Dithiolene Ligands

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Push–Pull Molybdenum Trisdithiolenes Allow Rapid Nonconventional Binding of Ethylene at Ligand Sulfur Atoms**

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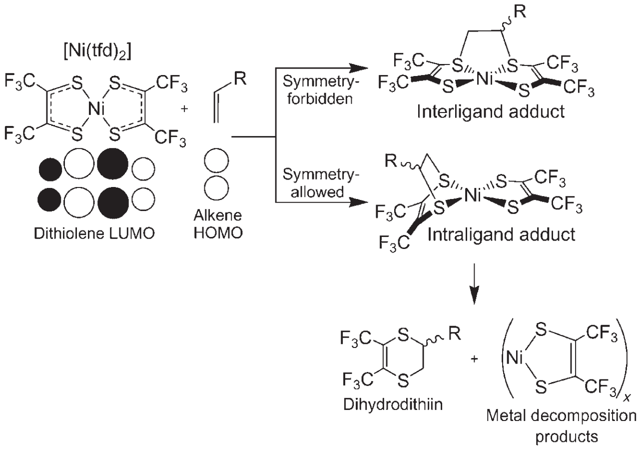
Molybdenum sulfides are used on a large industrial scale in hydrodesulfurization (HDS) processes.[1] In addition, many enzymes, such as oxotransferases[2,3] and nitrogenases,[4] rely on molybdenum bound to sulfur-based ligands.[5] Owing to their industrial and biological relevance, molybdenum complexes with sulfur donors have received much attention. Sulfur ligands can display unusual non-innocent behavior.[6] For sulfur-ligated complexes of molybdenum and other transition metals, increasing numbers of examples are surfacing where reactions with organic substrates occur at the sulfur atoms, rather than at the metal. Sulfur-centered reactivity has been observed, for example, in complexes with bridging sulfide groups ($[\{CpMo(\mu\text{-}S)\}_2S_2CH_2]$; $Cp^- = C_5H_5^-$),[7] terminal sulfide groups ($[ReS_4]^-$),[8] P,S chelates,[9] and sulfur centers in metal-bound dithiolene ligands ($[M(S_2C_2R_2)_2]$; M = Ni,Pd,Pt).[10–14]

Ligand-centered reactions are less well understood than reactions at metal centers, as illustrated by the reactivity of the nickel bisdithiolene $[Ni(tfd)_2]$ (tfd = $S_2C_2(CF_3)_2$) towards alkenes. While the binding of strained cyclic alkenes (e.g., norbornene) to the sulfur atoms of $[Ni(tfd)_2]$[11] and related nickel bisdithiolenes[10] has been known for decades, similar reactions of simple noncyclic mono-olefins (e.g., ethylene) were reported only in 2001,[12] and the mechanistic details behind this reactivity are just beginning to become clear.[13,15] In 2006, it was shown that alkene addition to $[Ni(tfd)_2]$ occurs, preferentially, in a symmetry-allowed, intraligand fashion to yield decomposition products (substituted 2,3-dihydro-1,4-dithiin and $[\{Ni(tfd)\}_x]$; Scheme 1), unless monoanionic $[Ni(tfd)_2]^-$ is present.[13] The monoanion reverses the product selectivity in favor of stable interligand adducts, by a mechanism that is still under investigation.[13]



Scheme 1. Reactions of $[Ni(tfd)_2]$ with alkenes.

Alkene-addition products of metal bisdithiolenes were initially proposed to be of the symmetry-allowed intraligand type.[10] However, all characterized alkene adducts have shown interligand binding.[11,13] In fact, intraligand addition products, with a metal-bound dihydrodithiin, are generally unstable and have not been directly observed for any metal. The present work is the first to investigate the reactivity of the well-known class of molybdenum trisdithiolenes towards alkenes. We achieved rapid alkene binding by employing unsymmetrical trisdithiolenes with electronically disparate ligands attached to the central metal ion.

We first investigated the reactions of the previously reported complexes $[Mo(tfd)_3]$[16] and $[Mo(bdt)_3]$[17] (bdt = $S_2(C_6H_4)$) with ethylene and found slow[18] reactions to give corresponding dihydrodithiins and decomposed metal species, presumably through intraligand alkene addition. We reasoned that push–pull trisdithiolenes, with a combination of electron-withdrawing and electron-donating dithiolene ligands ($[Mo(S_2C_2R_2)_2(S_2C_2R'_2)]$), would react more readily with alkenes. For example, in a trisdithiolene complex with one comparatively electropositive dithiolene ligand, the more electron-withdrawing dithiolene groups are expected to pull electron density from the more electron-releasing ligand.[19] Thus, we propose that the electron-releasing ligand is partially oxidized, relative to the electronegative ligands, and is poised for [2+4] cycloaddition reactions at the dithiolene sulfur centers (see below).

Metal trisdithiolenes with different dithiolene ligands are very rare and had not been crystallographically characterized previously.[19,20] We synthesized the new compounds $[Mo(bdt)_2(tfd)]$ and $[Mo(tfd)_2(bdt)]$, using the procedures shown in Scheme 2 (see the Supporting Information).

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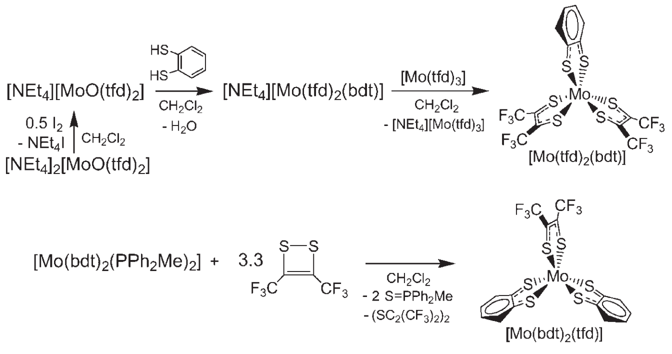


Scheme 2. Syntheses of $[Mo(tfd)_2(bdt)]$ and $[Mo(bdt)_2(tfd)]$.

An X-ray crystal structure analysis of $[Mo(bdt)_2(tfd)]$ reveals trigonal-prismatic geometry at the metal center (Figure 1),[21] as has been observed in the solid-state structures of a number of homoleptic trisdithiolenes.[5] Also, the dithiolene S_2C_2 planes are canted away from the MoS_2 planes, along the intraligand S···S axes ("ligand bend"). This ligand bending has been attributed to second-order Jahn–Teller effects; for homoleptic trisdithiolenes (e.g., $[Mo(S_2C_2H_2)_3]$), the distortion to lower symmetry ($D_{3h}\rightarrow C_{3h}$) is likely driven by mixing of ligand π orbitals (L_π^v) and the metal d_{z^2} orbital (Figure 2a).[22]

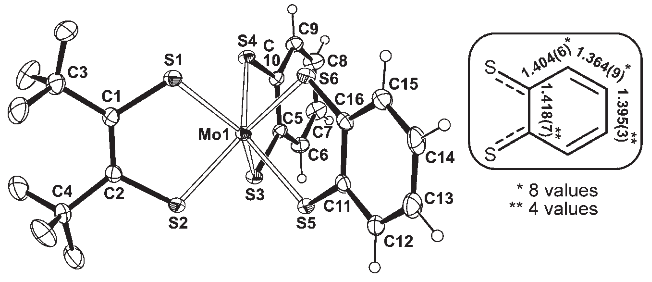


Figure 1. Molecular structure of $[Mo(bdt)_2(tfd)]$. One of two crystallographically independent molecules in the unit cell is shown, and thermal ellipsoids are set at 30% probability. A ligand-bend angle is defined as the angle between the ligand plane (least-squares plane through S-C-C-S) and the metal coordination plane (through S-Mo-S). Selected distances [Å] and angles [°]: Mo1–S1 2.367(1), Mo1–S2 2.366(1), Mo1–S3 2.371(1), Mo1–S4 2.359(1), Mo1–S5 2.363(1), Mo1–S6 2.363(1); S1-Mo1-S2 81.44(4), S3-Mo1-S4 82.39(4), S5-Mo1-S6 82.58(5); the average C–C distances of the bdt ligands are given in the inset, along with a limiting Lewis structure for oxidized[6] bdt. Ligand-bend angles [°]: 17.9(1) for the tfd ligand, 23.8(1) for both bdt ligands (values for the second molecule are 18.0(1) and 20.6(1), respectively).

The reactions of the new mixed-ligand trisdithiolenes with ethylene are predicted to proceed in an intraligand manner (Figure 2b). As a first-order approximation, the known molecular orbitals (MOs) of symmetrical (homoleptic) trisdithiolenes can be used.[17a,22,23] The lowest unoccupied MO (LUMO) of the metal complex and the highest occupied MO (HOMO) of the alkene have symmetry properties allowing synfacial intraligand addition. For homoleptic trisdithiolenes, such as $[Mo(S_2C_2H_2)_3]$, computed in D_{3h} symmetry, extended Hückel[17a] and Fenske–Hall[22] computations predict the HOMO ($a_2'(L_\pi^v)$) and LUMO ($a_1'(d_{z^2})$; left-hand part of Figure 2a) to be close in energy. Further, by ligand bending along the S···S axes ($D_{3h}\rightarrow C_{3h}$ distortion; Figure 2), these orbitals can mix to form frontier orbitals with a mixture of metal d_{z^2} and ligand π (in-phase across intraligand sulfur atoms) character.[22] For the mixed-ligand species, the symmetry will be further lowered compared to the C_{3h} (homoleptic) case. We expect that the tfd sulfur atoms contribute more to bonding MOs, whereas the bdt sulfur atoms should have larger coefficients for antibonding MOs.

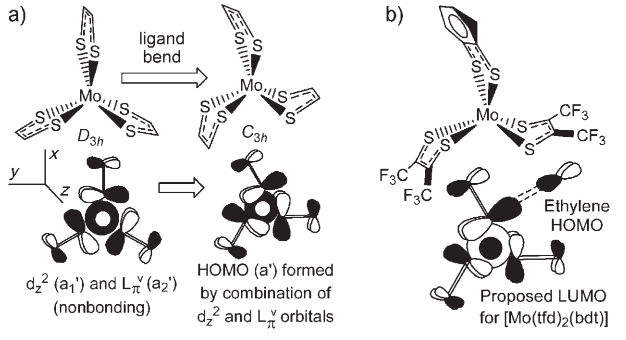
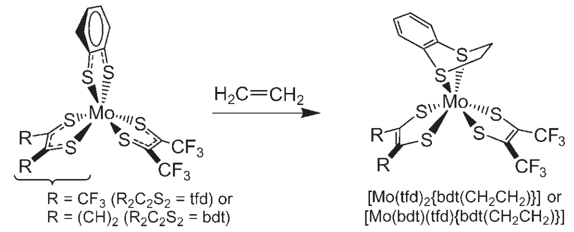


Figure 2. a) MO interactions that lead to ligand bending along the S···S intraligand axes (distortion to lower symmetry).[22] b) Proposed LUMO for $[Mo(tfd)_2(bdt)]$ and its symmetry-allowed interaction with ethylene.

It is likely that the bdt sulfur atoms significantly contribute to the LUMO, as shown schematically for $[Mo(tfd)_2(bdt)]$ in Figure 2b. Also, since structural data show larger ligand-bend angles for bdt compared to tfd, as well as evidence for a partially oxidized character of bdt (Figure 1), the bdt ligands appear to be more efficiently coupled to the d_{z^2} orbital; we propose that electron density from an alkene can be very efficiently transferred to the metal and tfd ligands through the π system of the bdt ligand.

Both $[Mo(bdt)_2(tfd)]$ and $[Mo(tfd)_2(bdt)]$ react with ethylene in the fashion predicted (Scheme 3). The reactions are rapid,[18] take place exclusively at the sulfur atoms of the bdt ligand, and selectively form the intraligand adducts $[Mo(tfd)_2\{bdt(CH_2CH_2)\}]$ and $[Mo(bdt)(tfd)\{bdt(CH_2CH_2)\}]$, where 2,3-dihydro-1,4-benzodithiin is denoted as $bdt(CH_2CH_2)$. Both adducts can be formed in high yield (> 80%), if the reactions are conducted in weakly coordinating solvents (chlorinated or aliphatic hydrocarbons). In the



Scheme 3. Reactions of $[Mo(tfd)_2(bdt)]$ and $[Mo(bdt)_2(tfd)]$ with ethylene to form intraligand alkene adducts at the bdt ligands.

presence of more-coordinating solvents (e.g., MeCN, THF), decomposition through the loss of 2,3-dihydro-1,4-benzodithiin is observed. [Mo(tfd)$_2${bdt(CH$_2$CH$_2$)}] is particularly stable and can be kept in CDCl$_3$ or CD$_2$Cl$_2$ at room temperature for days. We investigated [Mo(tfd)$_2${bdt(CH$_2$CH$_2$)}] with respect to reversibility of ethylene binding. Ethylene can be released from the metal-bonded dihydrodithiin to regenerate the dithiolene ligand,[24] such that [Mo(tfd)$_2$(bdt)] is restored at mildly elevated temperature: refluxing (21 h) a CDCl$_3$ solution of [Mo(tfd)$_2${bdt(CH$_2$CH$_2$)}] under argon yielded a mixture of unchanged [Mo(tfd)$_2${bdt(CH$_2$CH$_2$)}] (37 %) and the alkene-release product [Mo(tfd)$_2$(bdt)] (41 %), along with a small amount of dihydrodithiin (12 %; accompanied by corresponding metal decomposition products; see the Supporting Information). We expect that alkene dissociation from the alkene adduct of [Mo(tfd)$_2$(bdt)] is facilitated by back donation of an occupied d orbital (likely d$_{z^2}$) into the C–S σ* orbitals.[25]

X-ray quality crystals of [Mo(tfd)$_2${bdt(CH$_2$CH$_2$)}] were grown by allowing ethylene to slowly diffuse into a toluene solution of [Mo(tfd)$_2$(bdt)].[21] Its structure provides the first example of a 2,3-dihydro-1,4-dithiin chelating to a transition metal using the sulfur atoms in the 1,4-positions (Figure 3).

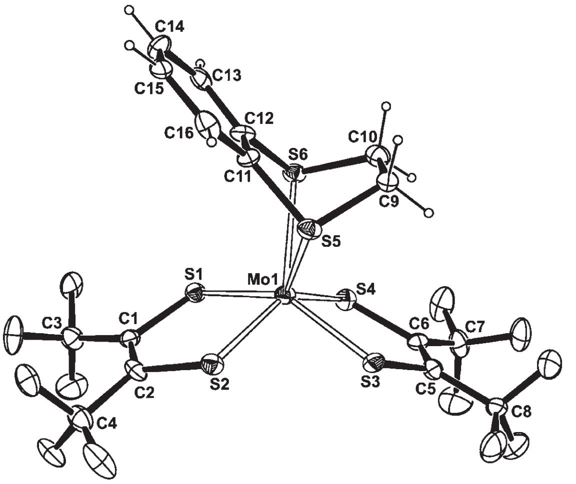
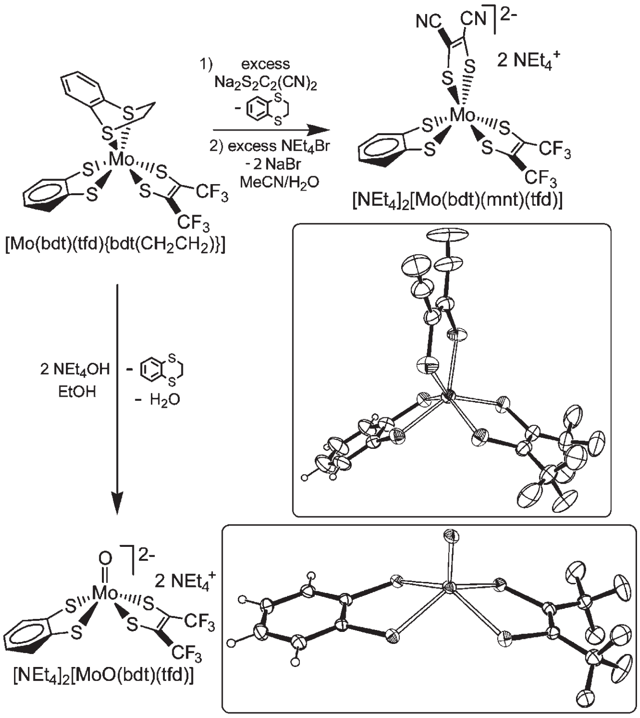


Figure 3. Molecular structure of [Mo(tfd)$_2${bdt(CH$_2$CH$_2$)}]. Thermal ellipsoids are set at 30% probability, and only one orientation is shown for the rotationally disordered trifluoromethyl groups involving C7 and C8. Selected distances [Å] and angles [°]: Mo1–S1 2.329(3), Mo1–S2 2.326(4), Mo1–S3 2.328(3), Mo1–S4 2.313(4), Mo1–S5 2.523(3), Mo1–S6 2.524(3), C9–C10 1.508(19), S5–C9 1.836(14), S6–C10 1.848(14); S1-Mo1-S2 82.3(1), S3-Mo1-S4 82.3(1), S5-Mo1-S6 72.4(1), C11-S5-C9 96.3(6), C12-S6-C10 97.9(1). Ligand-bend angles [°], as defined in Figure 1: 0.4(4) for the tfd ligand including S1 and S2, 4.5(4)(for the tfd ligand including S3 and S4, 52.1(4)(for the bdt–Mo substructure (using Mo1, S5, S6, C11, and C12).

We exploited the lability of the metal-coordinated dihydrodithiin to synthesize the new compounds [NEt$_4$]$_2$[Mo(bdt)(mnt)(tfd)] (mnt = S$_2$C$_2$(CN)$_2$) and [NEt$_4$]$_2$[MoO(bdt)(tfd)] in reasonable yields (67 %). We devised the synthetic procedures shown in Scheme 4 (see the Supporting Information).



Scheme 4. Reactions of [Mo(bdt)(tfd){bdt(CH$_2$CH$_2$)}] to form [NEt$_4$]$_2$[Mo(bdt)(mnt)(tfd)] and [NEt$_4$]$_2$[MoO(bdt)(tfd)]. The insets show the molecular structures of these products (thermal ellipsoids are set at 30% probability; NEt$_4^+$ cations are omitted). See the Supporting Information for bond lengths, bond angles, and other crystallographic details.

Dianionic [Mo(bdt)(mnt)(tfd)]$^{2-}$ is the first example of a metal trisdithiolene with three different dithiolene ligands. The mono-oxo bisdithiolene complex [MoO(bdt)(tfd)]$^{2-}$ is rare in that it contains two different dithiolene groups (Holm et al. reported [MoO(S$_2$C$_2$H$_2$)(mnt)]$^{2-}$ [26]). Molybdenum–oxo compounds with one or two dithiolene groups are of interest as models for the active sites in a variety of oxygen-atom-transfer enzymes.[2,3,5,26] Both [Mo(bdt)(mnt)(tfd)]$^{2-}$ and [MoO(bdt)(tfd)]$^{2-}$ were isolated in crystalline form as their NEt$_4^+$ salts. X-ray structure determinations confirmed the identity of the products (Scheme 4, insets).[21]

In conclusion, we have prepared new mixed dithiolene complexes of molybdenum. These compounds rapidly and cleanly bind ethylene in a nonconventional intraligand fashion to form metal-chelating 2,3-dihydro-1,4-dithiins. This alkene-binding reaction was shown to be reversible for [Mo(tfd)$_2$(bdt)], consistent with the view that 2,3-dihydro-1,4-benzodithiin can be regarded a protected form of ethylene. 2,3-Dihydro-1,4-dithiins have been previously used as protected forms of *cis* alkenes, and an excellent protocol for alkene release involves a heterogeneous reaction at the surface of Raney nickel.[27] Our demonstration of a 2,3-dihydro-1,4-dithiin chelating to a transition metal might provide a homogeneous model for the alkene-release step in such reactions, and could also be of relevance to the behavior of 1,4-disulfur heterocycles in hydrodesulfurization reactions. Furthermore, we demonstrated that molybdenum-coordinated 2,3-dihydro-1,4-benzodithiin can be labilized if desired, which opens new synthetic routes to dithiolene complexes of molybdenum possessing highly unsymmetrical structures. We think that further development of this field can provide both new insights into principles of reactivity, as well as useful applications.

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