Transition Metal Complexes with Sulfur Ligands, IV [1]

Synthesis and Reactions of Mo(IV) Complexes with the Tetradeutate Thioether-thiol Ligand 2,3,8,9-Dibenzo-1,4,7,10-tetrahiadiacene

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Molybdenum(IV) Sulfur Complexes, Synthesis, Reactions

Synthesis and characterization of non-oxo Mo(IV) complexes with the tetradeutate thioether-thiol ligand 2,3,8,9-dibenzo-1,4,7,10-tetrahiadiacene (dttd-H2) are reported. MoCl4(THF)2 reacts with dttd-H2 in THF at room temperature to give the paramagnetic (2.61 BM, 295 K) [Mo(dttd)Cl2]. The chlorine ligands in [Mo(dttd)Cl2] can be substituted by sulfur ligands yielding diamagnetic complexes as [Mo(dttd)(C6H4S2)]2 [6], [Mo(dttd)(SC6H4S)]2 [7] and [Mo(dttd)(SC6H4S)]2 [8]; with Na2S, NaHS or H2S, the di-^-sulfido bridged complex [(dttd)Mo(S)2Mo(dttd)] is obtained. The reduction of [Mo(dttd)Cl2] by various reducing agents in the presence of CO or NO yields labile carbonyl and nitrosyl species in solution. In contrast to [Mo(dttd)Cl2], the complexes with MoS8 chromophores showed no reactivity to CO or NO under reducing conditions.

1. Introduction

The occurrence of molybdenum in many redox enzymes, e.g. xanthine oxidase, sulfite reductase, nitrate reductase or nitrogenase, has stimulated the research on the coordination chemistry of molybdenum, particularly with a coordination sphere of sulfur [2]. In the case of nitrogenase, recent EXAFS data [3, 4] point to an all sulfur coordination sphere of the Mo centers. Much less is known about the oxidation state of the Mo centers in nitrogenase, however. The chemical reactivity points to low oxidation states, because CO blocks the N2 fixation completely. The difficulty to achieve complete CO substitution by other ligands in Mo(II) or Mo(0) complexes like [Mo(CO)3(dttd)] and [MMe4][Mo₂(CO)₆(C₆H₄S₂)₂] [5], prompted us to investigate the synthesis of Mo(IV) organosulfur complexes with the aim to test their ability of coordinating CO, N2 and other small molecules like NO or H2, under reducing conditions.

Non-oxo Mo(IV) sulfur complexes, especially with thioether, thiol or thioether-thiol ligands are relatively rare [2b, 2c]; examples are e.g. the pseudo octahedral [Mo(mes)₂], mes = (SC₆H₄SC₆H₄S)⁻ [6], or the tetrahedral [Mo(tert-C₆H₄S)₂] [7]. We have tried to obtain such complexes with the tetradeutate thioether-thiol ligand 2,3,8,9-dibenzo-1,4,7,10-tetrahiadiacene dttd-H2 [8], and o-benzenedithiol, 1,2-ethanedithiol, ethanethiol and C6H5SC6H5SC6H5H5, respectively, as coligands.

2. Results and Discussion

2.1. Synthesis and characterization of complexes

On reacting a suspension of MoCl4(THF)2 in THF with dttd-H2 according to eq. (1):

\[
\text{MoCl}_4(\text{THF})_2 + \text{dttd-H}_2 \xrightarrow{\text{THF}, 20^\circ\text{C}/3\text{h}} \text{MoCl}_4(\text{dttd})_2 \xrightarrow{+ 2 \text{HCl}} \text{MoCl}_4(\text{THF})_2 + \text{dttd-H}_2
\]

MoCl4(THF)2 dissolves and simultaneously precipitates from the reaction solution as dark violet microcrystals. They are paramagnetic (2.61 BM, 295 K, Faraday balance) and stable in air for a limited time. [Mo(dttd)Cl2] is slightly soluble in THF; in more polar solvents like DMSO or DMF one obtains intensely green solutions, probably due to dissociation.
Evaporating these solvents, [Mo(dttd)Cl₂] could not be regained, and only viscous residues were obtained. The FIR spectrum of [Mo(dttd)Cl₂] in nujol shows two strong ν(Mo-Cl) bands at 335 and 315 cm⁻¹ indicating a cis-position of the Cl ligands [9]; a band at 385 cm⁻¹ is assigned to ν(Mo-S) [10]. The UV-VIS spectrum of the complex shows high intensity absorptions at 13700, 20320, and 24570 cm⁻¹, probably due to S -> Mo charge transfer [6].

The chlorine ligands in [Mo(dttd)Cl₂] can be substituted by further sulfur ligands like o-C₆H₄S₂₂-, (SC₂H₄S)²⁻ and C₆H₅S⁻, respectively. According to eq. (2):

\[
[\text{Mo(dttd)Cl}_2] + \text{C}_6\text{H}_4\text{S}_2^{2-} \xrightarrow{\text{THF} \text{20}^\circ\text{C}} \quad [\text{Mo(dttd)}(\text{C}_6\text{H}_4\text{S}_2)] + 2\text{Cl}^{-}
\]

one obtains e.g. the benzenedithiolate complex. Analogously [Mo(dttd)(SC₂H₄S)] and [Mo(dttd)(SC₆H₅S)] are synthesised. All three complexes are dark green to greenish brown micro-crystalline diamagnetic solids. In the solid state the complexes are relatively stable in air, THF solutions, however, rapidly deposit dark colored products. The complexes are soluble in THF, but show only limited solubility in CH₂Cl₂ or acetone; they are insoluble in non-polar solvents. The ¹H NMR spectrum of [Mo(dttd)(C₆H₅S₂)] differs from the typical spectra of other dttd complexes as e.g. [Fe(dttd)(CO)₂] [11] with respect to the splitting of the proton signals. In the case of [Mo(dttd)(C₆H₅S₂)], one observes singlets of the aromatic as well as of the C₆H₄ protons at 7.3 and 3.45 ppm, respectively, which are only negligibly broadened. The low solubility of [Mo(dttd)(SC₂H₄S)] in CD₂Cl₂ prevented the registration of a well resolved ¹H NMR spectrum, but in the case of [Mo(dttd)(SC₆H₅S)] again the typical ¹H NMR pattern could be observed, with multiplets at 7.2 ppm (C₆H₄) and 3.2 ppm (C₆H₅); the SET protons yielded the usual triplet and quartet at 1.36 and 3.5 ppm, respectively.

The UV-VIS spectra of the complexes are listed in Table I. As in the case of [Mo(dttd)Cl₂], the intense absorptions might originate from S -> Mo charge transfer. The frequencies show relatively little variation, signalling that the organic substituents on the S atoms have little influence on the band positions and the electronic structure, respectively.

The chlorine ligands of [Mo(dttd)Cl₂] can be substituted also by sulfide, regardless if one uses Na₂S, NaHS or gaseous H₂S for the reaction with [Mo(dttd)Cl₂]. If one stirs, for instance, a THF suspension of [Mo(dttd)Cl₂] with solid Na₂S according to eq. (3):

\[
\text{[Mo(dttd)Cl₂] + Na₂S \rightarrow } \text{[Mo(dttd)(S₂)] + 2NaCl}
\]

The ¹H NMR spectrum of [Mo(dttd)(S₂)] differs from the typical spectra of other dttd complexes, with a triplet at 7.3 ppm and a quartet at 3.45 ppm, respectively. The UV-VIS spectra of the complexes are listed in Table I.

### Table I. Selected spectroscopic data.

<table>
<thead>
<tr>
<th>Complex</th>
<th>v_max [cm⁻¹]</th>
<th>1H NMR [ppm]</th>
<th>M⁺ mass spectrometrically</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. [Mo(dttd)Cl₂]</td>
<td>13700</td>
<td>paramagnetic</td>
<td>478</td>
</tr>
<tr>
<td>2. [Mo(dttd)(C₆H₄S₂)]</td>
<td>12655</td>
<td>7.3 (s)</td>
<td>547</td>
</tr>
<tr>
<td></td>
<td>17700</td>
<td>3.45 (s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21640</td>
<td>sh</td>
<td></td>
</tr>
<tr>
<td>3. [Mo(dttd)(SC₂H₄S)]</td>
<td>14180</td>
<td>~ 7.3 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17090</td>
<td>~ 3.1 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21970</td>
<td>~ 1.6 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25700</td>
<td>sh</td>
<td></td>
</tr>
<tr>
<td>4. [Mo(dttd)(SC₆H₅S)]</td>
<td>14080</td>
<td>7.2 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15030</td>
<td>3.2 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18180</td>
<td>3.5 (q)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20170</td>
<td>1.36 (t)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25700</td>
<td>sh</td>
<td></td>
</tr>
<tr>
<td>5. [(dttd)Mo(S)₂Mo(dttd)]</td>
<td>12980</td>
<td>7.3 (m)</td>
<td>876</td>
</tr>
<tr>
<td></td>
<td>15150</td>
<td>3.4 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17390</td>
<td>sh</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21000</td>
<td>sh</td>
<td></td>
</tr>
</tbody>
</table>

a In THF; b in CD₂Cl₂; s = singlet, m = multiplet, q = quartet, t = triplet, sh = shoulder.
2 [Mo(dttd)Cl₂] + 2 Na₂S → \[\text{THF} \atop 20 \degree C\] + 4 NaCl

\[
\text{Mo}
\begin{array}{c}
\text{S}
\end{array}
\begin{array}{c}
\text{S}
\end{array}
\begin{array}{c}
\text{Mo}
\end{array}
\begin{array}{c}
\text{S}
\end{array}
\begin{array}{c}
\text{S}
\end{array}
\]

A dark brown microcrystalline complex is obtained, the elemental analysis and spectroscopic data of which point to the binuclear complex with sulfide bridges shown in eq. (3). The complex is diamagnetic and shows the same solubility as the complexes mentioned above. In the \(^1\)H NMR spectrum (CD₂Cl₂), the ligand protons appear as multiplets centered at 7.3 ppm (C₆H₄) and 3.4 ppm (C₂H₄). The field desorption (FD) mass spectrum shows the molecular ion at \(m/e = 876\), [(dttd)Mo(S)₂Mo(dttd)] for \(^{98}\text{Mo} = 876\); besides the \(M^+\) ion only two fragment ions at \(m/e = 844\) and 812 can be registered. They result from the successive loss of the two sulfide bridges indicating the formation of dinuclear species like [Mo(dttd)]₂. A medium band at 435 cm\(^{-1}\) and a weak band at 344 cm\(^{-1}\) in the FIR spectrum of [Mo₂S₂(dttd)]₂ can be assigned to the four-membered Mo₂S₂ ring. This is in agreement with a recent assignment made for pentacoordinate di-µ-sulfido Mo(V)dithiocarbamato complexes like [Mo₂S₄(R₂dtc)] [12]. Similarly the weak band at 376 cm\(^{-1}\) is assigned to \(\nu\)(Mo–S) stretch. The UV–VIS spectrum of the complex again shows the typical high intensity absorption bands at 12980, 15150, 17390(sh) and 21000(sh) cm\(^{-1}\).

Attempts to synthesise Mo(IV) complexes with hexadentate sulfur ligands by template reactions of [Mo(dttd)(C₆H₄S₂)] as well as of [Mo(dttd)(SC₂H₄S)] with 1,2-dibromoethane failed.

2.2 Reductive carbonylation and nitrosylation reactions

Reductions of [Mo(dttd)Cl₂] were carried out in THF at room temperature using different reducers as e.g. Mg, LiBEt₃H and NaBH₄.

Adding Mg powder to a suspension of [Mo(dttd)Cl₂] in THF at room temperature under \(N₂\) resulted in a change of color from dark violet to dark brown, but no reaction with \(N₂\) could be observed even after 16h. Bubbling CO through this solution resulted in a dirty green solution, showing two strong \(\nu\)(CO) bands in the IR spectrum at 2030 and 1950 cm\(^{-1}\) (Fig. 1 a).

Fig. 1. IR spectra in THF of a) Mo(dttd)Cl₂ + Mg + CO, b) Mo(dttd)Cl₂ + 2 LiBEt₃H + CO, c) Mo(dttd)Cl₂ + 10 LiBEt₃H + CO, d) Mo(dttd)Cl₂ + NaBH₄ + CO, e) Mo(dttd)Cl₂ + LiBEt₃H + NO.
These bands indicate the formation of \([\text{Mo}(\text{dttd})(\text{CO})_3]\) according to reaction (4):

\[
\begin{align*}
\text{[Mo(dttdd)Cl]_2} & \xrightarrow{\text{Mg/THF} \quad 16 \text{ h}, \text{ CO}} \\
\text{[Mo(dttdd)(CO)H]_3} & + \text{by-products}
\end{align*}
\]

(4)

\([\text{Mo(dttdd)(CO)}_3]\) has been independently obtained recently by reaction (5) [5]:

\[
\begin{align*}
\text{Mo(CO)}_3\text{Cl}_2 & + \text{dttd-H} \xrightarrow{\text{EtOH} \quad \frac{\text{RT}}{\text{RT}}} \\
\text{[Mo(dttdd)(CO)}_3 & + \text{CO} + 2 \text{ HCl}
\end{align*}
\]

The reduction of \([\text{Mo(dttdd)Cl}]_2\) with \text{LiBEt}_2\text{H} and subsequent coordination of CO led to different results depending on the amount of \text{LiBEt}_2\text{H} used. If one reacts \([\text{Mo(dttdd)Cl}]_2\) with 2 equivalents of \text{LiBEt}_2\text{H} in the presence of CO, a dark purple solution is obtained, showing in the IR spectrum two \(\nu(\text{CO})\) bands at 1970 and 1910 cm\(^{-1}\) (Fig. 2b). This points to a cis-dicarbonyl species, possibly \([\text{Mo(dttdd)}(\text{CO})_2]^{3-}\) or \([\text{Mo(dttdd)}(\text{H})_3(\text{CO})_3]\), which, however, could not be crystallized. The evaporation of the solution led to complete loss of CO preventing further identification of the compounds.

Taking 10 equivalents of \text{LiBEt}_2\text{H} for reduction in the presence of CO, one obtains a deep green solution, which may contain an even lower oxidation state of Mo. Again two \(\nu(\text{CO})\) bands appear in the IR spectrum, at 1910 and 1800 cm\(^{-1}\) (Fig. 2c). This species, too, is so labile with respect to loss of CO, that it could not be isolated as a solid and identified.

Reducing \([\text{Mo(dttdd)Cl}]_2\) with \text{NaBH}_4 in the presence of CO, yields still another carbonyl complex or a mixture of carbonyl complexes with \(\nu(\text{CO})\) bands at 2000, 1920, 1895, 1845, 1800 and 1745 cm\(^{-1}\) (Fig. 1a); again all CO is lost on attempts to isolate complexes in the solid state.

Only preliminary experiments were carried out with NO. A mixture of \([\text{Mo(dttdd)Cl}]_2\) and 4 equivalents of \text{LiBEt}_2\text{H} in THF on reaction with NO yields a deep purple solution, which has two equally strong \(\nu(\text{NO})\) bands at 1720 and 1600 cm\(^{-1}\), pointing to a dinitrosyl complex. This species too is very unstable and was not investigated further.

In contrast to the behaviour of \([\text{Mo(dttdd)Cl}]_2\), the complexes \([\text{Mo(dttdd)}(\text{C}_6\text{H}_4\text{S}_2)]\), \([\text{Mo(dttdd)}(\text{SC}_2\text{H}_4\text{S})]\) as well as \([\text{Mo(dttdd)}(\text{SC}_3\text{H}_2\text{S})]\) showed no uptake of CO of NO under reducing conditions. This could be either due to a more difficult reduction of these \(\text{MoS}_4\) centers, or due to the fact that they are coordinatively saturated. However, when \([\text{Mo(dttdd)Cl}]_2\) is reacted with \text{LiBEt}_2\text{H} and CO in the presence of the thioether ligand \(\text{C}_6\text{H}_5\text{SC}_2\text{H}_4\text{SC}_6\text{H}_5\), in THF at room temperature, a deep blue solution was obtained, which had \(\nu(\text{CO})\) bands in the IR spectrum at 2000, 1975, 1900, 1800 and 1815 cm\(^{-1}\), indicating definitely the uptake of CO by the reduced species. Again the attempts to isolate the complex as a solid resulted in a carbonyl-free residue.

3. Experimental Part

All reactions and operations were carried out under nitrogen using the Schlenk technique. Solvents were dried and distilled under nitrogen before use. IR spectra (CaF\(_2\) cuvettes or KBr discs) were recorded on a Zeiss IMR 16 Infrared Spectrometer; F\(_2\)IR spectra (in nujol or polyethylene dises) were registered on a Beckman FT\(_2\)IR 720 Spectrometer. The solvent bands were compensated. Mass spectra were recorded on a Varian 212 MAT mass spectrometer, and \(^1\)H–NMR spectra on a Jeol PXM 60 MHz spectrometer.

2,3,8,9-dibenzo-1,4,7,10-tetraathiadecane, o-benzenedithiol, 1,2-di(phenylthio)ethane, MoCl\(_4\)(CH\(_3\)CN)\(_2\) and MoCl\(_4\)(THF)\(_2\) were prepared according to the literature. 1,2-ethanedithiol and ethanethiol (both Aldrich) were distilled under reduced pressure and stored under nitrogen. NaBH\(_4\), LiBEt\(_3\)H (1 molar in THF), NaS and NaHS (both anhydrous) were purchased from Alfa.

3.1. Synthesis of complexes

3.1.1. \([\text{Mo(dttdd)Cl}]_2\)

3.85 g (12 mmol) MoCl\(_4\)(CH\(_3\)CN)\(_2\) and 20 ml THF were stirred for 2 h. To the resulting suspension of MoCl\(_4\)(THF)\(_2\), 3.73 g (12 mmol) dttd-H\(_2\) in 15 ml THF were added with stirring. Further stirring for 3 h yielded a fine lustrous dark violet microcrystalline precipitate, which was filtered, washed with 2 \(\times\) 20 ml of THF, 2 \(\times\) 20 ml of ether, and dried in high vacuum for 10 h. Yield: 4.5 g (82%).

\[\text{Analysis for C}_{14}\text{H}_{12}\text{Cl}_2\text{S}_4\text{Mo} (475.31)}
\]

\[
\begin{align*}
\text{Found} & \quad \text{C} 35.65 \quad \text{H} 2.57, \\
\text{Caled} & \quad \text{C} 35.38 \quad \text{H} 2.52.
\end{align*}
\]

M\(^+\): 478 (Calc. for 98\% Mo = 478).

3.1.2. \([\text{Mo(dttdd)}(\text{C}_6\text{H}_4\text{S}_2)]\)

0.78 ml (1.26 mmol) of \(n\)-butyllithium in hexane were added dropwise to a solution of 0.09 g (0.63 mmol) o-benzenedithiol in 5 ml THF at 0 °C. The resulting clear solution was added dropwise under stirring to a suspension of 0.3 g (0.63 mmol)
Mo(dttd)Cl₂ in 20 ml THF. Immediately the initial violet color of the solution changed to red brown, and Mo(dttd)Cl₂ dissolved completely. After stirring for 4 h the solution was filtered and evaporated to dryness in vacuum. The residue was washed with 3 × 20 ml of ether to remove any organic material and extracted with 2 × 20 ml CH₂Cl₂. The CH₂Cl₂ solution was filtered through ca. 10 g silica gel as filter help, reduced to ca. 7 ml and kept overnight at —78 °C. The dark brownish green microcrystalline precipitate was separated, washed with 2 × 10 ml of ether, and recrystallised from CH₂Cl₂ at 20° —78 °C. Yield: 150 mg (45%).

Analysis for C₁₈H₂₈S₆Mo (544.67)

Found C 44.70 H 3.09,
Caled C 44.10 H 2.96.
M⁺: 547 (Calc. for ⁹⁸Mo = 547).

3.1.3. [Mo(dttd)(SC₂H₄S)]

A solution of 0.1 g (1.06 mmol) 1,2-ethanediethiol and 0.05 g (2.16 mmol) Na in 5 ml methanol was added dropwise with stirring to a suspension of 0.5 g (1.05 mmol) Mo(dttd)Cl₂ in 30 ml THF. Mo(dttd)Cl₂ dissolved completely and the initial violet color changed to dark red brown. After stirring for 4 h the solution was filtered and evaporated to dryness in vacuum. The residue was washed with 3 × 20 ml ether to remove organic impurities and extracted with 2 × 25 ml CH₂Cl₂. The CH₂Cl₂ solution was filtered through a cellulose pad, concentrated to ca. 10 ml and kept at —78 °C for 2 d. The resulting dark greenish brown microcrystalline product was separated, washed with 2 × 20 ml ether and dried in high vacuum for 12 h. Yield: 300 mg (57%).

Analysis for C₁₈H₂₈S₆Mo (496.58)

Found C 38.60 H 3.25,
Caled C 38.65 H 3.24.

3.1.4. [Mo(dttd)(SC₂H₅)₂]

2.3 ml (3.57 mmol) n-butyllithium (in hexane) were added to 0.13 ml (1.78 mmol) C₅H₅S in 5 ml THF at —30 °C, when a voluminous white precipitate was formed, which was redissolved by adding 2 ml of methanol. This clear solution was added dropwise under stirring to a suspension of 0.425 g (0.89 mmol) Mo(dttd)Cl₂ in 25 ml THF. The Ma(dttd)Cl₂ dissolved and the color of the solution was dark orange red. After stirring for 5 h the solution was filtered and evaporated to dryness in vacuum. The residue was washed with 3 × 20 ml ether and extracted with 40 ml CH₂Cl₂. The CH₂Cl₂ solution was filtered through a cellulose pad and concentrated to ca. 15 ml. After adding 20 ml of petrol ether (60–80 °C), the mixture was kept at —78 °C for two days yielding a dark brown microcrystalline precipitate which was collected, washed with ether and dried in high vacuum for 12 h. Yield: 200 mg (78%).

Analysis for C₁₈H₂₈S₆Mo (526.65)

Found C 41.11 H 4.22,
Caled C 41.04 H 4.20.

3.1.5. [(dttd)Mo(S)₂Mo(dttd)]

0.07 g (0.89 mmol) Na₂S (anhydrous) in solid form were added to a suspension of 0.42 g (0.88 mmol) Mo(dttd)Cl₂ in 30 ml THF. The mixture was stirred for 5 h, during which time Mo(dttd)Cl₂ dissolved. The resulting brown solution was filtered through a cellulose pad and evaporated to dryness in vacuum. The residue was washed with 3 × 20 ml ether and extracted with 2 × 25 ml CH₂Cl₂. The CH₂Cl₂ extract was filtered, concentrated to ca. 10 ml and kept at —78 °C for two days. The resulting dark brown microcrystalline product was collected, washed with ether and dried in high vacuum for 10 h. Yield: 300 mg (78%).

Analysis for C₁₈H₂₈S₆Mo₂ (872.95)

Found C 38.70 H 2.82 S 36.60,
Caled C 38.60 H 2.80 S 36.70.
M⁺: 876 (Calc. ⁹⁸Mo = 876).

The same complex can also be prepared by reaction of [Mo(dttd)Cl₂] with NaHS or by passing gaseous H₂S through a suspension of Mo(dttd)Cl₂ in THF.

3.2. Reductive carbonylation and nitrosylation reactions of [Mo(dttd)Cl₂]

3.2.1. Reduction with Mg

A suspension of 0.2 g (0.42 mmol) Mo(dttd)Cl₂ and 0.25 g (10.2 mmol) Mg powder in 20 ml THF was stirred under N₂ for 16 h. After bubbling CO through the dark brown solution for 1 h, v(CO) bands were detected IR-spectroscopically; after 4 h the color of the solution had changed to dirty green and its IR spectrum showed two strong v(CO) bands at 1930 and 1850 cm⁻¹ indicating the formation of [Mo(dttd)(CO)]₃.

3.2.2. Reduction with LiBEt₃H

a) On addition of 1.3 ml (1.3 mmol) LiBEt₃H to a stirred suspension of 0.3 g (0.63 mmol) Mo(dttd)Cl₂ in 20 ml THF, Mo(dttd)Cl₂ dissolved giving a dark red brown solution which was stirred for 4 h. At this stage 200 ml gaseous CO were introduced into the Schlenk tube. Within 10 min the initial red brown color of the solution started changing to purple, and v(CO) bands were detected IR-spectroscopically; after 1 h a deep purple solution resulted showing two v(CO) bands at 1970 and 1910 cm⁻¹. Attempts to isolate the complex resulted in complete loss of CO.
b) In another reaction, addition of 8.4 ml (8.4 mmol) LiBEt₃H to a suspension of 0.4 g (0.84 mmol) Mo(dttd)Cl₂ in 30 ml THF yielded a clear dark red brown solution. After stirring for 4 h, CO was bubbled through the solution, whereupon a rapid reaction occurred in ca. 5 min. The color of the solution changed to deep green and ν(CO) bands at 1910 and 1800 cm⁻¹ were detected after 15 min; after 3.5 h no further increase of the ν(CO) bands (Fig. 2) was observed. Attempts to isolate the complex in solid state resulted in complete loss of CO.

3.2.3. Reduction with NaBH₄

Addition of 0.41 g (10.8 mmol) NaBH₄ to a stirred suspension of 0.4 g (0.84 mmol) Mo(dttd)Cl₂ in 35 ml THF yielded a clear orange brown solution. After stirring for 4 h, CO was bubbled through the solution causing a rapid color change to green; after 4 h the solution had become deep green showing the IR spectrum of Fig. 1d. Here again, the attempts to isolate the complex resulted in complete loss of CO.

3.2.4. Reduction with LiBEt₃H and reaction with NO

Addition of 3.8 ml (3.8 mmol) LiBEt₃H to a suspension of 0.45 g (0.94 mmol) Mo(dttd)Cl₂ in 25 ml THF gave again a clear red brown solution. After stirring for 4 h, 200 ml NO gas were introduced into the Schlenk tube. The solution turned rapidly to purple; after stirring for a total of 0.5 h, the deep purple solution showed two strong ν(NO) bands at 1720 and 1605 cm⁻¹. This species is very unstable and was not further characterized.

3.2.5. Reaction of Mo(dttd)Cl₂ with C₆H₅SC₂H₄SC₂H₅, LiBEt₃H and CO

0.33 g (1.32 mmol) C₆H₅SC₂H₄SC₂H₅ in 10 ml THF was added to a suspension of 0.63 g (1.32 mmol) Mo(dttd)Cl₂ in 40 ml THF. After stirring for 1 h, 5.3 ml (5.3 mmol) LiBEt₃H were added resulting in complete dissolution of Mo(dttd)Cl₂ and a clear dark red brown solution. After stirring for 3 h, CO was bubbled through the solution for 3.5 h; a rapid color change to blue violet was observed and ν(CO) bands could be detected after 0.5 h. After 3.5 h the solution had a deep blue violet color and showed ν(CO) bands in the IR spectrum at 2000, 1975, 1900, 1860 and 1815 cm⁻¹. Attempts to isolate the complex again resulted in a carbonyl free product.

In another experiment an equivalent quantity of CO was used. However, there was no change in the number or the position of the ν(CO) bands in the IR spectrum.

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