ (M = Mo, W),[7] and they have been used as convenient precursors for various heterometallic sulfido clusters with late transition metals.[8] The other known examples of di and trisulfido complexes include

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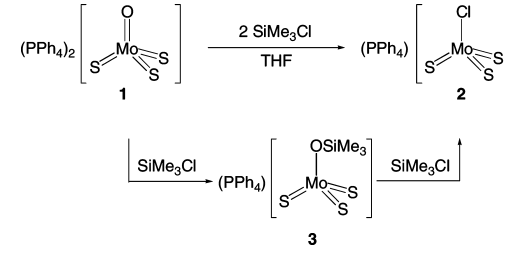
$[MoS_nO_{4-n}]^{2-}$ ($n = 1$–4),[9] $[MoS_3(OSiMe_3)]^-$,[10] *cis*-$Mo(S)_2(\eta^2$-$C_5H_{10}NO)_2$,[11] *cis*-$Mo(S)_2(\eta^2$-$Et_2NO)_2$,[12] *trans*-$Mo(PMe_3)_4(S)_2$,[13] *trans*-Mo(diphosphine)$_2(S)_2$,[14] *trans*-{Me_8[16]aneS_4}-$Mo(S)_2$,[15] and (^{t}Bu$_3$tacn)$Mo(S)_3$.[16] We and Boorman et al. have independently demonstrated that alkylation reactions of tetrathiomolybdate and tetrathiotungstate, $[MS_4]^{2-}$ (M = Mo, W), by alkylhalides give rise to trithio-thiolato complexes $[MS_3(SR)]^-$.[17] The related reaction of molybdate $[MoO_4]^{2-}$ with trialkylchlorosilane was reported to give $[MoO_3(OSiR_3)]^-$ and $[MoO_2(OSiR_3)_2]$.[18]

In this paper, we describe the facile synthesis and reactions of trithio-chloro molybdate $[MoClS_3]^-$ (**2**) from trithiomolybdate $[MoOS_3]^{2-}$ and trimethylchlorosilane. The unique mononuclear molybdenum complex carrying only sulfide and chloride was readily generated from trithiomolybdate $[MoOS_3]^{2-}$ and 2 equiv of trimethylchlorosilane, and complex **2** was found to provide versatile synthetic routes to a series of mononuclear trisulfido complexes of molybdenum. For instance, the reaction of **2** with a citric acid ester produced $[MoS_3\{OCCH_2CO_2Me\}_2(CO_2Me)]]$ (**9**), which is relevant to the molybdenum site of the FeMo-cofactor of nitrogenase.

Results and Discussion

Preparation and Characterization of $[PPh_4][MoClS_3]$. Treatment of trithiomolybdate $[PPh_4]_2[MoOS_3]$ with 2 equiv of Me_3SiCl in THF at −80 °C gave first a dark red solution with precipitation of PPh_4Cl. The color of the solution gradually turned to dark green upon warming to room temperature, and the trithio-chloro molybdate $[PPh_4][MoClS_3]$ (**2**) was isolated in 81% yield as green crystals after a standard workup (Scheme 1). The complex anion of **2** was detected in the electrospray ionization (ESI)-mass spectrum of the dark green reaction solution, where the observed isotope pattern was consistent with calculations. The IR spectrum of **2** isolated as crystals exhibits characteristic Mo=S stretching bands at $\nu_{Mo=S} = 517, 496\ cm^{-1}$. These frequencies are comparable to those of $[MoS_3(OSiMe_3)]^-$ ($\nu_{Mo=S} = 512, 503\ cm^{-1}$).[10] Whereas complex **2** is isolable in pure form from a tetrahydrofuran (THF) solution at room temperature, the complex is not thermally stable in THF, CH_3CN, or dimethylformamide (DMF). For instance, gentle heating of a THF solution of **2** to 40–50 °C resulted in a gradual color change to dark brown, and insoluble materials precipitated.

Scheme 1



The molecular structure of **2** was determined by X-ray diffraction analysis. The crystals of **2** possess crystallographic T_d symmetry, where both phosphorus of PPh_4^+ and molybdenum of $MoClS_3^-$ sit at site of $\bar{4}$ (S_4 point group) of symmetry. Thus, three sulfides and one chloride of $MoClS_3^-$ are fully disordered over four positions, as indicated in Figure 1. The Mo=S distances of the related trisulfido complexes $[MoS_3X]^-$ are 2.148(2) Å for X = S^{t}Bu[17a] and 2.154(6) Å for X = $OSiMe_3$,[10] while the Mo−Cl distances in the four-coordinate (2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$Mo{Si(SiMe$_3$)$_3$}Cl and (2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$Mo{N(SiMe$_3$)$_2$}Cl are in the range of 2.3093(14)–2.3353(11) Å.[19] The observed Mo−S/Cl distance of **2** (2.1727(1) Å) is close to a weighted average of the Mo=S and Mo−Cl bond lengths.

It is likely that the reaction of $[MoOS_3]^{2-}$ with 2 equiv of Me_3SiCl was initiated by a nucleophilic attack of the terminal oxo ligand at the silicon atom of Me_3SiCl. A possible intermediate of the formation of **2** would be the siloxy compound $[MoS_3(OSiMe_3)]^-$ (**3**).[10,18] To explore this possibility, complex **1** was treated with 1 equiv of Me_3SiCl in THF at −50 °C. The ESI-mass spectrum of the resultant red solution showed an intense band of isotopic clusters centered at $m/z = 282.7$, in addition to the signals associated with **2** ($m/z = 228.7$), which fits the theoretical mass pattern

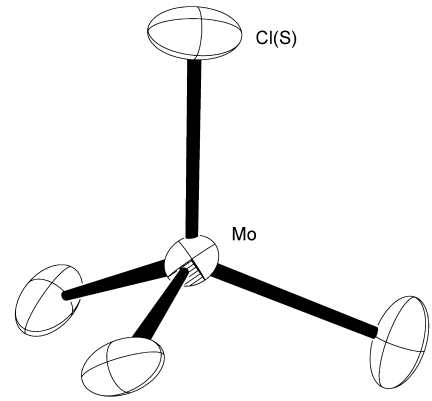


Figure 1. Structure of the complex anion of $[PPh_4][MoClS_3]$ (**2**) with thermal ellipsoids at 50% probability level. Mo−S(Cl) 2.1727(1) Å.

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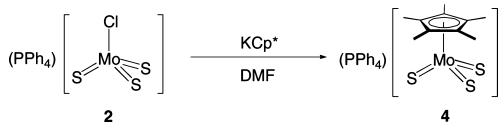
Scheme 2



2 4

of **3**. Analytically pure **3** was isolated successfully in 47% yield from the reaction mixture, after stirring the red solution at −50 °C for 36 h. As expected, the reaction of **3** with 1 equiv of Me_3SiCl in THF at room temperature immediately afforded a green suspension, from which **2** was isolated in 73% yield. Thus, Me_3SiCl attacked the siloxy group of **3**, presumably liberating $Me_3SiOSiMe_3$. In this regard, it is interesting to note that the reaction of $[MoO_4]^{2-}$ with 2 equiv of triphenylchlorosilane was reported to give the doubly silylated product $MoO_2(OSiPh_3)_2$.[18a] An analogous reaction of tetrathiomolybdate $[PPh_4]_2[MoS_4]$ with 2 equiv of Me_3SiCl resulted in an unidentifiable complex mixture and did not show any sign of the formation of **2**.

Synthesis and Characterization of A Series of Molybdenum Trisulfido Complexes. Using the trithio-chloro molybdate **2**, we examined the reactions leading to various mononuclear trisulfido complexes of molybdenum.

(1) Reaction of 2 with KCp*. The reaction of **2** with KCp* in DMF at room temperature and subsequent crystallization from DMF/ether produced $[PPh_4][Cp^*MoS_3]$[7b] (**4**) in 52% yield as reddish brown crystals (Scheme 2). We have previously reported the synthesis of **4** in 51% yield, via C−S bond cleavage of $Cp^*Mo(S^tBu)_3$,[7b] which itself requires five steps starting from commercially available $Mo(CO)_6$. The use of **2** has advantages for the synthesis of **4** over the above procedure, because the precursor **2** can be prepared in two steps from inexpensive $[MoO_4]^{2-}$.

It was found, however, that the choice of solvent was important for the successful isolation of **4**. When the reaction was carried out in CH_3CN, the ESI-mass spectrum of the reaction mixture indicated formation of the dinuclear complex anion $[Cp^*Mo_2S_6]^-$. Interestingly, only a small signal of $[Cp^*MoS_3]^-$ was seen in the spectrum. X-ray structure analysis revealed that the product was $[PPh_4][Cp^*Mo(S)(\mu\text{-}S)_2Mo(S)(S_2)]$ (**5**). As shown in Figure 2, complex **5** contains a Cp^*MoS_3 fragment, to which $MoS(S_2)$ is connected via two μ-S bridges and a Mo(V)−Mo(V) bond. The dinuclear structure was perhaps produced by the reaction of preformed

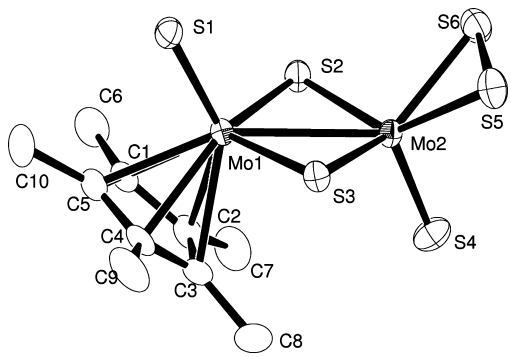


Figure 2. Structure of the complex anion of $[PPh_4][Cp^*Mo(S)(\mu\text{-}S)_2Mo(S)(S_2)]$ (**5**) with thermal ellipsoids at 50% probability level.

Scheme 3

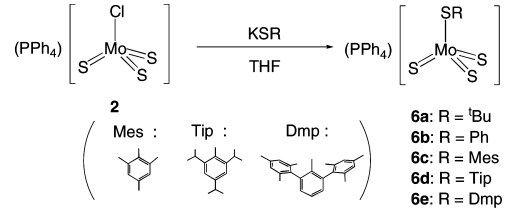


Table 1. Selected Bond Distances (Å) and Angles (°) for **5**

Mo(1)−Mo(2)	2.8731(4)	S(1)−Mo(1)−S(2)	104.27(4)
Mo(1)−S(1)	2.148(1)	S(1)−Mo(1)−S(3)	104.48(4)
Mo(1)−S(2)	2.3158(9)	S(2)−Mo(1)−S(3)	102.51(3)
Mo(1)−S(3)	2.3231(9)	Mo(1)−S(2)−Mo(2)	76.75(3)
Mo(2)−S(2)	2.3121(9)	Mo(1)−S(3)−Mo(2)	76.79(3)
Mo(2)−S(3)	2.3028(9)	S(2)−Mo(2)−S(3)	103.26(3)
Mo(2)−S(4)	2.122(1)	S(2)−Mo(2)−S(4)	105.81(4)
Mo(2)−S(5)	2.382(1)	S(2)−Mo(2)−S(5)	136.33(4)
Mo(2)−S(6)	2.356(1)	S(2)−Mo(2)−S(6)	90.88(4)
S(5)−S(6)	2.068(2)	S(3)−Mo(2)−S(4)	107.97(4)
		S(3)−Mo(2)−S(5)	91.62(4)
		S(3)−Mo(2)−S(6)	133.23(4)
		S(4)−Mo(2)−S(5)	108.11(4)
		S(4)−Mo(2)−S(6)	110.52(4)
		S(5)−Mo(2)−S(6)	51.73(4)

4 with $[MoClS_3]^-$ (**2**) and the reduction of the two Mo centers accompanied by oxidative coupling of two thio ligands to give S_2^{2-}. It is known that dinuclear Mo(V) complexes are occasionally generated in the reactions of $[MoS_4]^{2-}$, with concomitant S−S bond formation.[20] Complex **5** was selectively generated in CH_3CN, probably because KCp* is hardly soluble in CH_3CN while both **2** and **4** dissolve readily, making the reaction between **2** and **4** feasible. On the other hand, DMF dissolves KCp* well, leading to a high concentration of KCp* which consumes all of **2** before it can react with **4**, so that DMF turned out to be the best solvent for the synthesis of **4**.

(2) Reactions of 2 with Various Thiolates. Mononuclear thiolate/sulfide complexes of Mo(VI) remain scarce. Thus, we have investigated the synthesis of a series of thiolate derivatives $[MoS_3(SR)]^-$ from **2**, taking an advantage of the successful isolation of **2** (Scheme 3). Complex **2** was treated with KS^tBu in THF at 0 °C, and $[PPh_4][MoS_3(S^tBu)]$ (**6a**) was isolated in 50% yield as dark brown crystals after recrystallizaion of the crude product from ether/THF. This complex was previously synthesized by the reaction between $[PPh_4]_2[MoS_4]$ and ^{t}BuBr,[17a] where the yield was lower (20%) because of the tendency of $[MoS_3(S^tBu)]^-$ to react further with ^{t}BuBr leading to insoluble materials. Likewise, various arylthiolato complexes $[PPh_4][MoS_3(SAr)]$ {**6b**, Ar = Ph; **6c**, Ar = Mes (Mes = mesityl); **6d**, Ar = Tip (Tip = 2,4,6-triisopropylphenyl); **6e**, Ar = Dmp (Dmp = 2,6-dimesitylphenyl)} were synthesized readily by the reactions of **2** with the corresponding potassium salts of these arylthiolates. In all the reactions, the products were obtained as dark brown crystals in moderate yields ranging from 57%

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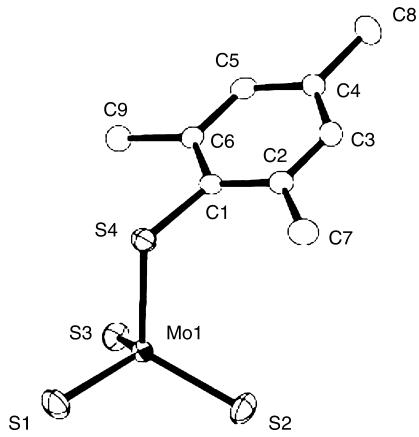


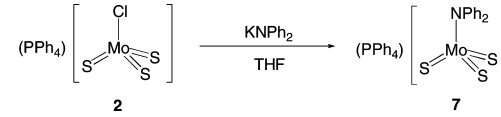
Figure 3. Structure of the complex anion of $[PPh_4][MoS_3(SMes)]$ (**6c**) with thermal ellipsoids at 50% probability level.

to 68%. Complexes **6b**−**e** were characterized by NMR, IR, and ESI-mass spectra, and the elemental analyses were satisfactory. The ESI-mass spectra of **6b**−**e** show isotope patterns in accordance with those calculated for $[MoS_3(SAr)]^-$ (Ar = Ph, Mes, Tip, Dmp), respectively. The IR spectra feature characteristic Mo═S stretching bands appearing at 507−514 cm^{-1} and at 482−486 cm^{-1}, the frequencies of which are somewhat lower than those of **2**. The crystal structure of **6c** was determined, and the ORTEP (Oak Ridge thermal ellipsoid plot) drawing and selected metric parameters are given in Figure 3 and Table 2, respectively. The Mo═S distances (2.1406(5)–2.1603(8) Å) and the Mo−$S_{thiolate}$ distance (2.3519(7) Å) are similar to those of **6a**,[17a] while the Mo(1)−S(4)−C(1) angle (108.54(8)°) is slightly smaller than **6a** (111.8(2)°).

This synthetic route to $[MoS_3(SR)]^-$ starting from $[MoClS_3]$ (**2**) is obviously advantageous over the alkylation of $[MoS_4]^{2-}$. Complex **2** reacts with KSR cleanly, and according to the ESI mass measurement of each reaction solution, the only detectable product was the expected trisulfido/thiolato complex. Furthermore, various potassium salts of arylthiolates readily react with **2** to give $[MoS_3(SAr)]^-$, while $[MoS_4]^{2-}$ does not react with arylhalides.

(3) Synthesis of $[PPh_4][MoS_3(NPh_2)]$. Transition metal amido complexes have been used as precursors for the synthesis of a wide range of organometallic complexes under mild conditions,[21] and a series of intriguing 4-coordinate molybenum complexes have also been synthesized from the reactions of amide ligands. For instance, Cummins et al. have prepared tris-alkoxide complexes $Mo(X)(OAd)_3$ (X = $C\{CH_2(SiMe_3)\}$, N, P; Ad = adamantylidene) via protonation of the amides in $Mo(X)[N(^iPr)(3,5\text{-}C_6H_3Me_2)]_3$ by adamantanol.[22] Schrock et al. expanded the scope of their ring-closing metathesis catalyst $Mo\{N(2,6\text{-}^iPr_2C_6H_3)\}(CHCMe_2Ph)(NPh_2)_2$ by the substitution reaction of amides with a chiral *R*-BINOL derivative to give Mo(NAr)(CHCMe$_2$Ph)(Biphen) (Biphen = 3,3′-^{t}Bu$_2$-5,5′,6,6′-Me$_4$-1,1′-biphenyl-2,2′-diolate).[23] We were thus interested in introducing amides into the trisulfido molybdenum moiety, anticipating that the resulting amide complexes may also serve as convenient precursors, being alternatives to **2**, for the synthesis of trisulfido molybdenum complexes.

Scheme 4



2 **7**

The reaction of **2** with $KNPh_2$ was carried out at room temperature in THF, and the subsequent workup and recrystallization from THF/ether gave $[PPh_4][MoS_3(NPh_2)]$ (**7**) as black crystals in 59% yield (Scheme 4). The ESI-mass spectrum features the signal of the $[MoS_3(NPh_2)]^-$ anion at m/z = 361.7. Complex **7** is highly moisture sensitive, but thermally stable at room temperature. Interestingly, a similar reaction with $KNEt_2$ resulted in a complex mixture of products, and the desired diethylamide complex could not be isolated. In the case of the reaction between **2** and $KN(SiMe_3)_2$, the ESI-mass spectrum indicated that $[MoS_3\{N(SiMe_3)_2\}]^-$ was the major product. However, isolation of the bis(trimethylsilyl)amide complex has not been successful.

The molecular structure of **7** as determined by X-ray diffraction is shown in Figure 4, and the selected bond distances and angles are summarized in Table 2. In the tetrahedral coordination geometry at molybdenum, the average S−Mo−S angle (108.72(4)°) is slightly smaller than the average S−Mo−N angle (110.22(7)°), while the Mo═S distances are normal. The sum of the bond angles at the amide nitrogen is 359.8°, pointing to a planar geometry. The maximum deviation from the planarity occurs at C(7) (0.13(1) Å). The effective N pπ−Mo dπ interaction is also incarnated in the short Mo−N distance of 2.004(2) Å, although it is somewhat longer than those of the dimethylamido molybdenum complexes, $Mo(NMe_2)_4$ (Mo−N (av) =

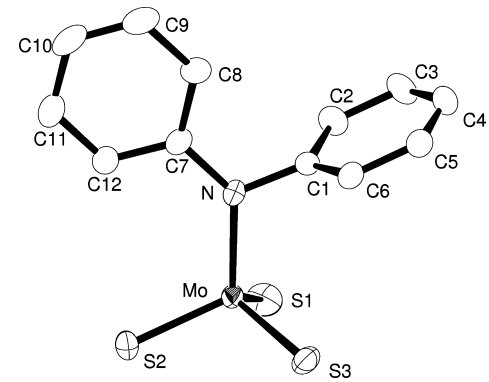


Figure 4. Structure of the complex anion of $[PPh_4][MoS_3(NPh_2)]$ (7) with thermal ellipsoids at 50% probability level.

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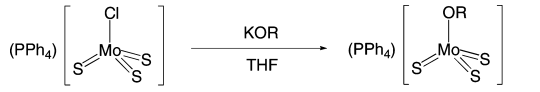
Table 2. Selected Bond Distances (Å) and Angles (°) for **6c** and **7**

6c		**7**	
Mo(1)−S(1)	2.1422(8)	Mo−S(1)	2.1518(7)
Mo(1)−S(2)	2.1603(8)	Mo−S(2)	2.1614(8)
Mo(1)−S(3)	2.1406(5)	Mo−S(3)	2.1433(8)
Mo(1)−S(4)	2.3519(7)	Mo−N	2.004(2)
S(4)−C(1)	1.790(2)	N−C(1)	1.450(4)
S(1)−Mo(1)−S(2)	111.74(3)	N−C(7)	1.423(3)
S(1)−Mo(1)−S(3)	111.17(2)	S(1)−Mo−S(2)	110.46(3)
S(2)−Mo(1)−S(3)	110.57(3)	S(1)−Mo−S(3)	107.13(4)
S(1)−Mo(1)−S(4)	100.50(3)	S(2)−Mo−S(3)	108.57(4)
S(2)−Mo(1)−S(4)	112.11(2)	S(1)−Mo−N	108.73(7)
S(3)−Mo(1)−S(4)	110.40(2)	S(2)−Mo−N	109.50(7)
Mo(1)−S(4)−C(1)	108.54(8)	S(3)−Mo−N	112.43(7)
		Mo−N−C(7)	133.1(2)
		Mo−N−C(1)	112.4(2)
		C(1)−N−C(7)	114.4(2)

Scheme 5



2

8a: R = ^{t}Bu
8b: R = Ph
8c: R = C(CH$_2$)^{t}Bu
8d: R = C(CH$_2$)Ph

1.926(6) Å) and $Mo_2(NMe_2)_6$ (Mo−N (av) = 1.98 Å).[24] The slight elongation of the Mo−N bond in **7**, relative to those of $Mo(NMe_2)_4$ and $Mo_2(NMe_2)_6$, is likely due to π-conjugation between a phenyl substituent and the amido nitrogen leading to weaker π-donation interaction with Mo. In fact, one phenyl ring orients in such a way that it sits coplanarly with the molybdenum and nitrogen atoms (interplane angle = 1.7(2)°), while the other phenyl ring is approximately perpendicular to it (interplane angle = 83.8(2)°). The different orientation of the phenyl rings also makes the two Mo−N−C angles distinct, Mo−N−C(1) = 112.4(2)° versus Mo−N−C(7) = 133.1(2)°, and the shorter N−C(7) bond (1.423(3) Å) relative to N−C(1) (1.450(4) Å) indicates the presence of N−C(7) π bonding.

(4) Synthesis of Alkoxide and Enolate Complexes. Whereas molybdenum complexes containing both Mo=S and Mo−OR groups are relevant to the active sites of xanthine oxidase/dehydrogenase, aldehyde oxidoreductase,[1] and nitrogenase,[2] there have been no monomeric molybdenum trisulfido complexes with alkoxy ligands. Thus, we investigated the substitution of the chloride in **2** with potassium salts of t-butoxide and phenoxide, and these reactions were found to proceed straightforwardly to give the desired trisulfido/alkoxo complexes.

The reaction of **2** with KOR (R = ^{t}Bu, Ph) in THF immediately proceeded at room temperature to afford $[PPh_4][MoS_3(OR)]$ (R = ^{t}Bu (**8a**), Ph (**8b**)), which were isolated in 56 and 81% yields, respectively (Scheme 5). As demonstrated in these reactions, both alkoxides and aryloxides are available for the replacement of the chloride in **2**. Such seemingly simple replacement of a chloride with an alkoxide is rare. However, some related reactions of chloro or oxo-chlorido complexes of molybdenum, $MoCl_4(THF)_2$, $MoCl_2O_2$, $MoCl_2O_2(MeCN)_2$, and Tp*$MoOCl_2$ with alkaline metal salts of alkoxides have been reported to give corresponding alkoxo complexes.[25] The ESI-mass spectra of **8a** and **8b** exhibited signals for anions centered at m/z = 266.7 and 286.7, respectively; their isotope patterns fit well with those of $[MoS_3(OR)]^-$ (R = ^{t}Bu, Ph). The ^{1}H NMR spectra of **8a** and **8b** exhibited a singlet for the ^{t}Bu group at δ 1.30 and the signals for the phenoxide group at δ 7.05 (2H), 6.98 (2H) and 6.79 (1H), respectively.

Transition metal enolate complexes have been postulated as intermediates in metal-mediated catalytic C−C bond formation.[26] Enolate ligands feature diverse coordinaton modes ranging from $\eta^1(O)$-enolate, to $\eta^1(C)$-2-oxoalkyl, and to $\eta^3(O,C,C)$-oxaallyl.[27] The reaction between **2** and potassium enolates resulted in the formation of the $\eta^1(O)$-enolate complexes $[PPh_4][MoS_3\{OC(CH_2)R\}]$ (R = ^{t}Bu (**8c**), Ph (**8d**)) in 51 and 29%. Consistent with the $\eta^1(O)$-enolate coordination, the signals for the terminal =CH_2 group of **8c** and **8d** were observed in the ^{1}H NMR at δ 4.31, 3.94 and δ 4.74, 4.73, respectively, and no intense C=O stretching band was found in the IR spectrum. The characteristic $\nu_{Mo=S}$ bands of **8a**−**d** appeared at 503–515, 484–490 cm^{-1}, which are close to those for the relevant trisulfido complexes $[MoS_3(S^tBu)]^-$ and $[MoS_3(SC_5H_{10}O)]^-$ (508–511, 482 cm^{-1})[17] and $[MoS_3(OSiMe_3)]^-$ (512, 503 cm^{-1}),[10] and are at higher frequencies than those for $[Cp^*MoS_3]^-$ (455, 445 cm^{-1}),[7] (^{t}Bu$_3$tacn)Mo(S)$_3$ (483, 473 cm^{-1}),[16] and $[MoO_{4-n}S_n]^{2-}$ (460–470 cm^{-1}).[9]

The molecular structures of **8a**−**8c** were determined by X-ray crystallography, and the perspective view of **8c** is shown in Figure 5. The selected bond lengths and angles of **8a**−**8c** are listed in Table 3. The molybdenum centers in the alkoxo complexes **8a** and **8b** are also tetrahedral like the other $[MoS_3X]^-$ (X = Cl, SR, NPh_2) complexes. The Mo=S distances, 2.1535(8)–2.1623(7) Å for **8a** and 2.1320(6)–2.1531(6) Å for **8b**, are slightly shorter than those for thiomolybdates $[MoO_nS_{4-n}]^{2-}$ (2.176(6)–2.2236(1) Å)[28] and are comparable to those of $[MoS_3(OSiMe_3)]^-$ (2.154(6)

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(28) (a) For $[MoO3S]^{2-}$, see ref 18b. For $[MoO2S2]^{2-}$, see Kutzler, F. W.; Scott, R. A.; Berg, J. M.; Hodgson, K. O.; Doniach, S.; Cramer, S. P.; Chang, C. H. *J. Am. Chem. Soc.* **1981**, *103*, 6083–6088. (b) For $[MoOS3]^{2-}$, see Krebs, B.; Müller, A.; Kindler, E. *Z. Naturforsch.* **1970**, *25B*, 222. (c) For $[MoS4]^{2-}$, see Lapasset, J.; Chezeau, N.; Belounge, P. *Acta Crystallogr.* **1976**, *B32*, 3087–3088. (d) Kanatzidis, M.; Coucouvanis, D. *Acta Crystallogr.* **1983**, *C39*, 835–838.

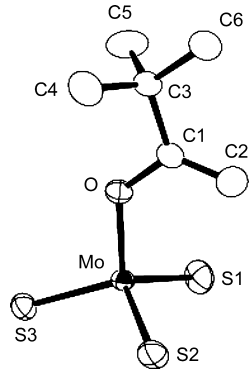

Figure 5. Structure of the complex anion of $[PPh_4][MoS_3\{OC(CH_2)^tBu\}]$ (**8c**) with thermal ellipsoids at 50% probability level.

Table 3. Selected Bond Distances (Å) and Angles (°) for **8a**−**c**

	8a	8b	8c
Mo(1)−S(1)	2.1623(7)	2.1471(6)	2.1448(7)
Mo(1)−S(2)	2.1574(8)	2.1531(6)	2.1442(7)
Mo(1)−S(3)	2.1535(8)	2.1320(6)	2.1559(5)
Mo(1)−O(1)	1.870(2)	1.916(2)	1.9108(18)
O(1)−C(1)		1.377(3)	1.377(2)
O(1)−C(2)	1.447(3)		
C(1)−C(2)			1.316(4)
S(1)−Mo(1)−S(2)	109.73(3)	110.57(2)	108.85(3)
S(1)−Mo(1)−S(3)	108.64(3)	107.44(3)	110.09(2)
S(2)−Mo(1)−S(3)	109.09(3)	109.39(3)	110.24(2)
S(1)−Mo(1)−O(1)	107.94(6)	109.77(6)	109.37(5)
S(2)−Mo(1)−O(1)	110.19(7)	108.62(5)	108.03(6)
S(3)−Mo(1)−O(1)	111.23(7)	111.05(6)	110.22(5)
Mo(1)−O(1)−C(1)		128.7(1)	129.08(16)
Mo(1)−O(1)−C(2)	139.1(2)		

Å)[10] and $[MoS_3(S^tBu)]^-$ (2.148(2) Å).[17a] The short Mo−O distances of **8a** (1.870(2) Å) and **8b** (1.916(2) Å) are indicative of δ-donation from oxygen to molybdenum. The Mo−O(alkoxo) distance of **8a** is similar to those for $Mo_2(OCH_2CMe_3)_6$ (Mo−O = 1.88(2) Å)[29] and Mo[OC(Ad)(Mes)]$_4$ (Mo−O = 1.866(3), 1.869(3) Å, Ad = adamantylidene).[25a] A rather shorter Mo−O(alkoxo) bond can be seen in $Mo_2(O^iPr)_6Br_4$ (Mo−O (av) = 1.81 Å).[30] As indicated by the difference in the Mo−O distances between **8a** and **8b**, δ-donation from the electron rich *tert*-butoxide group in **8a** is more efficient than that from the phenoxide in **8b**. The weaker δ-donation in **8b** possibly results from conjugation within the −OPh ligand. In fact, the O−C(1) distance of **8b** (1.377(3) Å) is significantly shorter than the corresponding O−C(2) bond in **8a** (1.447(3) Å). Such a structural feature is also found in the $\eta^1(O)$-enolate complex **8c**. As can be seen in Figure 5 and Table 3, the electronic effect of the vinyl group on the Mo−O−C bonding array is similar to that of a phenyl group, since the bond lengths of Mo−O (1.9108(18) Å) and O−C(1) (1.377(2) Å) are close to those for the phenoxide complex **8b**. The Mo−O−R angles parallel the trend of the Mo−O distances, in such a way that the shorter Mo−O bond of **8a** accompanies the larger Mo−O−R angle.

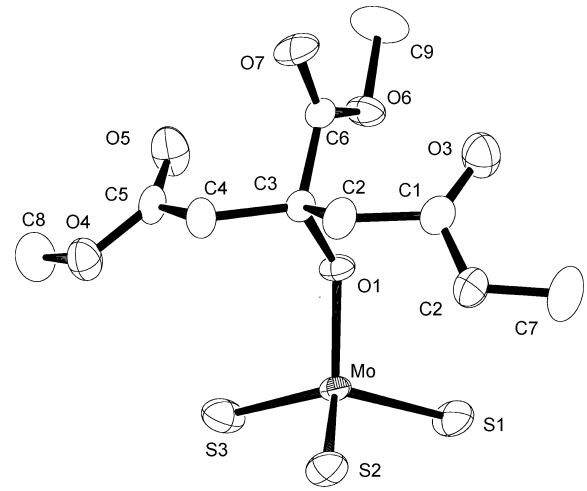

Figure 6. Structure of the complex anion of $[PPh_4][MoS_3(Me_3cit)]$ (**9**) with thermal ellipsoids at 50% probability level.

Scheme 6

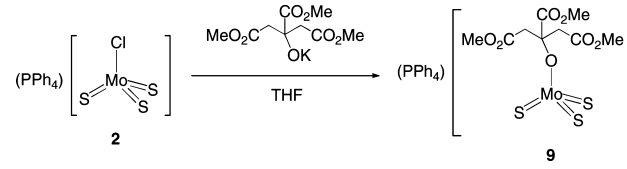

Table 4. Selected Bond Distances (Å) and Angles (°) for **9**

Mo−S(1)	2.1538(7)	S(1)−Mo−S(2)	110.09(3)
Mo−S(2)	2.1447(6)	S(1)−Mo−S(3)	109.31(3)
Mo−S(3)	2.1553(7)	S(2)−Mo−S(3)	108.34(3)
Mo−O(1)	1.890(2)	S(1)−Mo−O(1)	107.89(5)
O−C(3)	1.408(3)	S(2)−Mo−O(1)	111.96(5)
		S(3)−Mo−O(1)	109.22(5)
		Mo−O(1)−C(3)	141.9(1)

(5) Synthesis of $[PPh_4][MoS_3(Me_3cit)]$ (Me_3cit = $OC(CH_2CO_2Me)_2(CO_2Me)$). The molybdenum site in the nitrogenase FeMo-cofactor carries an *R*-homocitrate and a histidine residue.[2] Molybdenum trisulfide complexes with citrate derivatives could serve as suitable building blocks for structural models of the FeMo-cofactor and may provide information regarding reactivity at the molybdenum site. Thus, we have extended the reactions of **2** with alkoxides to the introduction of a citric acid ester to the MoS_3 unit.

Treatment of **2** with the potassium salt of citric acid trimethyl ester led to the formation of a trisulfido complex $[PPh_4][MoS_3(Me_3cit)]$ (**9**, Me_3cit = $OC(CH_2CO_2Me)_2(CO_2Me)$) in 73% yield as a red solid (Scheme 6). The ^1H NMR spectrum of **9** clearly indicated the presence of the Me_3cit moiety, showing two singlets for methyl groups at δ 3.67 and 3.49, and an AB-doublet for the methylenes at δ 3.07 and 2.99. The ESI mass spectrum confirmed the formation of $[MoS_3(Me_3cit)]^-$, showing a molecular ion peak at m/z = 426.7 with an appropriate isotope pattern.

The X-ray derived structure of the anion of **9** is shown in Figure 6. The selected bond distances and angles are listed in Table 4. The Me_3cit group is bound to molybdenum at the alkoxy-oxygen, and the ester portions do not interact with molybdenum. As a result, complex **9** again possesses a

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(30) Chisholm, M. H.; Kirkpatrick, C. C.; Huffman, J. C. *Inorg. Chem.* **1981**, *20*, 871–876.

tetrahedral coordination geometry, and the Mo═S distances are similar to those of **6c**, **7**, **8a**, and **8b**. The absence of interactions between the ester-oxygens and molybdenum points to coordinative saturation of **9** with three terminal sulfides. It might be that coordination of the sulfides to iron(s) would facilitate further coordination of one of the ester-oxygens mimicking the geometry at the molybdenum of the FeMo-cofactor. The Mo−O(1) bond is relatively short, that is shorter than those for relevant citrate (cit^{4-}) complexes of molybdenum, $[Mo(Hcit)(CO)_3]^{3-}$ (Mo−O = 2.230(2) Å)[31] and $K_4[MoO_3(cit)]$ (Mo−O = 2.052(2) Å).[32] The Mo−O(1) distance and the large Mo−O(1)−C(3) angle are similar to those for **8a**. Similarity between **8a** and **9** can be also seen in the IR spectrum, where the Mo═S bands appeared at 509, 490 cm^{-1} for **9** and at 503, 486 cm^{-1} for **8a**.

Summary

The oxo ligand in $[MoOS_3]^{2-}$ (**1**) was found to be selectively replaced by chloride in the reaction with trimethylchlorosilane, giving rise to the molybdenum trisulfidochloro complex $[MoClS_3]^-$ (**2**). This new complex was shown to be a useful and versatile precursor for a series of monomeric trisulfido complexes of molybdenum, and Cp*, thiolato, amido, and alkoxo complexes were readily obtained from the substitution of the chloride with the corresponding alkaline metal reagents. This synthetic method also allowed us to prepare a citrate derivative of molybdenum trisulfide, which should serve as a valuable building block for the synthesis of structural and reaction models of the FeMo-cofactor.

Experimental Section

General Procedures. All reactions were manipulated using standard Schlenk and vacuum line techniques under a nitrogen atmosphere. THF, CH_3CN, ether, and hexane were purified by the method of Grubbs, where the solvents were passed over columns of activated alumina and a supported copper catalyst supplied by Hansen & Co. Ltd. Degassed and distilled solvents from sodium benzophenone ketyl (hexane, ether, toluene, THF) or from CaH_2 (CH_3CN) were also used. DMF was dried over Molecular Sieve 4A. CD_3CN, $CDCl_3$, CD_2Cl_2, tetrahydrofuran-d_8, and trimethylchlorosilane were dried by CaH_2 and distilled prior to use. ^1H NMR spectra were recorded on a Varian INOVA-500 or a JEOL ECA600. The signals were referenced to the residual proton peak of the deuterated solvent. IR spectra were recorded on a JASCO FT/IR-410. UV/vis spectra were recorded on a JASCO V560. ESI-TOF-MS spectra were recorded on a Micromass LCT TOF-MS. Elemental analyses were recorded on a LECO-CHNS-932 elemental analyzer where the crystalline samples were sealed in silver capsules under nitrogen. X-ray diffraction data were collected on a Rigaku AFC7R, a Rigaku AFC8, or a Rigaku RA-Micro7 equipped with a CCD area detector by using graphite-monochromated Mo Kα radiation. $[PPh_4]_2[MoOS_3]$ was prepared according to the literature procedure.[9b]

All potassium salts of the ligands were prepared in THF. KCp* was prepared from the reaction of C_5Me_5H with 1 equiv of KH. After evaporation, KCp* was purified by washing with hexane. KSR (R = ^{t}Bu, Ph), $KNPh_2$, and KOR′ (R′ = ^{t}Bu, Ph, $C(CH_2)_2{}^t$Bu, $C(CH_2)_2Ph$) were prepared in a similar manner from the reactions of thiols, $HNPh_2$, or alcohols, with KO^{t}Bu (for KS^{t}Bu) or KH (others). KSAr (Ar = Mes, Tip, Dmp) were generated in situ and used without purification: KSMes was generated from MesSH (300 mg, 1.97 mmol) and KH (80 mg, 2.0 mmol); KSTip was generated from TipSH (486 mg, 2.06 mmol) and KH (83 mg, 2.1 mmol); KSDmp was generated from DmpSH (500 mg, 1.44 mmol) with KH (58 mg, 1.5 mmol). $K(Me_3cit)$ was prepared from citric acid trimethyl ester (271 mg, 1.16 mmol) and a toluene solution of $KN(SiMe_3)_2$ (0.5 M, 2.0 mL, 1.0 mmol) in THF at −80 °C, and was purified by washing with hexane.

Preparation of $[PPh_4][MoClS_3]$ (2). Treatment of a THF suspension of $[PPh_4]_2[MoOS_3]$ (555 mg, 0.626 mmol) with Me_3SiCl (185 μL, 1.46 mmol) at −80 °C gave a purple suspension. Upon warming to room temperature, the color of the suspension gradually turned dark green. After being centrifuged to remove insoluble materials, the solution was evaporated to dryness. The resulting green solid was extracted with THF (40 mL), and the extract was centrifuged again. After concentration of the extract, ether was layered. Slow diffusion of the layered solution led to the formation of dark green (almost black) crystals of **2** (288 mg, 0.508 mmol, 81%). IR (KBr): 3054(w), 1585(w), 1483(m), 1437(s), 1338(w), 1311(w), 1190(w), 1169(w), 1107(s), 997(m), 923(w), 760(w), 746(m), 723(s), 687(s), 526(s), 517(s, Mo═S), 496(sh, Mo═S) cm^{-1}. ESI-TOF-MS (THF, rt): m/z = 228.7. UV/vis (THF, rt): λ_{max} (ε) 581 (1.0×10^3), 425 (4.2×10^3), 315 nm (6.2×10^3). Elemental analysis calcd for $C_{24}H_{20}ClMoPS_3$: C 50.84, H 3.56, S 16.97; Found: C 50.77, H 3.66, S 16.70.

Reaction of $[PPh_4][MoOS_3]$ with one Equivalent of Me_3SiCl. To a THF suspension of $[PPh_4][MoOS_3]$ (500 mg, 0.564 mmol) was added Me_3SiCl (75 μL, 0.60 mmol) at −80 °C. After stirring for 36 h at −50 °C, the solvent was removed under reduced pressure. The residue was extracted with THF (50 mL) and the extract was centrifuged to remove insoluble materials. Concentration of the solution followed by slow diffusion of ether gave red crystals of $[PPh_4][MoS_3(OSiMe_3)]$ (**3**, 165 mg, 0.266 mmol, 47%). ^1H NMR (500 MHz, $CDCl_3$, rt): δ 7.88 (m, 4H, P*Ph*$_4$), 7.77 (m, 8H, P*Ph*$_4$), 7.66 (m, 8H, P*Ph*$_4$), 0.14 (s, 9H, Si*Me*$_3$). ESI-TOF-MS (CH_3CN, rt): 282.7. Elemental analysis calcd for $C_{27}H_{29}MoOPS_3Si$: C 52.24, H 4.71, S 15.50; Found: C 52.12, H 4.46, S 15.78.

Reaction of $[PPh_4][MoS_3(OSiMe_3)]$ (3) with Me_3SiCl. To a THF solution of $[PPh_4][MoS_3(OSiMe_3)]$ (72 mg, 0.12 mmol) was added Me_3SiCl (16 μL, 0.13 mmol) at room temperature. After stirring for 30 min, the solution was centrifuged and evaporated to dryness. The residue was extracted with THF, and the extract was centrifuged again. After evaporation under reduced pressure, the green solid was washed with ether (5 mL × 2) and dried under reduced pressure to give $[PPh_4][MoClS_3]$ (**2**, 48 mg, 0.084 mmol, 73%).

Preparation of $[PPh_4][Cp^*MoS_3]$ (4). To a DMF solution of **2** (173 mg, 0.305 mmol) was added a THF solution of KCp* (60 mg, 0.34 mmol) at room temperature. With vigorous stirring for 15 min, the reaction mixture afforded a reddish brown solution. After addition of acetonitrile (30 mL) to precipitate KCl, the brown suspension was centrifuged. The solution was concentrated, layered with ether, and kept standing at −40 °C. Reddish brown crystals of $[PPh_4][Cp^*MoS_3]$ (**4**, 106 mg, 0.159 mmol) were obtained in 52% yield. This compound gave identical spectral data with those reported.[7b]

Reaction of 2 with KCp* in CH_3CN. To an acetonitrile solution (20 mL) of **2** (111 mg, 0.196 mmol) was added a THF (5 mL) suspension of KCp* (38 mg, 0.218 mmol) at −20 °C. The reaction mixture was vigorously stirred to give a dark brown suspension.

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(32) Zhou, Z.; Wan, H.; Tsai, K. *Inorg. Chem.* **2000**, *39*, 59–64.

After warming to room temperature, the suspension was centrifuged to remove insoluble materials. The ESI-mass spectrum of the solution showed anionic signals at m/z = 518.4 (100%, $[Cp^*Mo_2S_6]^-$), 486.7 (20%, $[Cp^*Mo_2S_5]^-$), and 328.9 (5%, $[Cp^*MoS_3]^-$). After evaporation of the solvent, the dark brown residue was extracted with THF (20 mL), and the extract was centrifuged. The dark brown solution was concentrated and stored at −20 °C to produce black crystals of $[PPh_4][Cp^*Mo(S)(\mu\text{-}S)_2Mo(S)(S_2)]$ (**5**) and a dark brown powder. Single crystals of **5** for X-ray diffraction were manually separated from the precipitate.

Preparation of [PPh$_4$][MoS$_3$(S^{t}Bu)] (6a). The following manipulations were carried out at 0 °C because of thermal instability of the product. KS^{t}Bu was prepared by the reaction of ^{t}BuSH with KO^{t}Bu. To a THF solution of $[PPh_4][MoClS_3]$ (200 mg, 0.353 mmol) was added a THF suspension of KS^{t}Bu (59 mg, 0.46 mmol). After stirring for 30 min, the suspension was centrifuged. The resulting brown solution was diffused into ether at −40 °C to give dark brown crystals of $[PPh_4][MoS_3(S^tBu)]$ (**6a**, 112 mg, 0.177 mmol, 50%). The product gave identical spectral data with those reported by Boorman.[17a] ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.87 (m, 4H, P*Ph$_4$*), 7.76 (m, 8H, P*Ph$_4$*), 7.63 (m, 8H, P*Ph$_4$*), 1.44 (s, 9H, ^{t}Bu). ESI-TOF-MS (CH_3CN): m/z = 282.6. Elemental analysis calcd for $C_{28}H_{29}MoPS_4$: C 54.18, H 4.71, S 20.66; Found: C 53.86, H 4.76, S 20.58.

Preparation of [PPh$_4$][MoS$_3$(SPh)] (6b). The reaction of $[PPh_4][MoClS_3]$ (122 mg, 0.215 mmol) with KSPh (47 mg, 0.31 mmol) in THF was initiated at −80 °C. After warming to room temperature, the brown suspension was centrifuged, and the solution was diffused into ether at −40 °C to give dark brown crystals of $[PPh_4][MoS_3(SPh)]$ (**6b**, 78 mg, 0.122 mmol, 57%). Satisfactory ^{1}H NMR measurement was not available because of thermal instability and low solubility in $CDCl_3$ and CD_3CN. IR (KBr): 3049(w), 1585(w), 1481(m), 1434(s), 1315(w), 1184(w), 1160(w), 1108(s), 1022(w), 997(m), 746(m), 723(s), 688(s), 528(s), 514(s, Mo═S), 486(m, Mo═S) cm^{-1}. ESI-TOF-MS (CH_3CN): m/z = 302.7. UV/vis (CH_3CN, rt): λ_{max} (ε) 520 (1.0×10^3), 457 (5.0×10^3), 269 nm (1.7×10^4). Elemental analysis calcd for $C_{30}H_{25}MoPS_4$: C 56.24, H 3.93, S 20.02; Found: C 56.62, H 3.98, S 19.62.

Preparation of (PPh$_4$)[MoS$_3$(SMes)] (6c). A similar procedure as that for **6b** was used. The reaction of $[PPh_4][MoClS_3]$ (1.00 g, 1.76 mmol) with KSMes (1.97 mmol) gave a brown suspension. After addition of acetonitrile, the mixture was centrifuged. The solution was concentrated, and then diffused into ether to give dark brown crystals of $[PPh_4][MoS_3(SMes)]$ (**6c**, 821 mg, 1.20 mmol, 68%). ^{1}H NMR (600 MHz, CD_3CN, rt): δ 7.91 (m, 4H, P*Ph$_4$*), 7.74 (m, 8H, P*Ph$_4$*), 7.68 (m, 8H, P*Ph$_4$*), 6.82 (s, 2H, C$_6$*H$_2$*), 2.37 (s, 6H, *o*-C$_6$Me$_2$), 2.22 (s, 3H, *p*-C$_6$Me). IR (KBr): 3055(w), 1583(w), 1481(m), 1462(w), 1437(s), 1373(w), 1313(w), 1184(w), 1161(w), 1101(s), 1051(w), 1026(w), 995(m), 860(w), 758(m), 719(s), 690(s), 528(s), 511(s, Mo═S), 482(m, Mo═S) cm^{-1}. ESI-TOF-MS (CH_3CN): m/z = 344.7. UV/vis (THF, rt): λ_{max} (ε) 518 (3.1×10^3), 447 (6.2×10^3), 277 nm (2.1×10^4). Elemental analysis calcd for $C_{33}H_{31}MoPS_4$: C 58.05, H 4.58, S 18.79; Found: C 57.75, H 4.62, S 18.74.

Preparation of (PPh$_4$)[MoS$_3$(STip)] (6d). The same procedure as in the case of **6b** was used. The reaction of $[PPh_4][MoClS_3]$ (1.10 g, 1.94 mmol) and KSTip (2.06 mmol) in THF at −80 °C gave a brown suspension, from which dark brown crystals of $[PPh_4][MoS_3(STip)]$ (**6d**, 875 mg, 1.14 mmol, 59%) were isolated. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.82 (m, 4H, P*Ph$_4$*), 7.70 (m, 8H, P*Ph$_4$*), 7.63 (m, 8H, P*Ph$_4$*), 6.84 (s, 2H, C$_6$*H$_2$*), 3.86 (sep, J = 6.9 Hz, 2H, C*H*Me$_2$), 2.79 (sep, J = 6.7 Hz, 1H, C*H*Me$_2$), 1.19 (d, J = 6.7 Hz, 6H, CH*Me$_2$*), 1.13 (d, J = 6.9 Hz, 12H, CH*Me$_2$*). IR (KBr): 3053(w), 1585(w), 1483(m), 1460(w), 1437(s), 1360(w), 1311(w), 1186(w), 1163(w), 1107(s), 1059(w), 1028(w), 995(m), 883(w), 750(m), 723(s), 687(s), 526(s), 511(s, Mo═S), 484(m, Mo═S) cm^{-1}. ESI-TOF-MS (CH_3CN): m/z = 428.8. UV/vis (THF, rt): λ_{max} (ε) 509 (1.4×10^3), 443 (4.4×10^3), 277 nm (2.3×10^4). Elemental analysis calcd for $C_{39}H_{43}MoPS_4$: C 61.08, H 5.65, S 16.72; Found: C 61.38, H 5.56, S 16.72.

Preparation of [PPh$_4$][MoS$_3$(SDmp)] (6e). The same procedure as in the case of **6b** was used. The reaction of $[PPh_4][MoClS_3]$ (800 mg, 1.41 mmol) with KSDmp (1.44 mmol) in THF at −80 °C gave a brown suspension, from which dark brown crystals of $[PPh_4][MoS_3(SDmp)]$ (**6e**, 777 mg, 0.886 mmol, 63%) were isolated. ^{1}H NMR (600 MHz, CD_2Cl_2, rt): δ 7.89 (m, 4H, P*Ph$_4$*), 7.72 (m, 8H, P*Ph$_4$*), 7.60 (m, 8H, P*Ph$_4$*), 7.22 (t, J = 7.6 Hz, 1H, *p*-C$_6$*H*), 6.90 (d, J = 7.6 Hz, 2H, *m*-C$_6$*H*), 6.89 (s, 4H, C$_6$*H$_2$*Me$_3$), 2.28 (s, 6H, *p*-C$_6$*Me*), 2.10 (s, 12H, *o*-C$_6$*Me*). IR (KBr): 3051(w), 1583(w), 1483(m), 1437(s), 1383(w), 1315(w), 1181(w), 1165(w), 1107(s), 1028(w), 995(m), 847(m), 800(m), 746(m), 723(s), 688(s), 526(s), 507(s, Mo═S), 484(m, Mo═S) cm^{-1}. ESI-TOF-MS (THF): m/z = 538.7. UV/vis (THF, rt): λ_{max} (ε) 516 (2.7×10^3), 458 (5.8×10^3), 276 nm (2.0×10^4). Elemental analysis calcd for $C_{48}H_{45}MoPS_4$: C 65.73, H 5.17, S 14.62; Found: C 65.65, H 5.27, S 14.89.

Preparation of [PPh$_4$][MoS$_3$(NPh$_2$)] (7). To a THF solution of $[PPh_4][MoClS_3]$ (200 mg, 0.353 mmol) was added a THF solution of $KNPh_2$ (103 mg, 0.498 mmol) at room temperature. After stirring for 30 min, the solution was centrifuged and evaporated to dryness. The residue was extracted with THF, and the extract was centrifuged again. The resulting solution was diffused into ether to give black crystals of $[PPh_4][MoS_3(NPh_2)]$ (**7**, 145 mg, 0.207 mmol, 59%). ^{1}H NMR (500 MHz, CD_3CN, rt): δ 7.92 (m, 4H, P*Ph$_4$*), 7.75 (m, 8H, P*Ph$_4$*), 7.69 (m, 8H, P*Ph$_4$*), 7.20 (t, J = 8.0 Hz, 4H, N*Ph$_2$*), 7.16 (d, J = 7.5 Hz, 4H, N*Ph$_2$*), 6.97 (t, J = 7.3 Hz, 2H, N*Ph$_2$*). IR (KBr): 3057(w), 1583(m), 1479(s), 1437(s), 1319(w), 1226(m), 1174(m), 1153(m), 1108(s), 1026(w), 995(m), 928(m), 873(m), 856(w), 761(s), 750(w), 719(s), 690(s), 524(s), 505(s, Mo═S), 482(m, Mo═S), 444(w), 417(w) cm^{-1}. ESI-TOF-MS (CH_3CN): m/z = 361.7. UV/vis (CH_3CN, rt): λ_{max} (ε) 468 (8.1×10^3), 327 (9.3×10^3), 261 nm (1.8×10^4). Elemental analysis calcd for $C_{36}H_{30}MoNPS_3$: C 61.79, H 4.32, N 2.00, S 13.75; Found: C 61.43, H 4.46, N 2.04, S 13.78.

Preparation of [PPh$_4$][MoS$_3$(O^{t}Bu)] (8a). To a THF solution of $[PPh_4][MoClS_3]$ (300 mg, 0.529 mmol) was added KO^{t}Bu (74 mg, 0.66 mmol) at room temperature. After stirring for 30 min, the solution was centrifuged to remove insoluble materials. The resulting dark red solution was concentrated and diffused into ether to give red crystals of $[PPh_4][MoS_3(O^tBu)]$ (**8a**, 178 mg, 0.294 mmol, 56%). ^{1}H NMR (500 MHz, CD_3CN, rt): δ 7.91 (m, 4H, P*Ph$_4$*), 7.74 (m, 8H, P*Ph$_4$*), 7.69 (m, 8H, P*Ph$_4$*), 1.30 (s, 9H, ^{t}Bu). IR (KBr): 3053(w), 2970(w), 2915(w), 1585(w), 1483(w), 1435(s), 1385(w), 1359(w), 1342(w), 1315(w), 1232(w), 1161(m), 1107(s), 1025(w), 997(m), 931(s), 789(w), 752(m), 723(s), 688(s), 575(m), 526(s), 503(s, Mo═S), 486(sh, Mo═S) cm^{-1}. ESI-TOF-MS (THF, rt): m/z = 266.7. UV/vis (THF, rt): λ_{max} (ε) 541 (1.0×10^3), 411 (4.7×10^3), 283 nm (9.5×10^3). Elemental analysis calcd for $C_{28}H_{29}MoOPS_3$: C 55.62, H 4.83, S 15.91; Found: C 55.41, H 4.49, S 16.37.

Preparation of [PPh$_4$][MoS$_3$(OPh)] (8b). The same procedure as in the case of **8a** was used. The reaction of $[PPh_4][MoClS_3]$ (222 mg, 0.392 mmol) with KOPh (71 mg, 0.54 mmol) gave a red suspension, from which red crystals of $[PPh_4][MoS_3(OPh)]$ (**8b**, 198 mg, 0.336 mmol, 81%) were isolated. ^{1}H NMR (500 MHz,

Table 5. Crystal Data for **2**, **5**, **6c**, **7**, **8a**−**c**, and **9**

	2	**5**	**6c**	**7**	**8a**	**8b**	**8c**	**9**
formula	$C_{24}H_{20}ClMoPS$	$C_{38}H_{35}Mo_2OPS_6$	$C_{33}H_{31}MoPS_4$	$C_{36}H_{30}MoNPS_3$	$C_{28}H_{29}MoOPS_3$	$C_{30}H_{25}MoOPS_3$	$C_{30}H_{31}MoOPS_3$	$C_{33}H_{33}MoO_7PS_3$
mol wt (g mol^{-1})	566.97	922.91	682.76	699.73	604.63	624.62	630.69	764.71
crystal system	tetragonal	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$I\bar{4}$ (#82)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	Cc (#9)	$P2_1/n$ (#14)	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a (Å)	12.9808(8)	10.956(2)	11.187(2)	9.100(2)	14.612(3)	13.427(3)	15.415(3)	8.787(2)
b (Å)		11.307(2)	12.523(3)	16.719(4)	11.813(2)	11.008(2)	12.054(2)	17.862(4)
c (Å)	7.0844(8)	18.199(3)	12.906(3)	20.994(5)	17.210(3)	18.997(4)	16.960(3)	22.379(5)
α (°)		82.324(7)	106.7794(7)					
β (°)		84.800(7)	102.5378(17)	98.572(4)	110.744(2)	93.868(3)	110.835(3)	94.839(2)
γ (°)		61.785(4)	109.067(2)					
V (Å^3)	1193.7(2)	1967.8(5)	1536.1(6)	3158.4(13)	2777.9(9)	2801.5(10)	2945.2(10)	3499.9(1)
Z	2	2	2	4	4	4	4	4
d_{calc} (g cm^{-3})	1.577	1.557	1.476	1.471	1.446	1.481	1.422	1.451
μ (cm^{-1})	9.99	10.25	7.721	6.91	7.74	7.70	7.329	6.43
R^a	0.023	0.052	0.028	0.026	0.045	0.033	0.035	0.032
Rw^b	0.032	0.059	0.035	0.029	0.052	0.043	0.043	0.047
GOF^c	0.98	1.35	1.04	1.02	1.29	1.14	1.02	1.08

^{a} $R = \Sigma\triangle F_o| - |F_c\triangle/\Sigma|F_o|$. ^{b} $Rw = [\{\Sigma w\,(|F_o| - |F_c|)^2\}/\Sigma wF_o^2]^{1/2}$. ^{c} GOF $= [\{\Sigma w(|F_o| - |F_c|)^2\}/(N_o - N_p)]^{1/2}$, where N_o and N_p denote the number of data and parameters.

CD_3CN, rt): δ 7.83 (m, 4H, P*Ph*$_4$), 7.72 (m, 8H, P*Ph*$_4$), 7.60 (m, 8H, P*Ph*$_4$), 7.05 (m, 2H, OPh), 6.98 (m, 2H, OPh), 6.79 (m, 1H, OPh). IR (KBr): 3048(w), 1583(m), 1481(m), 1471(m), 1433(s), 1336(w), 1226(s), 1186(w), 1157(w), 1106(s), 997(m), 876(m), 752(m), 723(s), 687(s), 646(m), 526(s), 507(s, Mo═S), 487(m, Mo═S) cm^{-1}. ESI-TOF-MS (THF, rt): m/z = 286.7. UV/vis (CH_3CN, rt): λ_{max} (ε) 549 (1.6×10^3), 411 (5.4×10^3), 283 nm (1.6×10^4). Elemental analysis calcd for $C_{30}H_{25}MoOPS_3$: C 57.69, H 4.03, S 15.40; Found: C 57.74, H 4.05, S 15.41.

Preparation of [PPh$_4$][MoS$_3${OC(CH$_2$)^{t}Bu}] (8c). A similar procedure as that for **8a** was used. The reaction of [PPh_4][$MoClS_3$] (500 mg, 0.882 mmol) with KOC(CH$_2$)^{t}Bu (130 mg, 0.940 mmol) at −80 °C gave a red suspension, from which red crystals of [PPh$_4$][MoS$_3${OC(CH$_2$)^{t}Bu}] (**8c**, 285 mg, 0.452 mmol, 51%) were isolated. ^{1}H NMR (600 MHz, THF-d$_8$, rt): δ 7.91 (m, 4H, P*Ph*$_4$), 7.80 (m, 16H, P*Ph*$_4$), 4.31 (s, 1H, CH), 3.94 (s, 1H, CH), 1.01 (s, 9H, ^{t}Bu). IR (KBr): 3045(w), 1585(m), 1481(m), 1435(s), 1340(w), 1275(m), 1186(w), 1163(s), 1107(s), 995(m), 980(s), 812(m), 750(m), 723(s), 688(s), 634(m), 526(s), 509(s, Mo═S), 484(m, Mo═S) cm^{-1}. ESI-TOF-MS (THF, rt): m/z = 292.5. UV/vis (THF, rt): λ_{max} (ε) 550 (1.2×10^3), 410 (4.7×10^3), 287 nm (1.1×10^4). Elemental analysis calcd for $C_{30}H_{31}MoOPS_3$: C 57.13, H 4.95, S 15.25; Found: C 57.26, H 5.01, S 15.45.

Preparation of [PPh$_4$][MoS$_3${OC(CH$_2$)Ph}] (8d). The same procedure as in the case of **8c** was used. The reaction of [PPh_4][$MoClS_3$] (500 mg, 0.882 mmol) with KOC(CH$_2$)Ph (150 mg, 0.948 mmol) at −80 °C gave a red suspension, from which red crystals of [PPh$_4$][MoS$_3${OC(CH$_2$)Ph}] (**8d**, 165 mg, 0.254 mmol, 29%) were isolated. ^{1}H NMR (600 MHz, THF-d$_8$, rt): δ 7.89 (m, 4H, P*Ph*$_4$), 7.78 (m, 16H, P*Ph*$_4$), 7.53 (d, $^3J_{HH}$ = 7.6 Hz, 2H, *o*-Ph), 7.15 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-Ph), 7.09 (t, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-Ph), 4.74 (s, 1H, CH), 4.73 (s, 1H, CH). IR (KBr): 3042(w), 1481(m), 1434(s), 1311(w), 1271(m), 1072(m), 1107(s), 985(s), 812(m), 773(w), 748(w), 721(s), 688(s), 634(m), 526(s), 515(s, Mo═S), 490(m, Mo═S) cm^{-1}. ESI-TOF-MS (THF, rt): m/z = 312.8. UV/vis (THF, rt): λ_{max} (ε) 553 (1.3×10^3), 412 (5.5×10^3), 284 nm (1.8×10^4). Elemental analysis calcd for $C_{32}H_{27}MoOPS_3$: C 59.07, H 4.18, S 14.78; Found: C 58.91, H 4.47, S 14.91.

Preparation of [PPh$_4$][MoS$_3$(Me$_3$cit)] (9) (Me$_3$cit = OC(CH$_2$-CO$_2$Me)$_2$(CO$_2$Me)). A THF solution of K(Me$_3$cit) (1.0 mmol) was added to a THF solution of **2** (500 mg, 0.882 mmol) at room temperature. After stirring for 30 min, the dark red suspension was centrifuged to remove insoluble materials. The solution was evaporated to dryness, and the resulting red solid was washed with ether to give [PPh$_4$][MoS$_3$(Me$_3$cit)] (**9**, 491 mg, 0.643 mmol, 73%). Crystals for the X-ray diffraction were obtained by slow diffusion of ether to a THF solution of **9**. ^{1}H NMR (500 MHz, CD_3CN, rt): δ 7.93 (m, 4H, P*Ph*$_4$), 7.76 (m, 8H, P*Ph*$_4$), 7.69 (m, 8H, P*Ph*$_4$), 3.67 (s, 3H, O*Me*), 3.49 (s, 6H, O*Me*), 3.07 (d, J = 16 Hz, 2H, C*H*$_2$), 2.99 (d, J = 16 Hz, 2H, C*H*$_2$). IR (KBr): 1736 (vs, *C*═O), 1585(w), 1483(w), 1435(s), 1336(w), 1207(m), 1163(m), 1107(s), 1072(m), 997(m), 941(m), 835(w), 760(w), 721(s), 688(s), 530(s), 509(s, Mo═S), 490(s, Mo═S), 455(m) cm^{-1}. ESI-TOF-MS (THF): m/z = 426.7. UV/vis (THF, rt): λ_{max} (ε) 549 (1.1×10^3), 411 (3.7×10^3), 278 nm (9.5×10^3). Elemental analysis calcd for $C_{33}H_{33}MoO_7PS_3$: C 51.83, H 4.35, S 12.58; Found: C 51.72, H 4.35, S 12.54.

X-ray Structural Determination. Crystal data and refinement parameters of **2**, **5**, **6c**, **7**, **8a**−**c**, and **9** were summarized in Table 5. Single crystals were coated with oil (Immersion Oil, type B: Code 1248, Cargill Laboratories, Inc.) and mounted on loops. Diffraction data were collected on a Rigaku Mercury CCD diffractometer (for **2**, **5**, **7**, **8b**, and **8c**), Rigaku Saturn 70 CCD diffractometer (for **8a**), and Rigaku Saturn 70 CCD with Micromax (for **6c** and **9**), all equipped with a graphite monochromatized Mo Kα source (λ = 0.71070 Å). Data were collected on 676 oscillation images with oscillation range of 0.5° (for **2**), 720 oscillation images with oscillation range of 0.5° (for **5**, **6c, 7**, **8a**−**c**, and **9**). Intensity data were corrected for Lorentz-polarization effects and empirical absorption using the CrystalClear program package. All structures were solved by direct methods (SIR-92) using the TEXSAN or CrystalStructure program packages. Anisotropic refinement was applied to all nonhydrogen atoms, and all hydrogen atoms were placed at the calculated positions and were not refined. The S and Cl atoms in **2** overlap because of the crystallographic T_d symmetry, and they were analyzed as 75%(S) and 25%(Cl). The refinement was carried out by least-squares methods based on F with all measured reflections.

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Supporting Information Available: X-ray crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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