### Molybdenum Dithiolene Complexes as Structural Models for the Active Sites of Molybdenum(IV) Sulfide Hydrodesulfurization Catalysts

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The removal of sulfur (as  $H_2S$ ) from organosulfur species in petroleum feedstocks (hydrodesulfurization, HDS) is carried out on an enormous scale by using heterogeneous catalysts based on MoS<sub>2</sub> (usually doped with Co). Partially hydrogenated thiophenes are postulated intermediates in the MoS<sub>2</sub>catalyzed hydrodesulfurization of thiophene. The present contribution describes new molecular models for the proposed active sites in HDS catalysis. The models are derived from a mixed-ligand (push–pull) molybdenum trisdithiolene {[Mo(tfd)<sub>2</sub>(bdt)]; tfd = S<sub>2</sub>C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>, bdt = S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]: selective intraligand alkyne binding converts the bdt group to a labile Mo-chelating benzodithiin, which can be substituted with a variety of weak donor ligands. The complexes [Mo(tfd)<sub>2</sub>-(dht)<sub>2</sub>] and [Mo(tfd)<sub>2</sub>(tht)<sub>2</sub>] (dht = 2,5-dihydrothiophene; tht =

### Introduction

As high-grade petroleum reserves dwindle, lower and lower grades of petroleum resources must be brought into service to meet the continually growing energy demands. Environmental concerns require that the sulfur content of low-grade petroleum be reduced before use.<sup>[1]</sup> Hydrodesulfurization (HDS) processes - the removal of sulfur from organosulfur species as H2S - utilize catalysts based on molybdenum(IV) sulfide (MoS<sub>2</sub>; most commonly encountered as the hexagonal molybdenite, usually modified with cobalt for HDS applications) and hydrogen gas as a feedstock. As a greater and greater efficiency is being demanded of hydrodesulfurization techniques, the search for better catalysts has intensified. Of special interest is the desulfurization of thiophenes, which are less reactive in HDS than noncyclic thioethers and much-less reactive than thiols.<sup>[2,3]</sup> Thus, the removal of sulfur from thiophenes and related "stubborn" (refractory) compounds (deep desulfurization) is a formidable challenge. While some noble metal catalysts show excel-

3359 Mississauga Road N, Mississauga, Ontario L5L 1C6, Canada Fax: +1-905-828-5425 tetrahydrothiophene) were synthesized and crystallographically characterized. The Mo(tfd)<sub>2</sub> substructures closely resemble the presumed active site in MoS<sub>2</sub> HDS catalysts. The coordination geometries at molybdenum are approximately trigonal prismatic, and the metal bears two strongly bound dithiolene (tfd) groups and two comparatively weakly bound thioether ligands (dht or tht). Competitive binding experiments establish that tht binds more strongly to the Mo center than dht ( $K_{eq} = 6.5 \pm 0.5$ ). Preliminary reactivity studies reveal that [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] decomposes to [Mo(tfd)<sub>3</sub>], thiophene, and unidentified species upon heating. Further, [Mo(tfd)<sub>2</sub>(tht)<sub>2</sub>] induces the isomerization of 1,4-cyclohexadiene to 1,3-cyclohexadiene at elevated temperatures.

lent activity in deep desulfurization,<sup>[4]</sup> the high activity of those metals is offset by their cost. Developing increasingly active Mo-based catalysts is thus a worthwhile goal, and we focus here on molecular coordination compounds of molybdenum. Heterogeneous MoS<sub>2</sub>-based HDS catalysis has been investigated by experimental surface techniques as well as by computational (DFT) studies on cluster models.<sup>[5–7]</sup> However, small molecular (soluble) models mimicking the active sites in molybdenite HDS catalysts are rare.<sup>[8]</sup> Small molecule models should be useful for understanding the mechanism of HDS catalysis and could lead to the development of better catalysts.<sup>[6]</sup> It is thought that exposed (coordinatively unsaturated) edges of  $MoS_2$  sheets are the active sites and that the internal centers are inactive.<sup>[9]</sup> A fragment of the molybdenite structure is shown in Figure 1, which shows internal sites, edge sites, and key metric parameters.

As shown in Figure 1, the molybdenum edge sites possess pyramidal structures, with molybdenum at the apex of a square pyramid and four sulfur atoms forming the base of the pyramid. Current evidence suggests that thiophene coordinates to the molybdenum edge sites. The coordinated thiophene then undergoes hydrogenation to 2,5-dihydro-thiophene and, finally, desulfurization (through cycloreversion) of the organic moiety produces 1,3-butadiene and a terminal metal sulfide (Scheme 1).<sup>[13]</sup> Reduction of the metal sulfide with H<sub>2</sub> releases H<sub>2</sub>S and regenerates the unsaturated Mo center.



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Figure 1. Views of exposed molybdenum sites in hexagonal MoS<sub>2</sub>; (a) standard orientation, in which the hexagonal layers are oriented horizontally; (b) rotated to highlight the geometry<sup>[10]</sup> of the edge sites. The picture was generated with ORTEP,<sup>[11]</sup> by using MoS<sub>2</sub> coordinates<sup>[12]</sup> from the literature.



Scheme 1. Desulfurization of thiophene at a MoS<sub>2</sub> edge site.

Accurate structural models of MoS<sub>2</sub>-based HDS catalysts should have the square-pyramidal structure (with Mo at the apex and four sulfur donors forming the basal plane) as seen for the edge sites in molybdenite. Additionally, the model should incorporate vacant (or labile) sites to bind organosulfur substrates (e.g. thiophene derivatives). While many examples of molybdenum<sup>[14-18]</sup> (or tungsten<sup>[19]</sup>) complexes bearing four sulfur donors are known, they usually contain additional strongly bound ligands, such as thiolates or phosphanes, which cannot be displaced by thioether groups or other weakly coordinating sulfur donors. However, they do show catalytic activity toward nitrate and formate reduction, and in that area, are showing promise as models for enzymes. On the other hand, the few truly fourcoordinate  $MoS_4$  complexes {e.g.  $[Mo(SR)_4]$ , R = 2,4,6triisopropylbenzene} are extremely electrophilic toward small donor molecules and form a variety of MoS<sub>4</sub>L complexes, where L = (e.g.) alkyne, MeCN, tBuNC, CO.<sup>[20]</sup> However, these four-coordinate MoS<sub>4</sub> complexes have tetrahedral rather than pyramidal geometry at the metal, which makes them less desirable as model complexes for the molvbdenite edge sites. Monosulfided molybdenum<sup>[21]</sup> or tungsten<sup>[19]</sup> species with dithiolene ligands ["SM( $S_2C_2R_2$ )<sub>2</sub>"] have also been produced, and they may be regarded to be excellent models for the intermediate obtained after butadiene loss (right-hand side of Scheme 1). Schrauzer et al. produced thioether complexes on tungsten-based dithiolenes by methylation of one of the dithiete ligands.<sup>[22]</sup> [Mo(CO)<sub>2</sub>- $(S_2C_2Me_2)_2$ ] complexes are known and offer both the square-pyramidal MoS<sub>4</sub> structure as well as labile CO groups.<sup>[19,23]</sup> While CO is a labile ligand in such complexes (as we also confirmed experimentally, see below), we provide here an alternative approach to the opening up of two labile sites at "S4Mo".

The first coordination sphere of neutral molybdenum trisdithiolenes resembles the environment of the internal (non-edge sites) molybdenum atoms in molybdenite - in both cases, the metal geometry is approximately trigonal prismatic with six sulfur-donor ligands. Our group has previously reported that mixed-ligand molybdenum trisdithiolenes { $[Mo(tfd)_2(bdt)]$  and  $[Mo(bdt)_2(tfd)]$  with tfd =  $S_2C_2(CF_3)_2$ , bdt =  $S_2C_6H_4$ } react with ethylene through the sulfur atoms of one bdt ligand (i.e. intraligand alkene addition) to form a metal-chelating dihydrobenzodithiin moiety.<sup>[24]</sup> The weakly bound dihydrobenzodithiin can be substituted with a variety of nucleophiles, which allows access to new molybdenum bis- and trisdithiolene complexes. In this paper we extend this versatile method to create molybdenum bisdithiolenes with thioether ligands (partially hydrogenated thiophenes), which provide structural models for postulated intermediates in MoS<sub>2</sub>-based HDS catalysis.

### **Results and Discussion**

The syntheses of our structural models exploits the ligand-based reactivity of  $[Mo(tfd)_2(bdt)]$ : treatment of the trisdithiolene with bis(trimethylsilyl)acetylene (btmsa)<sup>[25]</sup> gave  $[Mo(tfd)_2\{bdt(btmsa)\}]$ , which was subjected to ligand substitution with excess dht or tht (dht = 2,5-dihydrothiophene; tht = tetrahydrothiophene) to yield  $[Mo(tfd)_2-(dht)_2]$  or  $[Mo(tfd)_2(tht)_2]$ , respectively, upon loss of the metal-coordinated benzodithiin (Scheme 2, see experimental section for details). The resulting complexes were characterized by multinuclear NMR spectroscopy, elemental analysis, and X-ray crystallography. However, this approach failed to produce any complexes with *thiophene* ligand.



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

Figure 2 shows the crystallographically determined structures of  $[Mo(tfd)_2(dht)_2]$  and  $[Mo(tfd)_2(tht)_2]$ . Crystallographic data are summarized in the Exp. Sect. (Table 3).





Figure 2. Top: structure of  $[Mo(tfd)_2(dht)_2]$ . Bottom: structure of  $[Mo(tfd)_2(tht)_2]$ . Non-hydrogen atoms are displayed by using 30% thermal ellipsoids.

The structures of [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] and [Mo(tfd)<sub>2</sub>(tht)<sub>2</sub>] (Figure 2) are, expectedly, quite similar. In each case, the molybdenum centers are coordinated by six sulfur atoms. Two adjacent (cis) coordination sites are occupied by thioether ligands (dht or tht); these labile sites will possibly allow access to mechanisms utilizing two coordination sites on the same Mo atom. In  $[Mo(tfd)_2(dht)_2]$ , the  $\pi$  bonds of the dht ligands do not interact with the metal (i.e. dht binds in an  $\eta^1$ -S fashion), consistent with experimental (NEXAFS) data for dht adsorbed on a sulfided molybdenum surface.<sup>[26]</sup> The "locked" conformation of the thioether ligands is likely enforced by crystal packing. NMR spectroscopy (19F) indicates apparent  $C_{2\nu}$  symmetry for [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] and [Mo(tfd)<sub>2</sub>(tht)<sub>2</sub>], which indicates interconversion between ring conformers in solution. The crystal structure determinations for [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] and [Mo(tfd)<sub>2</sub>(tht)<sub>2</sub>] have yielded detailed information on the sulfur environment in such species, which is very consistent across the two structures. Key structural data are summarized in Table 1. The Mo-S(tfd) bond lengths (Table 1) for [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] and [Mo(tfd)<sub>2</sub>(tht)<sub>2</sub>] [average 2.335(1) Å and 2.333(1) Å, respectively] are marginally shorter than the analogous Mo–S(tfd)

Table 1. Selected structural data for [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] and [Mo(tfd)<sub>2</sub>(tht)<sub>2</sub>].

	[Mo(tfd) <sub>2</sub> (dht) <sub>2</sub> ]	[Mo(tfd) <sub>2</sub> (dht) <sub>2</sub> ]		[Mo(tfd) <sub>2</sub> (tht) <sub>2</sub> ]	
Bond lengths (Å)					
Mo–S(tfd)	Mo1–S1 Mo1–S2 Mo1–S3	2.336(2) 2.329(2) 2.337(2)	Mo1–S1 Mo1–S2 Mo1–S3	2.331(1) 2.336(1) 2.324(1)	
Mo–S(thioether)	Mo1–S4 Mo1–S5 Mo1–S6	2.337(2) 2.520(2) 2.520(2)	Mo1–S4 Mo1–S5 Mo1–S6	2.343(1) 2.513(1) 2.523(1)	
Bond angles [°]					
S–Mo–S (tfd)	S1–Mo1–S2 S3–Mo1–S4	81.28(6) 81.76(6)	S1–Mo1–S2 S3–Mo1–S4	81.50(5) 81.55(5)	
S–Mo–S (thioether) S–Mo–S ( <i>trans</i> S)	S5-Mo1-S6 S1-Mo1-S4 S1-Mo1-S5 S3-Mo1-S2 S3-Mo1-S5 S6-Mo1-S2 S6-Mo1-S4	75.20(6) 142.11(6) 127.77(6) 137.21(6) 136.69(6) 134.27(6) 129.85(6)	S5-M01-S6 S3-M01-S2 S1-M01-S4 S3-M01-S5 S1-M01-S5 S2-M01-S6 S4-M01-S6	73.85(4) 139.92(5) 138.83(5) 130.58(5) 133.30(5) 128.73(5) 135.44(5)	
Nonbonded distances [Å]					
S–S (trigonal face) inter-tfd	S1–S3 S2–S4 S3_S6	3.170(2) 3.132(2) 3.230(2)	\$1-\$3 \$2-\$4 \$3 \$6	3.117(2) 3.167(2) 3.277(2)	
	S1-S6 S2-S5 S4-S5	3.233(2) 3.150(2) 3.242(2)	SJ-S6 S1-S6 S2-S5 S4-S5	3.151(2) 3.268(2) 3.232(2)	
S–S (prism edge) inter-tfd	S1–S2 S3–S4	3.038(2) 3.059(2)	S1–S2 S3–S4	3.047(2) 3.048(2)	
inter-thioether	S5–S6	3.075(2)	S5–S6	3.026(2)	
S–S–S	S3-S1-S6 S1-S3-S6 S1-S6-S3 S4-S2-S5 S2-S4-S5 S2-S4-S5	60.77(6) 60.58(6) 58.65(6) 62.14(6) 59.21(6)	\$3-\$1-\$6 \$1-\$3-\$6 \$1-\$6-\$3 \$4-\$2-\$5 \$2-\$4-\$5	63.04(5) 58.99(5) 57.97(5) 60.29(5) 61.4(5)	
interplanar angle	52-55-54 \$1-\$3-\$6 to \$2-\$4-\$5	0.59(11)	52–55–54 S1–S3–S6 to S2–S4–S5	0.57(8)	

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bonds in  $[Mo(bdt)_2(tfd)]^{[24]}$  and  $[Mo(tfd)_3]^{[27]}$  [average 2.367(1) Å and 2.355(4) Å, respectively]. Particularly striking is the fact that the thioether ligands are apparently very weakly bonded, with Mo–S bond lengths that are much longer, by almost 0.2 Å, than the Mo–S(tfd) bonds. Indeed, the Mo–S(thioether) bond lengths (thioether = dht or tht, 2.51–2.52 Å) are among the longest molybdenum–sulfur bonds known.

There are few examples of structurally characterized Mo–thioether complexes available for comparison. The most similar one is the ethylene adduct [Mo(tfd)<sub>2</sub>-{bdt(CH<sub>2</sub>CH<sub>2</sub>)}], with an average distance of 2.523 Å to the sulfur atoms on the dihydrobenzodithiin ligand.<sup>[24]</sup> The closest non-dithiolene-based Mo<sup>IV</sup> system is an octahedral molybdenum "S<sub>4</sub>-crown" thioether complex, with slightly shorter Mo–S(thioether) distances (2.469–2.498 Å).<sup>[28]</sup>

Computed Mo–S distances for dht and tht bound to a  $Mo_3S_9$  catalyst model fragment are 2.53 Å and 2.50 Å, respectively.<sup>[29]</sup> Thus,  $[Mo(tfd)_2(dht)_2]$  and  $[Mo(tfd)_2(tht)_2]$  can be regarded as being structurally very similar to the active sites they are modelling.

In both compounds, the coordination geometry at molybdenum is very close to trigonal prismatic. Figure 3 shows the bond angles used to corroborate this statement. By using the three largest S-M-Strans angles (Figure 3a) to position the structures on the scale ranging from perfect octahedron (0%) to perfect trigonal prism (100%),<sup>[30]</sup> [Mo- $(tfd)_2(dht)_2$  and  $[Mo(tfd)_2(tht)_2]$  were found to have 92% and 94% trigonal-prismatic character, respectively.<sup>[31]</sup> The largest deviations<sup>[32]</sup> in the SMS<sub>trans</sub> angles were ca. 14° {for  $[Mo(tfd)_2(dht)_2]$  and ca. 11° {for  $[Mo(tfd)_2(tht)_2]$ }. The triangular faces of the trigonal prisms contain S-S-S (formally nonbonded) angles very close to 60° (Figure 3b) the largest deviation is ca. 3° in both cases (Table 1). This observation is surprising insofar as the large difference between the Mo-S(tfd) and Mo-S(thioether) bond lengths could be expected to lead to a more distorted MoS<sub>6</sub> substructure.



Figure 3. Bond angles used for analysis; (a) example for  $S-M-S_{trans}$  angle, (b) example for S-S-S (nonbonding) angle.

Trigonal-prismatic geometry, which maximizes ligandmetal and interligand  $\pi$  interactions,<sup>[33]</sup> is quite common for high-valent (oxidized) metal trisdithiolenes (e.g. neutral group six trisdithiolenes). Reduced analogues, on the other hand, usually exhibit distortion toward octahedral geometries, thereby relieving ligand–ligand repulsion in these comparatively electron-rich systems. To illustrate, the metal geometry in neutral [Mo(tfd)<sub>3</sub>] is very close to trigonal prismatic<sup>[27]</sup> (99% by using the S–M–S<sub>trans</sub> angle criterion, see above),<sup>[31]</sup> while dianionic [Mo(tfd)<sub>3</sub>]<sup>2–</sup> has considerably more octahedral character<sup>[27]</sup> (70% trigonal prismatic).<sup>[32]</sup> In general, trigonal-prismatic structures are more likely for complexes with low d electron counts (i.e.  $d^n$ ,  $n \le 2$ ).<sup>[34]</sup> This has been explicitly discussed for MoS<sub>2</sub> by using crystal field theory.<sup>[35]</sup> Analogous effects have been shown computationally and experimentally for [Mo(butadiene)<sub>3</sub>] complexes<sup>[36]</sup> and computationally for M(CH<sub>3</sub>)<sub>6</sub><sup>n</sup> complexes (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Tc, Re, Ru, Os; n = -2,  $-1, 0, \pm 1$ .<sup>[37]</sup> The two complexes synthesized for the present study  $- [Mo(tfd)_2(dht)_2]$  and  $[Mo(tfd)_2(tht)_2] - are charge$ neutral and formally Mo<sup>IV</sup> (d<sup>2</sup>) species, with two ene-dithiolate donors and two neutral thioether ligands. Similarly, neutral group VI metal trisdithiolenes, such as [Mo(tfd)<sub>3</sub>], can be reasonably formulated as a d<sup>2</sup> species, with two dianionic dithiolene ligands and one neutral, weakly donating dithioketone ligand.<sup>[38]</sup> The trigonal-prismatic geometries observed at the metals in [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] and [Mo(tfd)<sub>2</sub>-(tht)<sub>2</sub>] can, therefore, be rationalized on the basis of low d electron counts and neutral charge states for both complexes, with analogy to group VI metal trisdithiolenes. The observed trigonal prismatic geometries mimic the environment of the Mo centers in molybdenum(IV) sulfide.

The S–Mo–S angles involving the thioether ligands are very acute  $\{75.2^{\circ} \text{ for } [Mo(tfd)_2(dht)_2] \text{ and } 73.9^{\circ} \text{ for} [Mo(tfd)_2(tht)_2]\}$ . The S–Mo–S angles in the dithiolene chelate rings are much wider (ca. 82°) for both complexes. Interestingly, there are many examples in the literature of Mo (or W) bisdithiolene complexes with various non-dithiolene ligands that also exhibit this acute non-dithiolene ligand angle and wider dithiolene ligand bite angles. Relevant examples are summarized in Table 2. Despite a large variation in non-dithiolene ligands (which are of variable steric demand), the non-dithiolene and the dithiolene bite angles remain remarkably consistent.

This narrow non-dithiolene ligand angle is intriguing. A similar observation was made by Holm and co-workers<sup>[39]</sup> when narrow C–M–C bond angles for  $M(CO)_2(S_2C_2Me_2)_2$ were observed:  $83.5^{\circ}$  for M = Mo and  $84.1^{\circ}$  for M = W. These bond angles became smaller even more upon stepwise reduction (monoanion, dianion), down to 72.3° for the dianions. CO is, of course, a very special ligand because of its  $\pi$ -acceptor properties, and Fomitchev, Lim and Holm<sup>[39]</sup> concluded that the observed effect is "suggestive of a weak bonding interaction between the carbonyl ligands". For those ligands that are not  $\pi$  acceptors, ligands such as dht and tht in this work, alternative explanations are needed. The lowest-lying empty orbitals of the Mo(tfd)<sub>2</sub> fragment points toward an explanation. Using density functional theory (DFT), we found that both a pseudo-tetrahedral structure and the pyramidal structure that is relevant here are minima on the hypersurface for Mo(tfd)<sub>2</sub>, as confirmed by geometry optimization and subsequent frequency analysis (no imaginary frequency). The pyramidal structure (uphill relative to the pseudo-tetrahedral structure by 12.3 kcal/ mol) has two low-lying empty orbitals (LUMO and NLUMO), shown in Figure 4, that contain some p-orbital contribution from the sulfur atoms but are largely metalbased and correspond roughly to  $d_{x^2-v^2}$  (LUMO) and  $d_{vz}$ 



	Non-dithiolene bite angle [°]	Dithiolene bite angle (av.) [°]	Trigonal-prismatic character <sup>[31]</sup> [%]	Deviation <sup>[32]</sup> [°]	Ref.
$\overline{[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{SCH}_2\text{CH}_2\text{OH})_2(\text{mnt})_4]}$	68	83	82	25	[15]
$[Et_4N]_2[Mo_2(SPh)_2(mnt)_4]$	67	82	96	12	[15]
$[Et_4N]_2[W_2(SCH_2Ph)_2(mnt)_4]$	68	83	95	10	[15]
$[Et_4N]_2[W_2(SCH_2CH_3)_2(mnt)_4]$	67	82	87	21	[15]
$[Et_4N]_2[W_2(SCH_2CH_2OH)_2(mnt)_4]$	68	83	92	18	[15]
$[Et_4N]_2[W_2(SPh)_2(mnt)_4]$	66	82	93	14	[15]
$[Et_4N]_2[Mo_2(SCH_2Ph)_2(mnt)_4]$	67	83	91	20	[15]
$[Et_4N]_2[Mo_2(SCH_2CH_3)_2(mnt)_4]$	68	82	86	22	[15]
$[Et_4N]_2[Mo(NCS)_2(mnt)_2]$	66	86	88	23	[16]
[Ph <sub>4</sub> P] <sub>2</sub> [W(SPh) <sub>2</sub> (mnt) <sub>2</sub> ]•0.5(CH <sub>3</sub> ) <sub>2</sub> CHOH	72	82	98	7	[15]
[Et <sub>4</sub> N][Mo(PPh <sub>3</sub> )(NCS)(mnt) <sub>2</sub> ]	76	83	83	21	[16]
$[Et_4N][Mo(PPh_3)(SC_6H_4-4-Me)(mnt)_2]$	77	82	93	10	[16]
[Ph <sub>3</sub> PNPPh <sub>3</sub> ][Mo(PPh <sub>3</sub> )(SC <sub>6</sub> H <sub>4</sub> -2-COOH)(mnt) <sub>2</sub> ]	76	82	73	29	[16]
[Et <sub>4</sub> N][Mo(SPh)(PPh <sub>3</sub> )(mnt) <sub>2</sub> ]·CH <sub>2</sub> Cl <sub>2</sub>	77	82	90	17	[17]
[PPh <sub>4</sub> ][Mo(PPh <sub>3</sub> )(SCH <sub>2</sub> CH <sub>3</sub> ) (mnt) <sub>2</sub> ]·CH <sub>2</sub> Cl <sub>2</sub>	76	83	74	28	[18]
[PPh <sub>4</sub> ][Mo(PPh <sub>3</sub> )(SCH <sub>2</sub> Ph)(mnt) <sub>2</sub> ]	77	81	94	14	[18]
$[Et_4N][Mo(PPh_3)(Br)(mnt)_2]$	78	83	81	23	[18]
$[Mo(tfd)_{2}{bdt(CH_{2}CH_{2})}]$	72	82	86	20	[24]
$[Mo(tfd)_2(dht)_2]$	75	82	92	14	this work
[Mo(tfd) <sub>2</sub> (tht) <sub>2</sub> ]	74	82	94	11	this work

Table 2. A comparative sampling of bite angles (°) in bisdithiolenes with various ligands  $[mnt = S_2C_2(CN)_2]$ .

(NLUMO), where the labeling assumes that we define the paper plane to be the xy plane with y being vertical and x horizontal. The system will be "frustrated" every time a Lewis acid/Lewis base adduct is formed with *two* added lone-pair donors L: an L–Mo–L bond angle close to 90° would optimize overlap with the NLUMO, which, however, leads to poor overlap with the LUMO. Good overlap with the orbital that is the LUMO in Mo(tfd)<sub>2</sub> necessitates a narrow L–Mo–L bond angle.



Figure 4. DFT-computed (B3LYP/SDD, see Experimental Section) low-lying molecular orbitals (Kohn–Sham orbitals; left: LUMO, -0.205 eV; right: NLUMO, -0.185 eV; plotted at 0.06 isovalue) of geometry-optimized (local minimum but not global minimum) pyramidal Mo(tfd)<sub>2</sub>. Note the similarity of the free pyramidal fragment to the Mo(tfd)<sub>2</sub> substructure in [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] and [Mo(tfd)<sub>2</sub>-(tht)<sub>2</sub>], shown in Figure 2 in a similar orientation.

While the narrow bite angle described above is a deviation from a perfect trigonal-prismatic geometry, the "trigonal" planes in  $[Mo(tfd)_2(dht)_2]$  and  $[Mo(tfd)_2(tht)_2]$  are almost perfectly parallel.

If the S1–S3–S6 and S2–S4–S5 faces of both complexes are taken to define planes, the angle between the two planes is  $0.59^{\circ}$  and  $0.57^{\circ}$  for [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] and [Mo(tfd)<sub>2</sub>(tht)<sub>2</sub>], respectively (i.e. essentially parallel as in a true triangular prism). In each triangular face, the sulfur atoms are essentially closest packed. A diagram showing the van der Waals spheres for the sulfur atoms of [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] is shown in Figure 5 (the structure of the tht complex leads to a virtually identical picture). Visually, the impression of a very symmetrical arrangement of closest-packed sulfur atoms (Figure 5A) is striking, which is quantitatively re-enforced by the very consistent nonbonded distances (Table 1).



Figure 5. View of the sulfur environment of  $[Mo(tfd)_2(dht)_2]$ , by using the van der Waals radii for the sulfur atoms; **A**: view perpendicular to S2–3–S6 "close-packed" plane; **B**: view onto S5–S6 edge.

While the preference for trigonal-prismatic (instead of octahedral) geometry is electronic in origin (as is the acuteness of one S–Mo–S angle), the resulting structure is surprisingly consistent with a closest-packing model in which the two closest-packed "S<sub>3</sub>" triangles are stacked on top of another and in which the central Mo is dislocated from the center toward the more donating sulfur atoms. In both  $[Mo(tfd)_2(dht)_2]$  and  $[Mo(tfd)_2(tht)_2]$ , the sulfur atoms are found in a geometric arrangement very similar to that observed for molybdenum inside solid MoS<sub>2</sub>, including the overlapping Van der Waals radii for adjacent sulfur centers.

#### Reactivity

The new complexes show some interesting and promising reactivity at slightly elevated temperatures (60–120 °C), which, unfortunately, is accompanied by decomposition.  $[Mo(tfd)_2(dht)_2]$  and  $[Mo(tfd)_2(tht)_2]$  are stable for days at room temperature in nonpolar/noncoordinating solvents

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(e.g.  $C_6D_6$ ), but rapidly react with coordinating solvents such as thf and acetonitrile (color change to green or red, respectively, observed immediately upon dissolution). Both complexes are somewhat unstable in chloroform, decaying within a few days at room temperature, and within 1 h at 60 °C. The decomposition products were identified by <sup>19</sup>F/ <sup>1</sup>H NMR as [Mo(tfd)<sub>3</sub>] and free thioethers (dht or tht). Presumably molybdenum metal is also deposited, as a faint darkening of the NMR tubes can be observed; this film is insoluble in organic solvents but dissolves in inorganic acids. The complexes are considerably more stable in C<sub>6</sub>D<sub>6</sub>: only minor decomposition was observed after heating either complex to 60 °C for 1 d.

The complexes are sufficiently stable (in CDCl<sub>3</sub>) to determine the relative binding constant of dht vs. tht with respect to coordination to the  $Mo(tfd)_2$  fragment. We found that tht binds more strongly by a factor of 6.5(5) at a temperature of ca. 22 °C (Figure 6). The lesser binding affinity for dht, relative to that for tht, is likely because of the electronwithdrawing alkene group in dht, which can be expected to decrease the  $\sigma$ -donor ability of the thioether ligand. Substitution of dht with thiophene was not observed at any concentration of thiophene in CDCl<sub>3</sub> or with neat thiophene. These results can be compared to a recent computational paper by Joshi et al. in which the adsorption energies of various sulfur-containing molecules onto MoS<sub>2</sub> is reported.<sup>[40]</sup> The lowest binding energies for an unsaturated molybdenum edge structure with tht and dht were found to be -1.67 eV and -1.60 eV, respectively, which corresponds to an energy difference of -6.75 kJ/mol. Our experimentally determined equilibrium constant corresponds to a difference in binding free energy of -4.6(2) kJ/mol (for tht vs. dht), quite consistent with the calculated value. Joshi et al. also calculated the binding energy of thiophene to be -1.04 eV, compared with -1.60 eV for dht (difference: -0.56 eV or -54 kJ/mol). This energy difference would yield



Figure 6. Determination of the equilibrium constant for the binding of tht vs. dht at 22 °C in CDCl<sub>3</sub>, according to the equation: Mo-dht + tht  $\rightleftharpoons$  Mo-tht + dht. The model, predicting a linear dependence of the ratio [Mo-tht]/[Mo-dht] vs. the ratio of free thioethers ([tht]/[dht]), fits the data very well ( $R^2 = 0.9991$ ). No cooperativity is observed, and the two labile sites behave independently in this process. The slope yields  $K_{eq} = 6.5 \pm 0.5$  (tht binds more strongly, by a factor of close to seven, than dht). See Experimental Section for details.

an equilibrium constant (at 22 °C) of  $3.7 \times 10^9$  in favor of dht binding and thus explains the inability of thiophene to displace dht.

When [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] was heated in deuterated chloroform (60 °C, 1 h), thiophene (12%, relative to original concentration) was identified by <sup>1</sup>H NMR spectroscopy as one of the decomposition products. [Mo(tfd)<sub>3</sub>] was also observed, as well as a smaller percentage of unidentified decomposition products (by <sup>19</sup>F NMR spectroscopy). It therefore appears that the dht ligands in the  $[Mo(tfd)_2(dht)_2]$ complex are dehydrogenated to thiophene, although free hydrogen gas was not observed in the <sup>1</sup>H NMR spectrum. These reactions were not catalytic when excess dht was present. At the temperatures accessible to this system (before decomposition occurs), we have not been able to reproducibly demonstrate desulfurization. Butadiene, which would be expected to form upon desulfurization of dht (Scheme 1), was not observed in any of the reactions we screened. Performing of the same reaction after an atmosphere of hydrogen was sealed into the tubes produced no change in the product type or distribution. All hydrogen reactions where done under a pressure of 1 atm; greater pressures may be needed to observe any reactivity. Many proposed HDS mechanisms invoke the action of the surrounding sulfur atoms,<sup>[41,42]</sup> and/or multiple metal centers,<sup>[43,44]</sup> in MoS<sub>2</sub> to facilitate the hydrodesulfurization of thiophene. Such pathways may not be accessible at the relatively low temperatures we tried (60-120 °C, as necessitated by the temperature-sensitivity of our model complexes; cf. 300-400 °C for industrial HDS processes<sup>[2]</sup>). It will be the goal of future studies (with more temperature-stable analogs) to investigate whether a HDS cycle can be achieved with a single molybdenum center or whether the participation of more than one metal is required.<sup>[44]</sup>

However, we observed the isomerization of 1,4-cyclohexadiene to 1,3-cyclohexadiene at 110 °C in  $[D_{12}]$ cyclohexane in the presence of  $[Mo(tfd)_2(tht)_2]$ . Performing of the same reaction with  $[Mo(tfd)_2(bdt)]$  did not yield any isomerized diene.

Finally, we would like to address the question of how the lability of carbon monoxide (which binds weakly to molybdenum bisdithiolenes, see Introduction) relates to the lability of thioethers. When a slow stream of carbon monoxide is bubbled through a solution of [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] in  $C_6D_6$  for a total of 4 h, a new complex is observed by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy [ca. 70-90% conversion, as determined by <sup>19</sup>F NMR spectroscopy, with 3,5-bis(trifluoromethyl)bromobenzene internal standard]. The new species is assigned as [Mo(tfd)<sub>2</sub>(dht)(CO)]: NMR integration of the dht protons yields that only one dht molecule is bound per molybdenum. In addition, the amount of free dht observed matches the dht bound to the new complex, in accord with expectations from mass balance. When a large excess of dht was added, the equilibrium shifted back to [Mo(tfd)2-(dht)<sub>2</sub>]. Thus, carbon monoxide and thioethers have a similar binding strength when coordination to Mo(tfd)<sub>2</sub> fragments is involved. Some metal bisdithiolene complexes containing carbonyls are already known,<sup>[19,23]</sup> and it may be-



come useful knowledge for future syntheses that CO and thioethers can be of comparable lability in such systems.

### Conclusions

The molecular compounds [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] and [Mo(tfd)<sub>2</sub>-(tht)<sub>2</sub>] were synthesized and characterized as structural models for the hydrodesulfurization catalyst molybdenum disulfide. X-ray crystallography shows that they are excellent models for the proposed active site of molybdenum disulfide. Preliminary investigations show some intriguing reactivity consistent with transfer dehydrogenation, yet temperature-sensitivity hampers full exploration of this avenue. It may be anticipated that molecular compounds for actual HDS catalysis will have to be designed to be more robust at high-temperature conditions, which will likely necessitate departure from a close structural model. Additionally, it may be necessary to consider models containing more than one metal site (e.g. homo- or heterodimetallic complexes of Mo). The new complexes are useful, however, to test equilibria at room temperature, as demonstrated with a dht/tht competition on a sulfur-ligated Mo<sup>IV</sup> center.

### **Experimental Section**

[Mo(tfd)<sub>2</sub>(bdt)] was prepared by literature methods.<sup>[24]</sup> Grubbs' second generation catalyst, tetrahydrothiophene (tht) (99%) and bis-(trimethylsilyl)acetylene (btmsa) (99%) were obtained from Sigma Aldrich. Tetrahydrothiophene was redistilled and dried with molecular sieves (3 Å) before use. Bis(trimethylsilyl)acetylene was used directly. Solvents were dried on a MBraun Solvent Purification System (MB-SPS). NMR spectroscopic data were collected on a Bruker Avance III 400 MHz spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra were referenced to the CDCl<sub>3</sub> solvent peaks, ( $\delta$  =7.26 ppm and 77.23 ppm, respectively). <sup>1</sup>H spectra were also referenced to the  $C_6D_6$  solvent peaks where applicable ( $\delta = 7.16$  ppm). <sup>19</sup>F was referenced to an external capillary of neat trifluoroacetic acid ( $\delta$  = -78.5 ppm). Elemental analysis was performed by Chemisar Laboratories, Guelph, Ontario, Canada. DFT calculations were performed on a Desktop PC by using Gaussian 03W Rev D.01<sup>[45]</sup> on closed-shell singlets (charge-neutral molecules) with the B3LYP<sup>[46]</sup> functional and SDD basis set (ECP) for molybdenum. The SDD basis set is the combination of the Dunning/Huzinaga double- $\zeta$  basis set<sup>[47]</sup> on lighter elements with the Stuttgart-Dresden relativistic effective core potential<sup>[48]</sup> (RECP) on heavier elements.<sup>[49]</sup> To improve the accuracy of the calculation, d functions were added to all sulfur atoms [as polarization functions; d coefficients from the 6-311G(d,p) basis set]. No symmetry restrictions were used, and default convergence criteria were employed.

Synthesis of  $[Mo(tfd)_2(tht)_2]$ : In air:  $[Mo(tfd)_2(bdt)]$  (51.3 mg, 74.5 µmol) was dissolved in dry hexanes (10 mL) along with tetrahydrothiophene (63.4 µL, 719 µmol) and btmsa (80.4 µL, 360 µmol), and the mixture was left to stand. Brown crystals slowly came out of solution over ca. 1 h, and the solution turned redpurple. After 18 h, the crystals were recovered by filtration and washed three times with 5 mL portions of hexane. The crystals were dried in vacuo to give  $[Mo(tfd)_2(tht)_2]$  (39 mg, 54 µmol, 72%). The crystals were stored under inert atmosphere and were found to be stable at room temperature. X-ray quality crystals were obtained directly from the hexane reaction mixture. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.28 (m, 8 H, tht), 3.54 (m, 8 H, tht) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -54.9 [s, 12 F, (CF<sub>3</sub>)<sub>2</sub>×2] ppm. <sup>13</sup>C{<sup>1</sup>H}

NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 30.109 (s, C<sub>β</sub>, tht),  $\delta$  = 42.31 (s, C<sub>α</sub>, tht) ppm. C<sub>16</sub>H<sub>16</sub>F<sub>12</sub>MoS<sub>6</sub> (724.59): calcd. C 26.52, H 2.23, S 26.55; found C 26.82, H 1.97, S 26.23.

Synthesis of 2,5-Dihydrothiophene: Grubbs' second generation catalyst, 1,3-bis(2,4,6-trimethylphenyl)-2-(imidazolidinylidene)(dichlorophenylmethylene)(tricyclohexylphosphane)ruthenium, (75 mg, 88.3 µmol) was added to diallyl sulfide (75 mL of a 0.1 M solution) in dry chloroform (7.5 mmol). The solution was stirred under a stream of argon for 24 h. The volatiles were vacuum transferred to a new container and heated to 70 °C until the volume was reduced to ca. 1 mL. The solution was vacuum-distilled a second time to a new container and stored under nitrogen. NMR spectroscopy showed the sample to consist of ca. 70% 2,5-dihydrothiophene and ca. 30% chloroform. Volumes used were adjusted for actual 2,5-dihydrothiophene content.

**Synthesis of [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>]:** The procedure for [Mo(tfd)<sub>2</sub>(tht)<sub>2</sub>] was repeated but with [Mo(tfd)<sub>2</sub>(bdt)] (52.4 mg, 76.1 µmol), 2,5dihydrothiophene solution (50 µL), and btmsa (50 µL, 224 µmol). The crystals were dried in vacuo to give [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] (24.4 mg, 33.8 µmol, or 44%). The crystals were stored under an inert atmosphere and were stable at room temperature. X-ray quality crystals were obtained directly from the hexane solution. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.35 [m, 8 H, (CH<sub>2</sub>)×4], 5.99 [m, 4 H, (CH)×4] ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = 48.78 (s, CH<sub>2</sub>),  $\delta$  = 126.62 (s, CH) ppm. C<sub>16</sub>H<sub>16</sub>F<sub>12</sub>MoS<sub>6</sub> (720.56): calcd. C 26.67, H 1.68, S 26.70; found C 26.89, H 1.49, S 26.04.

Attempted Synthesis of  $[Mo(tfd)_2(thiophene)_2]$ :  $[Mo(tfd)_2(bdt)]$ (2 mg) was placed into an NMR tube with C<sub>6</sub>D<sub>6</sub> (500 µL), btmsa (ca. 10 µL), and thiophene (ca. 5uL), and 3,5-bis(trifluoromethyl)bromobenzene (ca. 3 µL) as an internal standard. After 2 h only unreacted  $[Mo(tfd)_2(bdt)]$  and btmsa along with a smaller quantity of the  $[Mo(tfd)_2\{bdt(btmsa)\}]$  adduct {20% yield relative to unreacted  $[Mo(tfd)_2(bdt)]\}$  were identified by NMR spectroscopy and integration. No new products could be detected. The procedure for  $[Mo(tfd)_2(tht)_2]$  was also repeated but by substituting tht with thiophene. After 24 h, the solution remained green and no crystals were observed.

**Thermal Decomposition of** [**Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>**]: [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>] (2.5 mg, 3.5 µmol) was placed in an NMR tube with CDCl<sub>3</sub> (600 µL), and 3,5-bis(trifluoromethyl)bromobenzene (ca. 5 µ L) as an internal standard. The mixture was heated to 60 °C for 20 h. Thiophene {12% yield relative to starting [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>]} was identified in the products by using NMR spectroscopy and integration.

Noncatalytic Dehydrogenation of dht with [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>]: [Mo(tfd)<sub>2</sub>-(dht)<sub>2</sub>] (0.7 mg, 0.967 µmol) was placed in an NMR tube with dht (600 µL of a 0.062 м solution) in CDCl<sub>3</sub> along with 3,5-bis(trifluoromethyl)bromobenzene (ca. 5 µL) as an internal standard. The tube was heated to 60 °C for 24 h and then to 120 °C for 5 h. Thiophene was identified by NMR spectroscopy in a 43% yield based on the reagent Mo (tfd)<sub>2</sub>(dht)<sub>2</sub>.

**Hydrogen Reactivity:** Both the thermal decomposition and the noncatalytic dehydrogenation experiments were repeated, but before heating, the NMR tubes were thoroughly degassed by freeze-pumpthaw cycling. Hydrogen at atmospheric pressure was admitted to the tubes (ca. 1 mL) and then sealed. Heating proceeded as described previously. No new products or significant changes in product distribution were observed by NMR spectroscopy.

**Isomerization of 1,4-Cyclohexadiene:**  $[Mo(tfd)_2(tht)_2]$  (0.5 mg, 0.69 µmol) and 1,4-cyclohexadiene (5 µL, 52.9 µmol) were added

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to  $C_6D_{12}$  (500 µL) in an NMR tube and sealed. The contents were heated to 110 °C for 24 h. <sup>1</sup>H NMR spectroscopy revealed isomerization to 1,3-cyclohexadiene (35% by NMR integration).

Reaction with Carbon Monoxide to Produce [Mo(tfd)<sub>2</sub>(dht)(CO)]:  $[Mo(tfd)_2(dht)_2]$  (2 mg, 2.77 µmol) was added to C<sub>6</sub>D<sub>6</sub> (400 µL) in an NMR tube along with 3,5-bis(trifluoromethyl)bromobenzene (ca. 5 µL) as an internal standard. Carbon monoxide gas was gently bubbled into the solution for a total of 4 h with occasional refilling of the solvent to make up for evaporation losses. The yellowishbrown solution turned bright orange, and a new complex was identified by  $^{19}\mathrm{F}$  NMR spectroscopy and integration {70–90% yield relative to [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>]}. <sup>1</sup>H NMR spectroscopy and integration showed an equal amount of free dht and bound dht on this complex {excluding dht bound to known [Mo(tfd)<sub>2</sub>(dht)<sub>2</sub>]}. The sample was degassed by freeze-pump-thaw cycling, and dht (300 µL of a 0.067 m solution) in  $C_6D_6$  (20 µmol) was added, followed by shaking. After 2 h, NMR integration revealed 85% [Mo(tfd)<sub>2</sub>-(dht)<sub>2</sub>] and 15% [Mo(tfd)<sub>2</sub>(dht)(CO)], which indicates that the equilibrium shifted back to the starting materials. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta = 2.66$  [m, 8 H, (CH<sub>2</sub>)×4], 4.60 [m, 4 H, (CH)×4] ppm. <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -54.92 [s, 12 F, (CF<sub>3</sub>)<sub>2</sub>×2] ppm.

Determination of  $K_{eq}$  (Preferred Binding of tht Over dht): A stock solution of dht in CDCl<sub>3</sub> was prepared by adding diallyl sulfide (200 µL ) to CDCl<sub>3</sub> (16 mL) and Grubb's catalyst (10 mg). After 24 h, the reaction was checked for completion by NMR spectroscopy, and the volatiles were purified by vacuum transfer. The concentration of the stock solution was approximately 0.097 m. The method used for the determination of the equilibrium constant is based on relative ratios (by NMR integration) and not on absolute amounts. [Mo(tfd)<sub>2</sub>(tht)<sub>2</sub>] (2 mg) was added to CDCl<sub>3</sub> (400 µL) in an NMR tube. The NMR spectra were recorded at 22 °C. After each spectrum, a small amount of dht in CDCl<sub>3</sub> was added. The ratios of the various species were determined by NMR integration: Mo-bound tht ("Mo–tht"), Mo-bound dht ("Mo–dht"), free dht, and free tht were independently observed and quantified by NMR

Table 3. Crystal data and structure refinement for  $[Mo(tfd)_2(dht)_2]$  and  $[Mo(tfd)_2(tht)_2]$ .

	[Mo(tfd) <sub>2</sub> (dht) <sub>2</sub> ]	[Mo(tfd) <sub>2</sub> (tht) <sub>2</sub> ]
Empirical formula	C <sub>16</sub> H <sub>12</sub> F <sub>12</sub> Mo <sub>1</sub> S <sub>6</sub>	C <sub>16</sub> H <sub>16</sub> F <sub>12</sub> Mo <sub>1</sub> S <sub>6</sub>
Formula mass	720.56	724.59
Crystal size [mm]	$0.08 \times 0.06 \times 0.02$	$0.24\!\times\!0.16\!\times\!0.10$
Crystal system	triclinic	monoclinic
Space group	PĪ	$P2_{1}/c$
a [Å]	8.3184(3)	12.0316(5)
<i>b</i> [Å]	12.1554(8)	25.0104(6)
<i>c</i> [Å]	12.9245(9)	8.4960(4)
a [°]	76.092(3)	90
β [°]	90.074(4)	109.275(1)
γ [°]	69.878(3)	90
V[Å <sup>3</sup> ]	1186.03(12)	2413.27(16)
Ζ	2	4
<i>T</i> [K]	150(2)	150(1)
λ [Å]	0.71073	0.71073
F(000)	708	1432
Data/restraints/ parameters	4826/0/317	5440/0/316
$D_{\rm calcd.} [\rm mgm^{-3}]$	2.018	1.994
$\mu [\mathrm{mm}^{-1}]$	1.181	1.161
Reflections (collected)	7732	13879
Reflections (unique)	4826	5440
GOF	1.164	1.041
$R1 \left[I > 2\sigma(I)\right]$	0.0553	0.0516
wR2 (all data9	0.1465	0.1358

integration. An excellent fit was obtained for the simple model Modht + tht  $\rightleftharpoons$  Mo-tht + dht, which demonstrates that the two labile sites at Mo have a very similar preference for binding tht vs. dht, i.e. no cooperativity is observed. The equilibrium constant (for the reaction as written, Mo-tht as the product of the reaction) is equal to ([Mo-tht]/[Mo-dht])([tht]/[dht])<sup>-1</sup>, and a straight line was indeed obtained from plotting the ratio [Mo-tht]/[Mo-dht] against the ratio [tht]/[dht] (Figure 5). The slope yields  $K_{eq} = 6.5(5)$ ; tht binds more strongly than dht by that factor. A similar experiment was performed with thiophene (NMR, 20 °C). No substitution was observed at any concentration including neat thiophene.

CCDC-762433 and CCDC-762434 for  $[Mo(tfd)_2(tht)_2]$  and  $[Mo(tfd)_2(dht)_2]$  (Table 3), respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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