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Supporting Information (16 pages)

**The Direct Synthesis of Isothiocyanates from Isonitriles by  
Molybdenum-Catalyzed Sulfur Transfer with Elemental Sulfur**

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## Experimental Section

**General Remarks.** All solvents were dried and distilled prior to use.<sup>S1</sup> Acetone was degassed by three freeze-pump-thaw cycles. All reactions with catalyst **2** and complex **3** were carried out under an argon-gas atmosphere. The work-up was done under aerobic conditions.

**Caution:** Isonitriles are very toxic and a well ventilated hood is required; skin contact should be strictly avoided. For flash chromatography, Woelm silica gel (0.032–0.063 mm) was used. TLC detection was performed with Polygram SIL/UV 254 plates from Macherey-Nagel. The isonitriles spots were visualized by means of a ninhydrin solution. –The boiling points of the bulb-to-bulb distillations refer to oven temperatures.– Melting points are uncorrected – <sup>1</sup>H-NMR (200 or 250 MHz) and <sup>13</sup>C-NMR (50 MHz or 63 MHz) spectra were run in CDCl<sub>3</sub> solution, if not otherwise stated; the chemical shifts are expressed in  $\delta$  values relative to tetramethylsilane, and the multiplicities were determined by DEPT spectra. – IR spectra were measured as KBr plates and absorptions are expressed in  $\tilde{\nu}$  values. – Elemental analyses were carried out by the Microanalytical Division of the Institut für Anorganische Chemie, Universität Würzburg. –

**Materials.** Sodium molybdate dihydrate, isocyanocyclohexane (**4b**), 2-isocyano-2,4,4-trimethylpentane (**4c**), 2-isocyano-2-methylpropane (**4d**), isocyanomethylbenzene (**4f**), 2-isocyano-1,3-dimethyl-benzene (**4h**), sodium diethyldithiocarbamate trihydrate, 3,3-dimethyloxetane, mesitaldehyde and cinnamyl chloride were purchased. Isocyanomethane was a generous gift from Prof. H. Quast. The molybdenum complexes **1**<sup>S2</sup>, **2**<sup>S3</sup>, and **3**<sup>S4</sup> and the isonitriles (3-isocyano-2,2-dimethylpropoxy)trimethylsilane (**4e**)<sup>S5</sup>, (*E*)-(3-isocyano-1-propenyl)benzene (**4g**)<sup>S6</sup>, (*E*)-2-(2-isocyanoethenyl)-1,3,5-trimethyl-benzene (**4j**)<sup>S7</sup>, 1-isocyanocyclopentanol acetate (**4m**)<sup>S8</sup>, (1-isocyanoethenyl)-benzene (**4n**)<sup>S9</sup> were prepared as described in the literature. 1-Isocyanooctane (**4a**)<sup>S10</sup>, 1-isocyanonaphthalene (**4i**)<sup>S11</sup> and ethyl isocyanoacetate (**4k**)<sup>S12</sup> were prepared according to literature<sup>S13</sup>.

**3-Isocyano-2,2-dimethyl-1-propanol (4l):** 5.32 g (28.7 mmol) of isonitrile **4e** were dissolved in 80 mL of dry methanol, 2.13 g (57.4 mmol) of ammonium fluoride were added, and the solution stirred for 20 h at 20–25 °C. The methanol was removed (40 °C/20 mbar) and from the residue the isonitrile **4l** [2.53 g (78%)] was obtained as a colorless oil after distillation (b.p. 120 °C/10 mbar). <sup>1</sup>H NMR (200 MHz): 3.45 (t, <sup>2</sup>J = 3.91 Hz, 2H, CH<sub>2</sub>), 3.31 (t, <sup>4</sup>J = 1.89 Hz, 2H, CH<sub>2</sub>), 1.50 (br. s, 1H, OH), 1.00 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (50 MHz): 156.2 (tt, <sup>1</sup>J = 2.86 Hz), 68.0 (t), 49.1 (tt, <sup>1</sup>J = 6.65 Hz), 36.0 (s), 21.7 (q). IR (neat): 3427, 2967, 2877, 2148, 1639, 1475, 1052, 998, 943. Anal. Calcd. for C<sub>6</sub>H<sub>11</sub>NO (113.2) C, 63.69; H, 9.80; N, 12.38; found C, 63.20; H, 10.00; N, 12.10.

#### **General Catalytic Procedure for the Preparation of the Isothiocyanates **5** by the Molybdenum Oxo Complex **2** with Elemental Sulfur**

In a NMR tube were placed 2.50–3.00 mmol of isonitrile **4**, 10.2–12.3 mg (0.025–0.030 mmol) of catalyst **2** and 160–192 mg (5.00–6.00 mmol) of elemental sulfur in 1.0 mL acetone. The tube was sealed by means of a rubber stopper and *Parafilm* and heated in an oil bath at 56 °C for 72 h. The contents were diluted with 10.0 mL of petroleum ether (30–50 °C), and the suspended material removed by filtration. The solvent was evaporated (40 °C/200 mbar) and the dark oily residue was purified by bulb-to-bulb distillation at an oil-pump vacuum.

**1-Isothiocyanatooctane (5a):**<sup>S14</sup> Colorless oil [462 mg (93%)], b.p. 120 °C / 7 mbar (lit.<sup>S14</sup> 123 °C / 12 mbar). <sup>1</sup>H NMR (250 MHz): 3.50 (t, <sup>3</sup>J = 6.55 Hz, 2H, CH<sub>2</sub>), 1.60–1.78 (m, 2H, CH<sub>2</sub>), 1.48–1.18 (m, 10H, CH<sub>2</sub>), 0.95–0.80 (t, <sup>3</sup>J = 6.72 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (63 MHz): 129.5 (s), 45.0 (t), 31.6 (t), 29.9 (t), 28.9 (t), 28.6 (t), 26.4 (t), 22.5 (t), 13.9 (q).

**Isothiocyanatocyclohexane (5b):**<sup>S15</sup> Colorless oil [346 mg (92%)], b. p. 140 °C / 45 mbar (lit.<sup>15</sup> 117–118 / 13.3 mbar). <sup>1</sup>H NMR (250 MHz): 3.71–3.62 (m, 1H, CH), 2.00–1.80 (m, 2H, CH<sub>2</sub>), 1.79–1.54 (m, 4H, CH<sub>2</sub>), 1.54–1.04 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (63 MHz): 129.6 (s), 55.3 (d), 33.1 (t), 25.0 (t), 23.1 (t).

**2-Isothiocyanato-2,4,4-trimethylpentane (5c):**<sup>S16</sup> Colorless oil [375 mg (88%)], b.p. 110 °C / 20 mbar (lit.<sup>S16</sup> 91 °C / 19 mbar). <sup>1</sup>H NMR (250 MHz): 1.51 (s, 2H, CH<sub>2</sub>), 1.40 (s, 6H, CH<sub>3</sub>), 0.98 (s, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (63 MHz): 129.3 (s), 60.4 (s), 54.1 (t), 31.3 (q), 31.2 (s), 30.8 (q).

**2-Isothiocyanato-2-methylpropane (5d):**<sup>S17</sup> Colorless oil [276 mg (80%)], b.p. 35 °C / 13 mbar (lit.<sup>S17</sup> 55 °C / 47 mbar), R<sub>f</sub> (silica gel, 5:1 petroleum ether/dichloromethane): 0.50. <sup>1</sup>H NMR (250 MHz): 1.42 (s, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (63 MHz): 129.4 (s), 58.3 (s), 30.7 (q).

**3-Isothiocyanato-2,2-dimethyl-propoxy)-trimethylsilane (5e):** Colorless oil [498 mg (78%)], b.p. 90 °C / 8 mbar. <sup>1</sup>H NMR (250 MHz): 3.34 (s, 2H, CH<sub>2</sub>), 3.28 (s, 2H, CH<sub>2</sub>), 0.91 (s, 6H, CH<sub>3</sub>), 0.08 (s, 9H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (63 MHz): 129.5 (s), 67.8 (t), 51.9 (t), 37.4 (s), 21.6 (q), –1.2 (q). IR (neat): 3853, 3742, 2959, 2882, 2357, 2186, 2102, 1688, 1517, 1458, 1254, 1096, 843. Anal. Calcd. for C<sub>9</sub>H<sub>19</sub>NOSSi (217.4) C, 49.72; H, 8.81; N, 6.44; S, 14.75; found C, 49.81; H, 8.59; N, 6.28; S, 14.67.

**Isothiocyanatomethylbenzene (5f):**<sup>S18</sup> Colorless oil [268 mg (67%)], b.p. 170 °C / 13 mbar (lit.<sup>S18</sup> 82–85 °C / 0.8 mbar). <sup>1</sup>H NMR (250 MHz): 7.30–7.50 (m, 5H), 4.68 (s, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (63 MHz): 133.9 (s), 131.6 (s), 128.6 (d), 128.0 (d), 126.5 (d), 48.3 (t).

**(E)-(3-Isothiocyanatopropenyl)benzene (5g):**<sup>S14</sup> Colorless oil [356 mg (68%)], b.p. 150 °C / 0.8 mbar (lit.<sup>S14</sup> 159 °C / 13 mbar). <sup>1</sup>H NMR: 7.10–7.37 (m, 5H), 6.67 (dt, <sup>3</sup>J = 15.60 Hz, <sup>4</sup>J = 1.53 Hz, 1H), 6.17 (dt, <sup>3</sup>J = 15.60 Hz, <sup>3</sup>J = 5.50 Hz, 1H), 4.31 (dd, <sup>3</sup>J = 5.50 Hz, <sup>4</sup>J = 1.53 Hz, 2H). <sup>13</sup>C NMR (63 MHz): 135.6 (s), 133.1 (d), 132.4 (s), 128.7 (d), 128.3 (d), 126.6 (d), 121.3 (d), 46.8 (t).

**2-Isothiocyanato-1,3-dimethylbenzene (5h):**<sup>S19</sup> Colorless oil [446 mg (91%)], b.p. 120 °C / 20 mbar (lit.<sup>S19</sup> 119–121 / 16 mbar). <sup>1</sup>H NMR (250 MHz): 7.14–7.00 (m, 3H), 2.38 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (63 MHz): 135.0 (s), 129.5 (s), 127.9 (d), 126.9 (d), 18.6 (q).

**1-Isothiocyanatonaphthalene (5i):**<sup>S20</sup> b.p. 160 °C / 0.08 mbar, Colorless needles [350 mg (68%)], m.p. 53–54 °C (lit.<sup>S20</sup> m.p. 54–55 °C). <sup>1</sup>H NMR (250 MHz): 8.04–7.95 (m, 1H), 7.80–7.72 (m, 1H), 7.70–7.61 (m, 1H), 7.55–7.40 (m, 2H), 7.34–7.27 (m, 2H). <sup>13</sup>C NMR (63 MHz): 136.0 (s), 133.9 (s), 129.2 (2xs), 128.4 (d), 127.6 (d), 127.3 (d), 127.0 (d), 125.3 (d), 123.4 (d), 122.7 (d).

### **General Catalytic Procedure for the Preparation of Isothiocyanates 5 by the Molybdenum Oxo Complex 2 with Propene Episulfide**

Analogous to the general procedure for elemental sulfur (see above) 0.573–3.00 mmol of isonitrile **4**, 11.7–61.3 mg (0.025–0.030 mmol) of catalyst **2**, and 90.0–470 µL (1.15–6.00 mmol) of propene episulfide were dissolved in 1.0 mL dichloromethane and allowed to react at 20–25 °C for 72 h. After work-up as above, the dark oily residue was purified by silica gel chromatography for **5j**, and **5m** or by bulb-to-bulb distillation at an oil-pump vacuum for **5k** and **5l**.

**(E)-2-(2-Isothiocyanatoethenyl)-1,3,5-trimethylbenzene (5j):** Colorless needles [94.7 mg (81%)], b.p. 120 °C / 0.15 mbar, m.p. 55–56 °C, R<sub>f</sub> (silica gel, petroleum ether): 0.40. <sup>1</sup>H NMR (250 MHz): 6.88 (s, 2H), 6.72 (d, <sup>3</sup>J = 14.18 Hz, 1H), 6.14 (d, <sup>3</sup>J = 14.18 Hz, 1H), 2.28 (s, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (63 MHz): 138.1 (s), 136.7 (3xs), 130.0 (d), 129.6 (s), 129.3 (d), 119.1 (d), 20.7 (2xq), 20.6 (q). IR: 2915, 2133, 1606, 1442, 1289, 1031, 947, 856. Anal. Calcd. for C<sub>12</sub>H<sub>13</sub>NS (203.3) C, 70.90; H, 6.45; N, 6.85; S, 15.77; found C, 71.15; H, 6.54; N, 6.87; S, 15.61.

**Ethyl Isothiocyanatoacetate (5k):**<sup>S21</sup> Colorless liquid [380 mg (87%)], b.p. 80 °C / 0.27 mbar (lit.<sup>S21</sup> 104–106 °C / 9 mbar). <sup>1</sup>H NMR (250 MHz): 4.27 (q, <sup>3</sup>J = 7.02 Hz, 2H, CH<sub>2</sub>), 4.21 (s, 2H, CH<sub>2</sub>), 1.31 (t, <sup>3</sup>J = 7.02 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (63 MHz): 166.1 (s), 138.3 (s), 62.6 (t), 46.4 (t), 14.1 (q).

**3-Isothiocyanato-2,2-dimethyl-1-propanol (5l):**<sup>S22</sup> Colorless liquid [376 mg (81%)], b. p. 120 °C / 0.4 mbar (lit.<sup>S22</sup> no b.p.). <sup>1</sup>H NMR (200 MHz): 3.42 (s, 2H, CH<sub>2</sub>), 3.41 (s, 2H, CH<sub>2</sub>), 1.86 (br. s, 1H, OH), 0.97 (s, 6H, 2×CH<sub>3</sub>). <sup>13</sup>C NMR (50 MHz): 130.0 (s), 68.2 (s), 51.9 (t), 37.4 (s), 21.5 (q).

**1-Isothiocyanatocyclopentanol acetate (5m):** Colorless liquid [505 mg (89%)], R<sub>f</sub> (silica gel, 4:1 petroleum ether/diethyl ether): 0.41. <sup>1</sup>H NMR (250 MHz): 2.40–2.24 (m, 2H, CH<sub>2</sub>), 2.20–2.07 (m, 2H, CH<sub>2</sub>), 2.05 (s, 3H, CH<sub>3</sub>), 1.86–1.71 (m, 4H, 2×CH<sub>2</sub>). <sup>13</sup>C NMR (63 MHz): 168.8 (s), 138.4 (s), 96.8 (s), 40.2 (t), 22.4 (t), 21.4 (q). IR (neat): 3490, 2965, 2879, 2037, 1756, 1231, 1180, 1086, 1016. Anal. Calcd. for C<sub>8</sub>H<sub>11</sub>NO<sub>2</sub>S (185.2) C, 51.87; H, 5.99; N, 7.56; S, 17.31; found C, 52.00; H, 6.07; N, 7.43; S, 17.61.

### General Procedure for the Stoichiometric Sulfuration of the Isonitrile 4b by the Molybdenum Oxo Disulfur Complex 3

Analogous to the general catalytic procedure for elemental sulfur (see above), 27.5 μL (0.224 mmol) of isocyanocyclohexane (**4b**) was added to 55.6 mg (0.118 mmol) of the disulfur complex **3** in 0.5 mL deuteroacetone. The reaction mixture was heated at 56 °C for 150 min. After cooling to 20–25 °C, the contents were directly subjected to silica-gel chromatography and eluted with petroleum ether (30–50 °C), to afford a colorless oil [22.0 mg (70% based on complex **3**)], b.p. 140 °C / 45 mbar (lit.<sup>S15</sup> 117–118 / 13.3 mbar).

## UV/VIS and FT-IR Spectroscopy of a Mixture of the Molybdenum Oxo Complex **2** and Isonitriles **4**

### General Procedure for the UV/VIS-Spectral Experiments

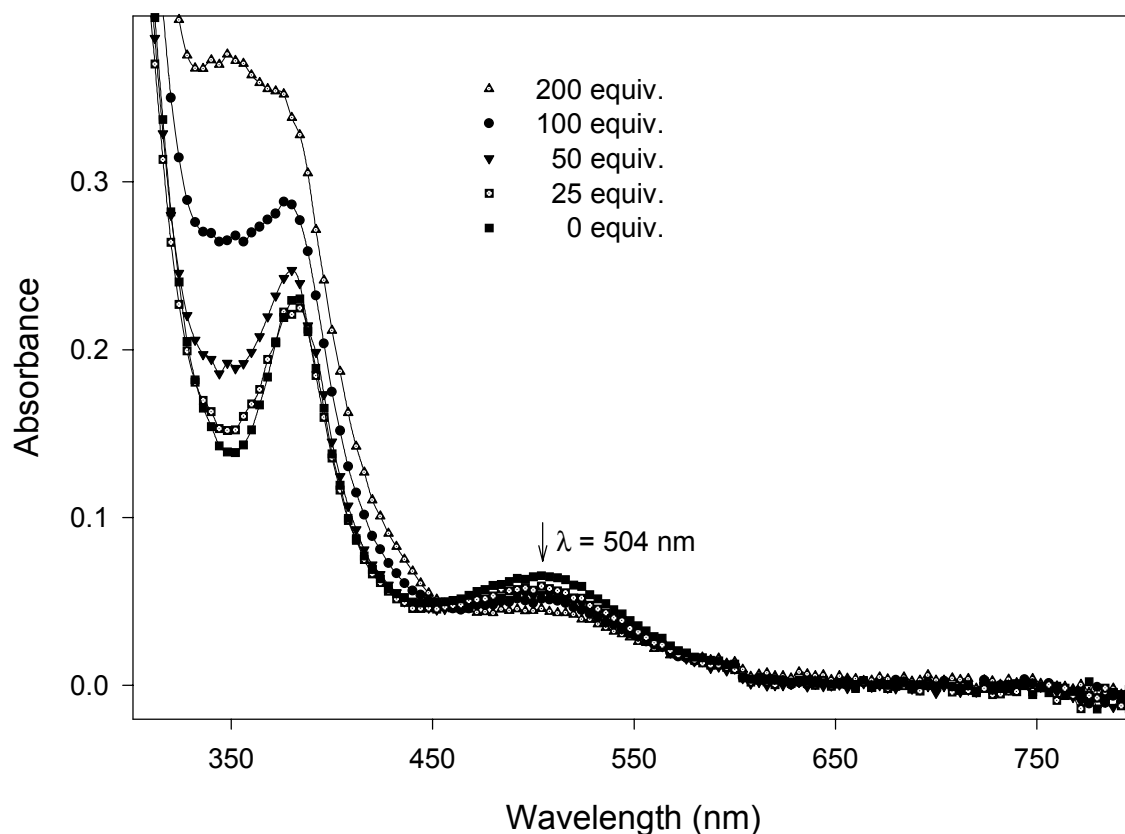
All operations were carried out in a glove box. A stock solution of complex **2** (Sol A) and of isonitrile **4** (Sol B) were prepared in deaerated dichloromethane. Into each of five 2-mL calibrated flasks were placed by means of an Eppendorf pipette 1.00 mL of Sol A and an aliquot of Sol B, as specified below and filled up to the 2-mL calibration mark with dichloromethane. After vigorous agitation for 2 min, ca. 1.5 mL of each sample was transferred to an UV Quartz cuvette (38 × 10 × 10 mm) and sealed with a Teflon stopper. The cuvette was removed from the glove box and the UV-Vis absorption spectra were immediately recorded (Figures S1 and S2).

**Isonitrile 4d:** For the preparation of the samples, aliquots of 0, 200, 220, 240, 260, 280, 300 and 1000 µL of Sol B (200 mM) were added to 1000 µL of Sol A (1.98 mM), which correspond to 0, 20, 22, 24, 26, 28, 30 and 100 equiv. of isonitrile **4d** relative to complex **2**.

**Isonitrile 4h:** For the preparation of the samples, aliquots of 0, 50, 100, 200 and 400 µL of Sol B (100 mM) were added to 1000 µL of Sol A (196 µM), which correspond to 0, 25, 50, 100 and 200 equiv. of isonitrile **4h** relative to complex **2**.

From the absorption band at 504 nm, the association constants of the adducts with the isonitriles **4d** and **4h** were calculated according to the Ketelaar equation<sup>S23</sup> (eq 1), where  $A_{\text{tot}}$  is the absorbance of the mixture,  $\epsilon_n$  the extinction coefficient of the component n,

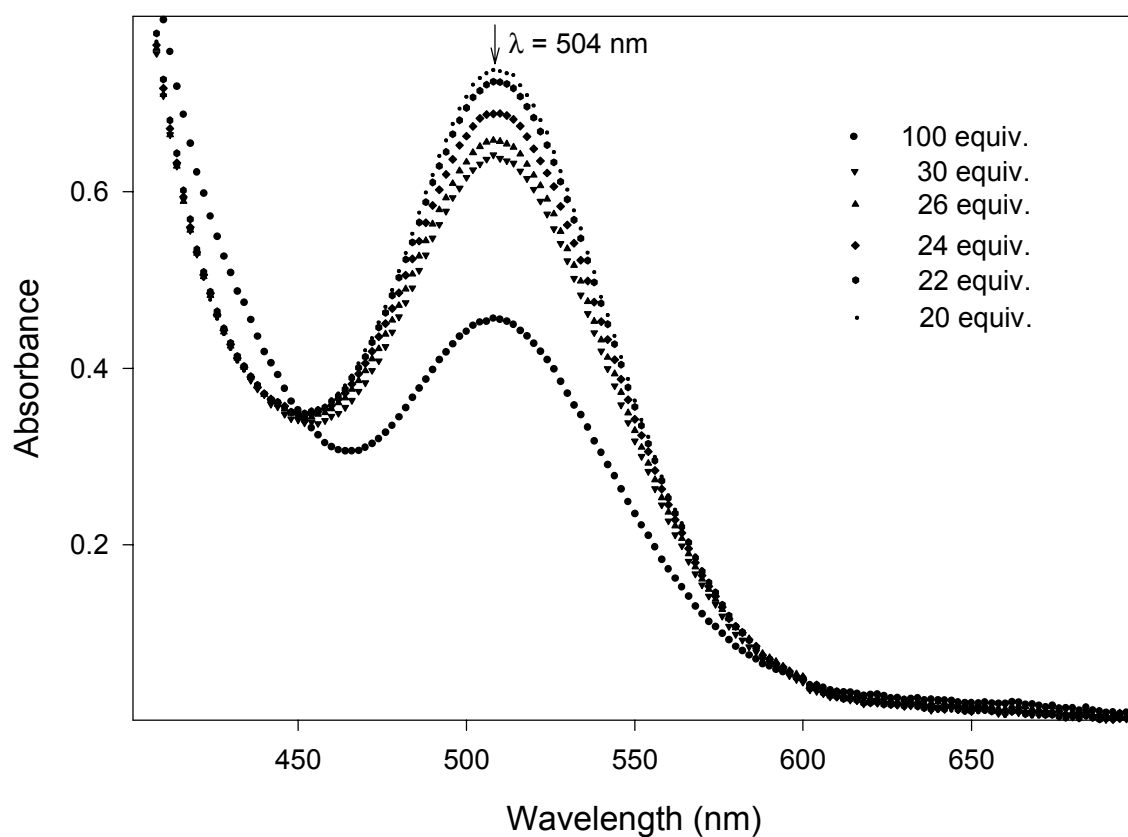
$$\frac{1}{\epsilon^* - \epsilon_2} = \frac{1}{K_c \cdot (\epsilon_4 - \epsilon_2)} \cdot \frac{1}{[4]_0} + \frac{1}{\epsilon_4 - \epsilon_2}, \text{ with } \epsilon^* = \frac{A_{\text{tot}}}{[2]_0 \cdot d} \quad (\text{eq 1})$$



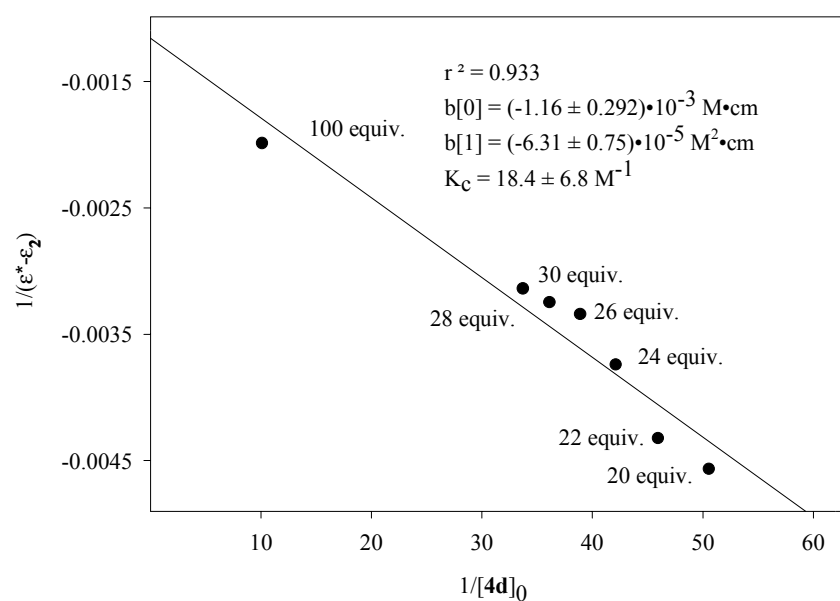
**Figure S1.** UV/VIS absorption spectra of the molybdenum oxo complex **2** ( $10^{-4}$  M) and isonitrile **4h** in  $\text{CH}_2\text{Cl}_2$  as a function of **4h** concentration; the arrows indicate increasing **4h** concentration.

$K_c$  is the association constant, and  $[n]_0$  the initial concentration of component  $n$ . The association constants ( $K_c$ ) were determined from the slopes  $[b(1)]$  and intercepts  $[b(0)]$  of the Figures S3 and S4 according to  $K_c = b(0) / b(1)$ .

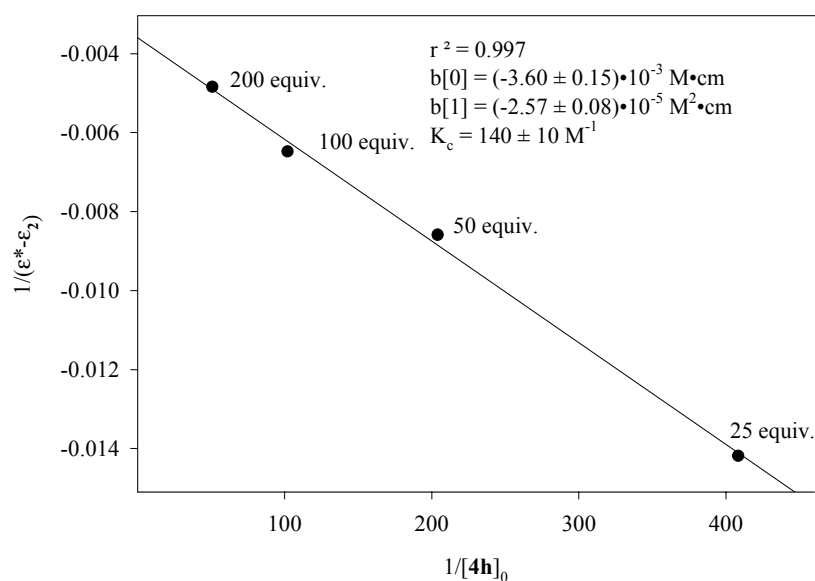




**Figure S2.** UV/VIS absorption spectra of the molybdenum oxo complex **2** ( $10^{-3}$  M) and isonitrile **4d** in  $\text{CH}_2\text{Cl}_2$  as a function of **4d** concentration; the arrows indicate increasing **4d** concentration.



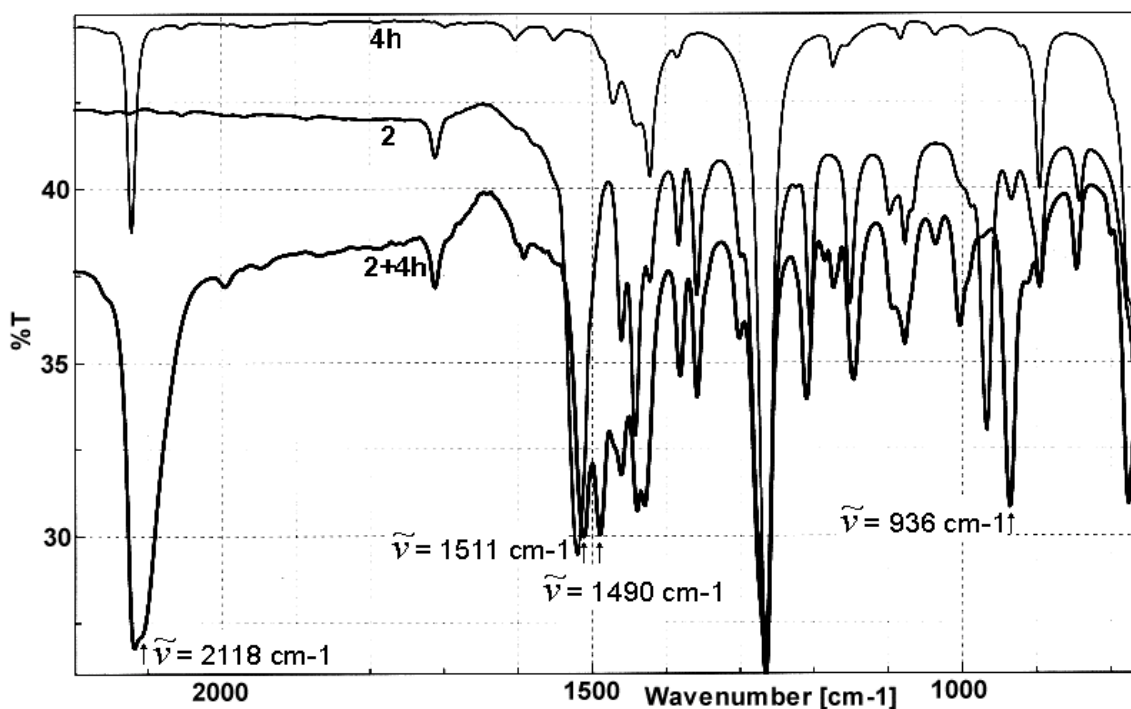
**Figure S3.** Determination of the association constant for the adduct of isonitrile **4d**.



**Figure S4.** Determination of the association constant for the adduct of isonitrile **4h**.

#### IR-Spectral Experiments of a Mixture of the Molybdenum Oxo Complex **2** and Isonitriles **4**

For the IR-spectral experiments, a solution of 490 mg (1.20 mmol) of oxo complex **2** in 3.2 mL of dry dichloromethane was prepared and an FT-IR spectrum (Figure S2) immediately recorded (NaCl plates). To this solution was added 346 mg (2.64 mmol) of the isonitrile **4h** was added, stirred for 5 min, and an FT-IR spectrum was measured again (Figure S5).

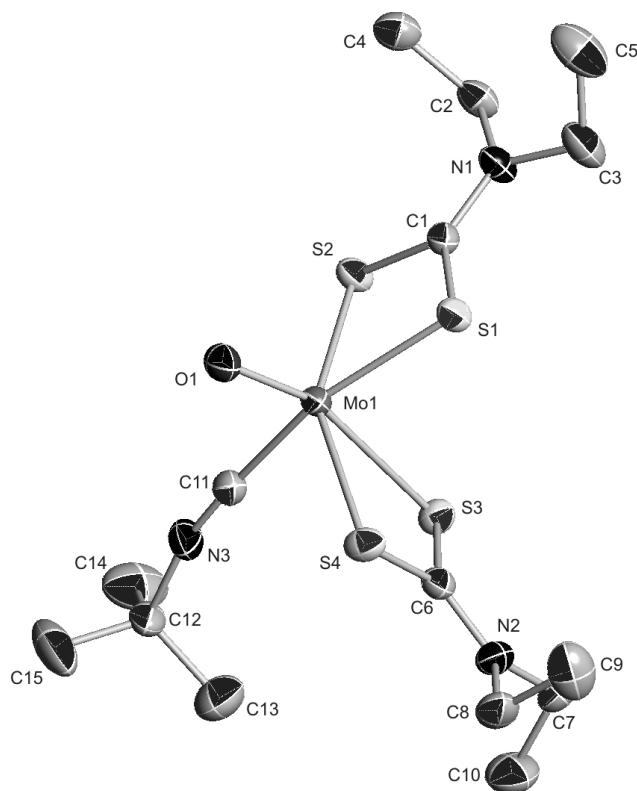


**Figure S5.** FT-IR spectrum of the mixture of the molybdenum oxo complex **2** and isonitrile **4h** in CH<sub>2</sub>Cl<sub>2</sub>.

#### Isolation of the Isonitrile Adduct 2/4d of Complex **2** and X-Ray Analysis

In a 5-mL Schlenk flask were placed under an argon-gas atmosphere 700 mg (1.71 mmol) of complex **2** in 1.36 mL of deaerated isonitrile **4d**. The Schlenk flask was immersed into a preheated (to 80 °C) oil bath and magnetically stirred until complete dissolution (ca. 5 min) of complex **2**. During heating, a color change from dark green to dark brown was observed. The reaction mixture was allowed to cool within 2 h to 20–25 °C, while an argon-gas flow was maintained during the cooling process. The Schlenk flask was capped with a glass stopper, sealed by means of Parafilm, and stored in the glove box for 9 d. The crystalline solid was collected on a sintered-glass funnel by filtration under an argon-gas atmosphere. A crystal was submitted to X-ray analysis, the structural data are summarized in Tables S1–S5, and the structure is given in Figure 1 (see main text). The remaining crystalline complex was dried (20–25 °C / 20 mbar) for 3 h to afford 736 mg (87%) of the adduct as green blocks. During

the drying process some molybdenum oxo complex **2** was regenerated, as revealed by FT-IR spectroscopy; thus, the isonitrile ligand is only weakly coordinated and readily departs.



**Figure S6:** Solid state structure of the adduct **2/4d** between the molybdenum oxo complex **2** and isonitrile **4d**. Anisotropic displacement parameters are depicted at 50% probability level. Selected bond lengths [ang] and angles[°]: Mo1-C11 2.116(2), Mo1-O1 1.6825(15), Mo1-S1 2.4595(5), Mo1-S2 2.4184(6), Mo1-S3 2.7107(6), Mo1-S4 2.5214(6); O1-Mo1-C11 92.48(8), C11-Mo1-S3 74.09(6), C11-Mo1-S4 90.21(6), C11-Mo1-S2 100.57(6), S(2)-Mo(1)-S(1) 71.862(18), S2-Mo1-S4 150.31(2).

**Table S1.** Crystal Data and Structure Refinement for Isonitrile Adduct **2/4d**

Identification code	<b>2/4d</b>
Empirical formula	C <sub>15</sub> H <sub>29</sub> Mo N <sub>3</sub> O S <sub>4</sub>
Formula weight	491.59
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
Unit cell dimensions	a = 12.2290(5) Å      α = 90°. b = 9.0120(4) Å      β = 97.3080(10)°. c = 20.6266(9) Å      γ = 90°.
Volume	2254.75(17) Å <sup>3</sup>
Z	4
Density (calculated)	1.448 Mg/m <sup>3</sup>
Absorption coefficient	0.960 mm <sup>-1</sup>
F(000)	1016
Crystal size	0.3 x 0.1 x 0.1 mm <sup>3</sup>
θ-range for data collection	1.99 to 26.41°.
Index ranges	-15 ≤ h ≤ 15, 0 ≤ k ≤ 11, 0 ≤ l ≤ 25
Reflections collected	36679
Independent reflections	4926 [R(int) = 0.0266]
Completeness to θ = 26.41°	99.7 %
absorption correction	empirical
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4612 / 0 / 224
Goodness-of-fit on F <sup>2</sup>	1.104
Final R indices <sup>a, b</sup> [I > 2σ(I)]	R1 = 0.0273, wR2 = 0.0662
R indices (all data)	R1 = 0.0290, wR2 = 0.0674
g <sub>1</sub> ; g <sub>2</sub> <sup>c</sup>	0.0314, 1.8744
Largest diff. peak and hole	0.952 and -0.310 eÅ <sup>-3</sup>

$$^a R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|,$$

$$^b wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{0.5},$$

$$^c w = [\sigma^2(F_o^2) + (g_1 P)^2 + g_2 P]^{-1}, P = 1/3[\max(F_o^2, 0) + 2F_c^2]$$

Crystal data for **Isonitrile Adduct 2/4d**: The data were collected from shock-cooled crystals on a BRUKER SMART-APEX diffractometer with D8 goniometer (graphite-monochromated

Mo-K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) equipped with a low temperature device in omega-scan mode at 193(2) K<sup>S24</sup>. The data were integrated with SAINT<sup>S25</sup> and an empirical absorption correction was applied.<sup>S26</sup> The structure was solved by direct methods (SHELXS-97)<sup>S27</sup> and refined by full-matrix least squares methods against  $F^2$  (SHELXL-97).<sup>S28</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms bonded to sp<sup>3</sup> carbon atoms were assigned ideal positions and refined using a riding model with  $U_{\text{iso}}$  constrained to 1.5 times the  $U_{\text{eq}}$  value of the parent atom.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 174715. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) + 44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

## References for Supporting Information

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# Structure Matrix

