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Reactivity of $Mo(PMe_3)_6$ towards Benzothiophene and Selenophenes: New Pathways Relevant to Hydrodesulfurization

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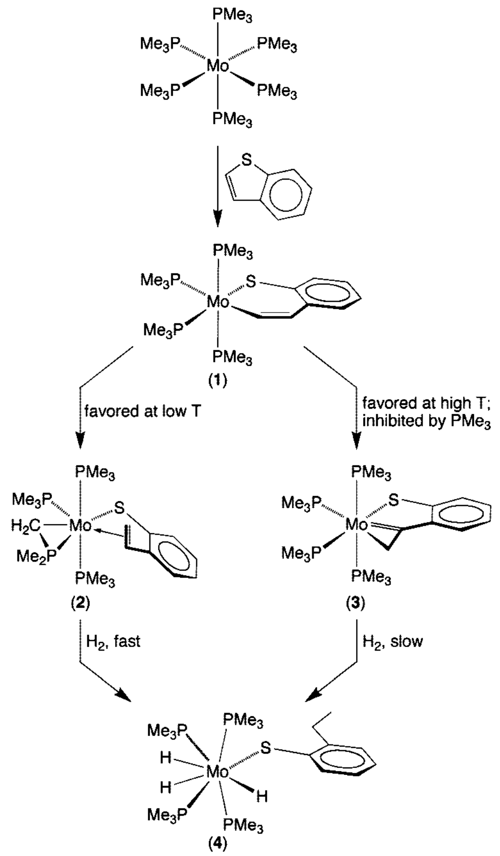
Hydrodesulfurization (HDS) is the critical industrial process by which sulfur is removed from compounds present in crude petroleum feedstocks prior to their use as fuel.[1,2] Of these compounds, thiophenes belong to the class of molecules that are most resistant towards HDS, such that they feature prominently in model studies to provide mechanistic insight into the industrial process.[2,3] Since molybdenum is an essential component of an HDS catalyst, it is of particular relevance to define its coordination chemistry with respect to thiophenes. In this regard, we have demonstrated that $[Me_2Si(C_5Me_4)_2]MoH_2$ and $Mo(PMe_3)_6$ exhibit interesting reactivity towards thiophene, including examples of κ^1-coordination, η^5-coordination, C−S bond cleavage, and formation of a butadiene−thiolate derivative.[4,5] Here we describe the reactivity of $Mo(PMe_3)_6$ towards benzothiophene and selenophenes that reveals new pathways which are relevant to mechanisms of hydrodesulfurization.

We previously demonstrated that $Mo(PMe_3)_6$ reacts with thiophene to give the isomeric η^5-thiophene and butadiene−thiolate complexes, $(\eta^5\text{-}C_4H_4S)Mo(PMe_3)_3$ and $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$, respectively. We now report that the corresponding reaction of $Mo(PMe_3)_6$ with benzothiophene follows a different course, thereby increasing our knowledge of the array of organic species that may exist and interconvert on the surface of an HDS catalyst. Specifically, $Mo(PMe_3)_6$ cleaves the C−S bond of benzothiophene to give paramagnetic $(\kappa^2\text{-}CHCHC_6H_4S)Mo(PMe_3)_4$ (**1**), which rapidly isomerizes to the olefin−thiophenolate and 1-metallacyclopropene−thiophenolate complexes, $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)Mo(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**2**) and $(\kappa^1,\eta^2\text{-}CH_2CC_6H_4S)Mo(PMe_3)_4$ (**3**), as illustrated in Scheme 1. While $(\kappa^2\text{-}CHCHC_6H_4S)Mo(PMe_3)_4$ (**1**) is simply the product of C−S bond cleavage,[6] $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)Mo(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**2**) and $(\kappa^1,\eta^2\text{-}CH_2CC_6H_4S)Mo(PMe_3)_4$ (**3**) are the results of more complex sequences involving hydrogen transfers, such that the termini of the thiolate fragments coordinate *via* η^2-olefin[7] and η^2-vinyl[8,9] modes, respectively. Of particular note, the latter coordination mode is without precedent for complexes derived from benzothiophene.[10]

The composition of the thiolate ligand of $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)Mo(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**2**) bears a close analogy to that of $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$, in the sense that both are a result of C−S cleavage and hydrogen transfer. An important difference, however, resides with their coordination modes. Thus, whereas the ligand derived from thiophene coordinates in a flat η^5-manner (i.e., as a butadiene−thiolate ligand), that derived from benzothiophene coordinates in a puckered κ^1,η^2-manner (i.e., as an olefin−thiolate ligand).[11] As a corollary of the different coordination modes, $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)Mo(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**2**) possesses an additional PMe_3 ligand to maintain an 18-electron configuration.

The relative amounts of $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)Mo(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**2**) and $(\kappa^1,\eta^2\text{-}CH_2CC_6H_4S)Mo(PMe_3)_4$ (**3**) in the product mixture depend critically on the reaction conditions. For example, $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)Mo(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**2**) is favored if the reaction is performed at low temperatures (10 °C), while the metallacyclopropene $(\kappa^1,\eta^2\text{-}CH_2CC_6H_4S)Mo(PMe_3)_4$ (**3**) is favored at high temperatures (80 °C). This situation reflects a kinetic preference because the isolated complexes do not interconvert thermally on a comparable time scale.[12] Furthermore, the relative amounts of the two isomers are influenced by the presence of PMe_3, such that the formation of the metallacyclopropene $(\kappa^1,\eta^2\text{-}CH_2CC_6H_4S)Mo(PMe_3)_4$ (**3**) is inhibited by increasing the concentration of PMe_3. These observations indicate that an important difference in the mechanisms for formation of $(\kappa^1,\eta^2\text{-}CH_2CC_6H_4S)Mo(PMe_3)_4$ (**3**) and $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)Mo(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**2**) is that isomerization to the metallacyclopropene (**3**) requires a sequence involving reversible dissociation of a PMe_3 ligand prior to the rate-determining step.

Scheme 1



Deuterium labeling studies employing d_1-2-D-benzothiophene and d_1-3-D-benzothiophene demonstrate that a methylene hydrogen atom of both $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)Mo(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**2**) and $(\kappa^1,\eta^2\text{-}CH_2CC_6H_4S)Mo(PMe_3)_4$ (**3**) is derived from a PMe_3 ligand. Furthermore, the reaction of $Mo(PMe_3)_6$ with d_1-2-D-benzothiophene at room temperature yields the isotopomer of $(\kappa^1,\eta^2\text{-}CHDCHC_6H_4S)Mo(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**2**) in which the deuterium is selectively located *cis* to the hydrogen on the adjacent carbon

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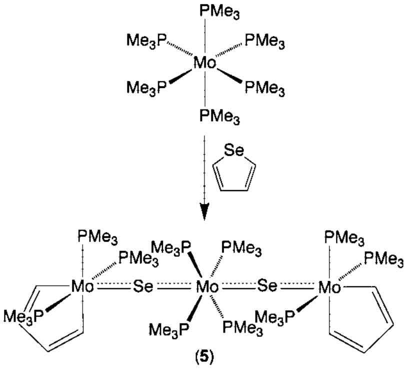
Scheme 2



atom.[13,14] This labeling pattern is consistent with a mechanism that involves oxidative addition of C−H bond of a PMe$_3$ ligand, followed by C−H bond reductive elimination of a {(κ^2-CHCHC$_6$H$_4$S)MoH} intermediate.[15,16]

Both (κ^1,η^2-CH$_2$CHC$_6$H$_4$S)Mo(PMe$_3$)$_3$(η^2-CH$_2$PMe$_2$) (**2**) and (κ^1,η^2-CH$_2$CC$_6$H$_4$S)Mo(PMe$_3$)$_4$ (**3**) react with H$_2$ at room temperature to yield Mo(PMe$_3$)$_4$(SC$_6$H$_4$Et)H (**4**),[17,18] thereby achieving partial hydrogenation of benzothiophene on a molybdenum center. The relative reactivity of the two isomers, however, differ considerably. Thus, whereas hydrogenation of the former occurs within minutes, hydrogenation of the latter requires a period of days to proceed to completion.

The reactivity of Mo(PMe$_3$)$_6$ towards selenophene derivatives is pertinent towards understanding the mechanisms of HDS because the products obtained could correspond to different stages of the reaction coordinate for the thiophene system. As such, an analysis of the reactivity of the selenophene systems furnishes insight into the types of transformations that may be achieved by molybdenum as a component of an HDS catalyst surface. It is, therefore, interesting that Mo(PMe$_3$)$_6$ reacts with selenophene to give the metallacyclopentadiene complex [(κ^2-C$_4$H$_4$)Mo(PMe$_3$)$_3$(Se)]$_2$-[Mo(PMe$_3$)$_4$] (**5**) in which the selenium has been completely abstracted from the selenophene moiety (Scheme 2).[19,20]

X-ray diffraction demonstrates that [(κ^2-C$_4$H$_4$)Mo(PMe$_3$)$_3$-(Se)]$_2$[Mo(PMe$_3$)$_4$] (**5**) possesses an almost linear chain of Mo−Se−Mo−Se−Mo atoms (Figure 1), in which the Mo−Se bond lengths for the central molybdenum atom [2.4617(4) and 2.4712(4) Å] are longer than those for the outer molybdenum atoms [2.3472(4) and 2.3512(4) Å]. These Mo−Se bond lengths are comparable to the terminal Mo═Se bonds in *trans*-Mo(PMe$_3$)$_4$(Se)$_2$ [2.381(1) Å and 2.385(1) Å][21] but considerably shorter than a Mo−Se single bond;[22] as such, it is evident that there is a degree of multiple bonding in the Mo−Se−Mo−Se−Mo chain. An analysis of the π-molecular orbitals indicates that there is a more significant π-bonding component for the outer Mo−Se bonds because the in-phase combinations of selenium 4p$_z$ and 4p$_y$ orbitals of the two selenium atoms are of appropriate symmetry to interact with 4d orbitals of the outer molybdenum atoms but are of incorrect symmetry for the 4d$_{xz}$ and 4d$_{yz}$ orbitals of the central molybdenum.[23,24]

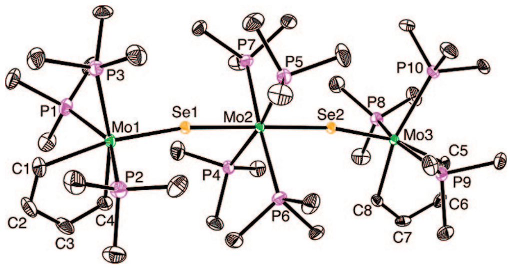
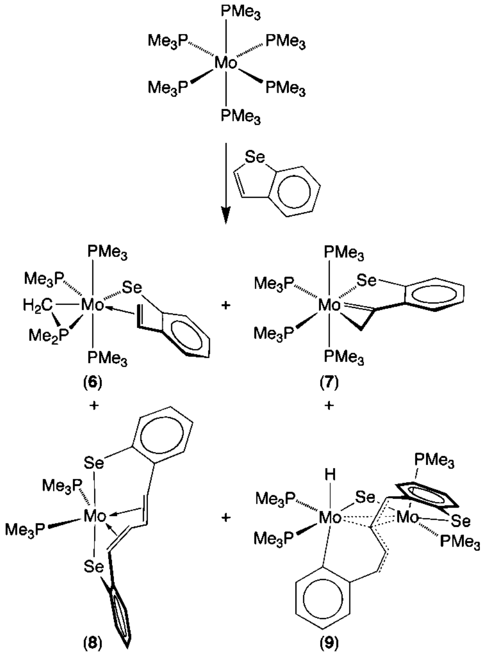


Figure 1. Molecular structure of [(κ^2-C$_4$H$_4$)Mo-(PMe$_3$)$_3$(Se)]$_2$[Mo(PMe$_3$)$_4$] (**5**).

Scheme 3



The ability of molybdenum to extract selenium from selenophene and generate the κ^2-butadienediyl C$_4$H$_4$ ligand suggests that a similar process could occur for thiophene on an HDS catalyst surface. The synthesis of [(κ^2-C$_4$H$_4$)Mo(PMe$_3$)$_3$(Se)]$_2$[Mo(PMe$_3$)$_4$] (**5**), therefore, indicates that consideration should also be given to HDS mechanisms that feature cleavage of *both* C−S bonds *prior* to hydrogenation. In this regard, Jones has reported an interesting nickel system where dibenzothiophene (but not benzothiophene or thiophene) undergoes desulfurization without any form of hydrogenation.[25,26]

The reaction of Mo(PMe$_3$)$_6$ with benzoselenophene is considerably more complex than the reaction with benzothiophene, with four products having been isolated. Thus, in addition to (κ^1,η^2-CH$_2$CHC$_6$H$_4$Se)Mo(PMe$_3$)$_3$(η^2-CH$_2$PMe$_2$) (**6**) and (κ^1,η^2-CH$_2$CC$_6$H$_4$Se)Mo(PMe$_3$)$_4$ (**7**), which correspond to two of the species observed in the benzothiophene reaction, products resulting from C−C coupling, namely [κ^2,η^4-Se(C$_6$H$_4$)(CH)$_4$-(C$_6$H$_4$)Se]Mo(PMe$_3$)$_2$ (**8**) and [μ-Se(C$_6$H$_4$)(CH)C(CH)$_2$(C$_6$H$_4$)]-(μ-Se)[Mo(PMe$_3$)$_2$][Mo(PMe$_3$)$_2$H] (**9**), are also formed (Scheme 3).

X-ray diffraction studies demonstrate that [κ^2,η^4-Se(C$_6$H$_4$)-(CH)$_4$(C$_6$H$_4$)Se]Mo(PMe$_3$)$_2$ (**8**) possesses a novel [Se(C$_6$H$_4$)(CH)$_4$-(C$_6$H$_4$)Se] ligand that may be conceptually viewed as being derived from C−C coupling of two ring-opened benzoselenophene molecules. While a similar ligand derived from thiophene has been observed to link two rhodium centers,[27] an interesting feature of [κ^2,η^4-Se(C$_6$H$_4$)(CH)$_4$(C$_6$H$_4$)Se]Mo(PMe$_3$)$_2$ (**8**) is that the [Se(C$_6$H$_4$)(CH)$_4$(C$_6$H$_4$)Se] ligand coordinates to a *single* molybdenum center and effectively occupies four coordination sites of an octahedral geometry. Specifically, the two selenolate donors occupy *trans* sites while the central butadiene component occupies two *cis* sites.

The asymmetric dinuclear complex [μ-Se(C$_6$H$_4$)(CH)C(CH)$_2$-(C$_6$H$_4$)](μ-Se)[Mo(PMe$_3$)$_2$][Mo(PMe$_3$)$_2$H] (**9**), which also features a C−C coupled ligand derived from benzoselenophene, can be viewed as originating from $[Se(C_6H_4)(CH)_4(C_6H_4)Se]$ *via* a sequence that involves both C−Se and C−H bond cleavage reactions. The bonding in this complex is highly delocalized, but a salient feature is that the "quaternary" carbon of the $[Se(C_6H_4)(CH)C(CH)_2(C_6H_4)]$ ligand interacts to a similar degree with both molybdenum atoms, with bond lengths [2.110(2) Å and 2.160(2) Å] that are comparable to the Mo−aryl interaction [2.107(2) Å]. Furthermore, the Mo−Mo separation [2.7394(3) Å] is in the range for a single bond, although bond distance alone is not a sufficient criterion for establishing bond orders in such systems.[28]

In summary, the reactions of $Mo(PMe_3)_6$ with benzothiophene, selenophene, and benzoselenophene reveal reaction pathways that are pertinent to the mechanisms of hydrodesulfurization. Of particular note, cleavage of the C−S bond of benzothiophene results in the formation of three isomers, namely $(\kappa^2\text{-CHCHC}_6H_4S)Mo(PMe_3)_4$ (**1**), $(\kappa^1,\eta^2\text{-CH}_2\text{CHC}_6H_4S)Mo(PMe_3)_3(\eta^2\text{-CH}_2PMe_2)$ (**2**), and $(\kappa^1,\eta^2\text{-CH}_2\text{CC}_6H_4S)Mo(PMe_3)_4$ (**3**), thereby providing evidence for the types of interconversions that may occur on the surface of an HDS catalyst. Furthermore, $Mo(PMe_3)_6$ undergoes a novel reaction with selenophene to give the metallacyclopentadiene complex $[(\kappa^2\text{-C}_4H_4)Mo(PMe_3)_3(Se)]_2[Mo(PMe_3)_4]$ $(\kappa^1,\eta^2\text{-CH}_2\text{CHC}_6H_4S)Mo(PMe_3)_3(\eta^2\text{-CH}_2PMe_2)$ (**5**), thereby demonstrating that the molybdenum is capable of completely abstracting selenium from the heterocycle.

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Supporting Information Available: Experimental details, computational data and crystallographic data in CIF format. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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(6) For another example of C−S cleavage of benzothiophene by molybdenum, see ref 4a.

(7) The metrical details associated with the molybdenum−olefin interaction of $(\eta^1,\eta^2\text{-CH}_2\text{CHC}_6H_4S)Mo(PMe_3)_3(\eta^2\text{-CH}_2PMe_2)$ indicate that there is a significant metallacyclopropane component to the bonding description, with $d(\text{Mo−C}) = 2.268(2)$ and 2.304(1) Å and $d(\text{C−C}) = 1.420(2)$ Å.

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(9) Compounds with $\eta^2\text{-C(R)=CR}_2$ ligands are also referred to as 1-metallacyclopropene complexes, a description that better portrays the bonding situation (See: Casey, C. P.; Brady, J. T.; Boller, T. M.; Weinhold, F.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 12500–12511.). In accord with this description, the Mo−C bond lengths of $(\kappa^1,\eta^2\text{-CH}_2\text{CC}_6H_4S)Mo(PMe_3)_4$ are 1.953(1) and 2.294(1) Å, corresponding to single and double bonds, respectively.

(10) A related ligand derived from thiophene, namely $\kappa^1,\kappa^1\text{-CH}_2\text{CCHCHS}$, has been reported, but the vinyl group only coordinates in a κ^1-manner with a five-membered thiametallacyclopentene motif. See ref 5a.

(11) Mononuclear compounds that feature the $[(\kappa^1,\eta^2\text{-CH}_2\text{CHC}_6H_4S)M]$ motif have been described for metals other than molybdenum. For example, see: (a) Bianchini, C.; Frediani, P.; Herrera, V.; Jiménez, M. V.; Meli, A.; Rincón, L.; Sánchez-Delgado, R.; Vizza, F. *J. Am. Chem. Soc.* **1995**, *117*, 4333–4346. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Moneti, S.; Herrera, V.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 4370–4381.

(12) Although the relative stabilities of $(\kappa^1,\eta^2\text{-CH}_2\text{CHC}_6H_4S)Mo(PMe_3)_3\text{-}(\eta^2\text{-CH}_2PMe_2)$ and $(\kappa^1,\eta^2\text{-CH}_2\text{CC}_6H_4S)Mo(PMe_3)_4$ are not known experimentally, density functional theory calculations (B3LYP and cc-pVTZ(-f)/LACV3P basis sets) predict that the latter is more stable by 7.2 kcal mol^{-1}.

(13) While the deuterium labeling of $(\kappa^1,\eta^2\text{-CHDCHC}_6H_4S)Mo(PMe_3)_3(\eta^2\text{-CH}_2PMe_2)$ is stereoselective at room temperature, upon heating at 60 °C the deuterium scrambles statistically into both sites of the methylene group. Significantly, this exchange occurs without accessing the η^2-vinyl complex $(\kappa^1,\eta^2\text{-CH}_2\text{CC}_6H_4S)Mo(PMe_3)_4$.

(14) It is pertinent to note that this labeling pattern is not observed upon formation of the butadiene−thiolate complex $(\eta^5\text{-C}_4H_5S)Mo(PMe_3)_2(\eta^2\text{-CH}_2PMe_2)$ *via* reaction of $Mo(PMe_3)_6$ with d_4-thiophene (see ref 4c), thereby indicating that the mechanisms for formation of $(\eta^5\text{-C}_4H_5S)Mo(PMe_3)_2(\eta^2\text{-CH}_2PMe_2)$ and $(\kappa^1,\eta^2\text{-CH}_2\text{CHC}_6H_4S)Mo(PMe_3)_3(\eta^2\text{-CH}_2PMe_2)$ are not analogous.

(15) For an example of isomerization of $\{(\kappa^2\text{-CHCHC}_6H_4S)MH\}$ to $\{(\kappa^1,\eta^2\text{-CH}_2\text{CHC}_6H_4S)M\}$, see ref 11.

(16) In this regard, it is pertinent to note that the formation of a butadiene−thiolate complex *via* addition of D^+ or D^- to η^5-thiophene complexes occurs with the deuterium being respectively incorporated into *cis* and *trans* sites relative to the adjacent CH group. These labeling patterns are consistent with C−S bond cleavage within a $\eta^4\text{-C}_4H_4DS$ species for which the deuterium is located respectively in the *endo* (for D^+) and *exo* (for D^-) positions. See: (a) Luo, S.; Rauchfuss, T. B.; Gan, Z. *J. Am. Chem. Soc.* **1993**, *115*, 4943–4944. (b) Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8515–8520. (c) Hachgenei, J. W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359–378.

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(19) $[(\kappa^2\text{-C}_4H_4)Mo(PMe_3)_3(Se)]_2[Mo(PMe_3)_4]$ may be conceptually viewed to be a result of $Mo(PMe_3)_6$ trapping two $[(\kappa^2\text{-C}_4H_4)Mo(PMe_3)_3(Se)]$ moieties.

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(22) For example, the Mo−Se bond length in $(\kappa^1,\eta^2\text{-CH}_2\text{CC}_6H_4Se)Mo(PMe_3)_4$, which is predicted to be a single bond on the basis of the 18-electron configuration, is 2.7101(4) Å (see Supporting Information).

(23) z corresponds to the 2-fold axis and x corresponds to the Se−Mo−Se axis for the central molybdenum.

(24) Note that the in-phase combinations of $4p_z$ and $4p_y$ orbitals of the two selenium atoms are of appropriate symmetry to interact with 4d orbitals of both the inner and outer molybdenum atoms.

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