Generation of "$Cp_2Mo{=}S$" and Cycloaddition of the Molybdenum Sulfido Bond with Di-*p*-tolylcarbodiimide

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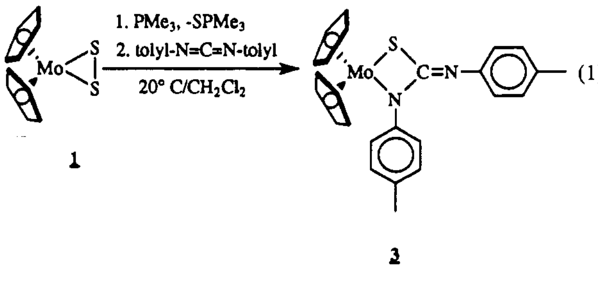
In a search of chemical probes for functional groups important to the catalytic chemistry of MoS_2,[1] we are developing the reaction chemistry of the sulfur-containing ligands of Mo^{IV} complexes. In particular, we are interested in the bis(cyclopentadienyl)molybdenum family of complexes {$Cp_2Mo(SH)_2$,[2] Cp_2MoS_2,[3] Cp_2MoS_4,[4] $Cp_2Mo(S_3C_2RR')$,[5] $Cp_2Mo(S_2C_2RR')$[5]} since this family contains the robust Cp_2Mo framework, which allows development of the ligand chemistry without changes in the remaining coordination or oxidation state of molybdenum. In this paper we present synthetic routes to "Cp_2MoS" and describe the trapping of this reactive monosulfido species. We envisioned two relatively simple routes to "Cp_2MoS" from existing complexes: (1) abstraction of a sulfur atom {S} from Cp_2MoS_2 and (2) stripping of H_2S from $Cp_2Mo(SH)_2$. In addition to allowing generation of "Cp_2MoS", these synthetic routes also permit us to investigate the reaction chemistry of the molybdenum disulfido and bis(hydrosulfido) complexes, respectively. Regardless of its mode of synthesis, "Cp_2MoS" is valuable for comparative study of its reaction chemistry with its oxo Cp_2MoO[6] and Cp_2WO[6] and carbonyl $Cp_2W(CO)$[7] counterparts and the sulfido complex "Cp_2ZrS".[8] Of particular interest is the formal [2 + 2] cycloaddition of the metal heteroatom bond with heterallenes and other unsaturated organic molecules.[6,8]

Although our evidence is indirect, we believe we have generated Cp_2MoS *in situ*. We have, however, direct evidence for the formal [2 + 2] cycloaddition product of the Mo=S bond of "Cp_2MoS" and the C=N bond of tolyl-N=C=N-tolyl (di-*p*-tolylcarbodiimide). Reaction of Cp_2MoS_2, **1**, with PMe_3 followed by the addition of di-*p*-tolylcarbodiimide, as shown in eq 1, yields Cp_2Mo{SC(=N-tolyl)N-tolyl}, **3**,[9] which has been the subject of a single-crystal X-ray study[10] as shown in Figure 1. Complex **3** is similar to other four-membered metallocycles of the bis(cyclopentadienyl)molybdenum family in that the four atoms Mo, S, N(1), and C(11) are nearly coplanar with 0.034, -0.041, -0.064, and 0.071 Å deviations from the plane, respectively. This plane bisects the dihedral angle formed by the cyclopentadienyl ligands. The Mo-S bond distance at 2.462(1) Å and the Mo-N bond distance at 2.128(4) Å are characteristic of molybdenum-sulfur and molybdenum-nitrogen single bonds, respectively. The C(11)-N(1) and C(11)-N(2) distances of 1.363(6) and 1.282(6) Å are best described as single and double bonds, respectively. The N(1)-Mo-S bond angle of 66(1)° is only slightly larger than the N-Mo-O bond angle of 61.9(1)° found in the complex Cp_2-



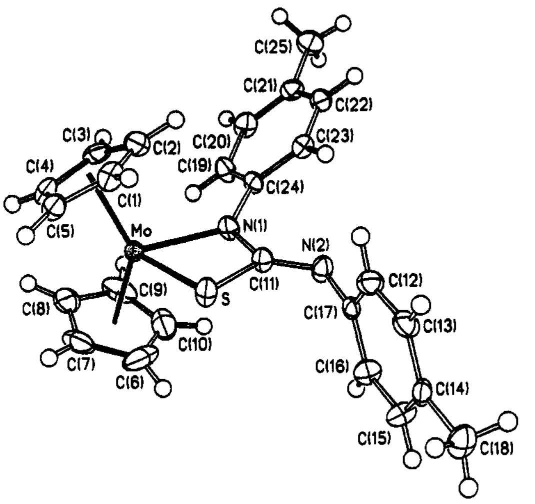


Figure 1. ORTEP drawing of Cp_2Mo{SC(=N-tolyl)N-tolyl}, **3**, with the thermal ellipsoids drawn at the 35% probability. Selected bond lengths (Å) and angles (deg): Mo-S, 2.462(1); Mo-N(1), 2.128 (4); S-C(11), 1.771(5); C(11)-N(1), 1.363(6); C(11)-N(2), 1.282(6); N(1)-C(24), 1.418(6); N(2)-C(17), 1.411(7); N(1)-Mo-S, 66.0(1); Mo-S-C(11), 81.6(2); Mo-N(1)-C(11), 105.4(3); S-C(11)-N(1), 106.0(3); S-C(11)-N(2), 126.8(4); N(1)-C(11)-N(2), 127.1(5).

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(9) Preparation of Cp_2Mo{SC(=N-tolyl)N-tolyl}, **3**, from **1**: Cp_2MoS_2, **1** (90 mg, 0.30 mmol), is dissolved in 10 mL of CH_2Cl_2, PMe_3 (25 mg, 0.33 mmol) is added, and the solution is allowed to stir for 4 h. The solution is filtered, and CH_2Cl_2 is removed under vacuum. The resulting solid is washed with 2 × 10 mL of Et_2O. The solid is redissolved in CH_2Cl_2 (2 mL) and di-*p*-tolyl dicarbodiimide (133 mg, 0.6 mmol) is added to the solution and allowed to stir for 2 days under a nitrogen atmosphere. An orange precipitate forms, which is filtered onto a fine frit. The solid is dissolved in CH_2Cl_2 (20 mL) and filtered. The CH_2Cl_2 is removed under vacuum to yield **3** as an orange analytically pure solid (59 mg, 0.123 mmol) in 41% yield. ^1H NMR (CD_2Cl_2): 7.30-6.80 (m, 8H, C_6H_4), 5.39 (s, 10H, C_5H_5), 2.28 (s, 3H, CH_3), 2.27 (s, 3H, CH_3). ^{13}C NMR (CD_2Cl_2): 177.4 (s, {S}(N)C=N), 149.7, 145.7, 131.4, 130.5, 129.4, 128.8, 123.7, 123.4 (s, C_6H_4), 97.3 (s, C_5H_5), 20.9 (s, CH_3), 20.7 (s, CH_3). MS (EI): 482 (M^+), 260 (M^+ – *p*-tolylcarbodiimide), 222 (*p*-tolylcarbodiimide). Anal. Calc for $C_{25}H_{24}MoN_2S$: C, 62.5; H, 5.03; N, 5.83. Found: C, 62.3, H, 4.98, N, 5.88.

(10) Crystal data for **3**: $C_{25}H_{24}MoN_2S$, $M = 480.44$, $C2/c$, $a = 15.312(3)$ Å, $b = 17.580(3)$ Å, $c = 15.719(3)$ Å, $\beta = 97.89(2)°$, $V = 4191.3(16)$ Å^3, $Z = 8$, $D_c = 1.523$ g cm^{-3}, $T = 295$ K, and $\mu = 7.2$ cm^{-1} (no correction for absorption was warranted). A Nicolet R3m diffractometer was used to collect 3559 data (red-orange specimen, $4° \leq 2\varphi \leq 48°$) of which 2402 independent data with $F_o \geq 4\sigma(F_o)$ were observed using graphite-monochromated Mo Kα radiation. With all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions, $R(F) = 3.85\%$, $R_w(F) = 4.12\%$, and GOF = 1.042.

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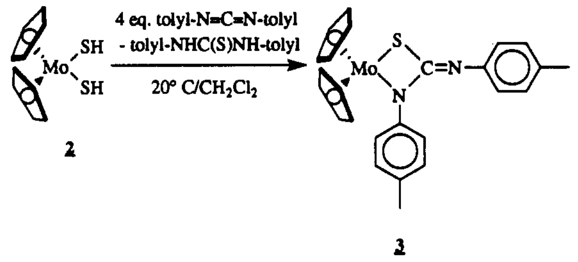
Mo{OC(=O)NPh}, which also contains a four-membered metallocycle.[6] The N(1)–Mo–S bond angle of **3** is substantially smaller than that found in the five-membered sulfur-containing metallocycle $Cp_2Mo(S_2C_2RR')$, where the S–Mo–S bond angle is 81.9(1)° (R = quinoxaline and R′ = C(O)Me).[5]

We have investigated the reaction of **1** with di-*p*-tolylcarbodiimide without the addition of PMe_3 and find that no reaction occurs over a 2-day period as monitored by ^1H NMR. Given the unreactive nature of **1**, the isolation of $SPMe_3$ in reaction 1, and the established reactions of the oxo analogues with heteroallenes, we propose that the monosulfido complex Cp_2MoS has been formed. Although we have been unable to isolate an analytically pure sample, we have made attempts to characterize Cp_2MoS *in situ*. The reaction of 1 equiv of PMe_3 with **1** leads to a new ^1H NMR (CD_2Cl_2) resonance at δ 5.59, which we attribute to the cyclopentadienyl ligands of Cp_2MoS. The (EI) mass spectrum of the reaction mixture shows a cluster of peaks with an isotope pattern of a single mononuclear molybdenum complex with the highest intensity peak at $m/z = 260$ corresponding to $[Cp_2MoS]^+$ in the gas phase. Thus, we suggest that Cp_2MoS is mononuclear in analogy with $(MeC_5H_4)_2MoO$,[11] which has been shown crystallographically to be mononuclear in the solid state. However, we have not unequivocally ruled out the possibility that Cp_2MoS is a dimer or oligomer in solution.

We have also attempted to prepare Cp_2MoS by heating $Cp_2Mo(SH)_2$, **2**, in the solid state at 90 °C under vacuum. We hypothesized that such treatment would simply eliminate H_2S. However, no stable new Cp_2Mo complex was observed in the periodic ^1H NMR monitoring of the reaction, although the complete consumption of **2** eventually occurred. While thermal elimination of H_2S from **2** did not allow isolation of Cp_2MoS, complex **2** can nevertheless be used to prepare Cp₂Mo{SC(=N-tolyl)N-tolyl}. Complex **2** reacts with excess tolyl-N=C=N-tolyl over a 2-day period in CH_2Cl_2 to generate **3** in 34% yield as shown in eq 2.[12] We have tried to isolate Cp_2MoS from the addition of a single equivalent of tolyl-N=C=N-tolyl to **2** and again observed the resonance at δ 5.59 in the ^1H NMR but also observed the cyclopentadienyl resonances due to **2** and **3** at δ 5.19 and 5.39, respectively. These results suggest that Cp_2MoS is generated but that it reacts with tolyl-N=C=N-tolyl almost as rapidly as H_2S is abstracted from $Cp_2Mo(SH)_2$ by tolyl-N=C=N-tolyl. It seems likely that H_2S is abstracted from **2** in the reaction with tolyl-N=C=N-tolyl as it is unlikely that $Cp_2Mo(SH)_2$ eliminates H_2S. Solutions of $Cp_2Mo(SH)_2$ are stable under nitrogen and do not react with NEt_3, which would be expected to trap H_2S. In related work, we have found that the sulfhydryl groups of **2** do not rapidly exchange with H_2S (2 atm) in CD_2Cl_2 as monitored by a lack of saturation transfer in the ^1H NMR from H_2S to $Cp_2Mo(S\mathit{H})_2$. This behavior contrasts with that of $Cp_2Ti(SH)_2$,[13,14] which at least exchanges the hydrogen atoms (and probably the entire S–H groups) of the sulfhydryl ligand with those of H_2S on the ^1H NMR time scale as evidenced by the saturation transfer from H_2S to $Cp_2Ti(S\mathit{H})_2$ under 2 atm of H_2S.[15]



(2)

We are continuing to develop the reaction chemistry of the sulfur-containing complexes of the bis(cyclopentadienyl)molybdenum family including the chemistry of "Cp_2MoS". We are also attempting to extend the reactions developed on the bis(cyclopentadienyl)molybdenum framework to MoS_2 in an attempt to probe for the presence of certain Mo–S functional groups on the surface of the heterogeneous catalyst.

Supplementary Material Available: Tables of crystallographic data, including complete atomic coordinates, bond distances and angles, and anisotropic thermal parameters, for complex **3** (5 pages). Ordering information is given on any current masthead page.

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(12) Preparation of Cp₂Mo{SC(=N-tolyl)N-tolyl}, 3, from 2: $Cp_2Mo(SH)_2$, 1 (90 mg, 0.30 mmol), is dissolved in CH_2Cl_2 (2 mL), and di-*p*-tolyl)-carbodiimide (266 mg, 1.2 mmol) is added to the solution, which is allowed to stir for 2 days under a nitrogen atmosphere. An orange precipitate forms, which is filtered onto a fine frit. The solid is dissolved in CH_2Cl_2 (20 mL), and the mixture is filtered. CH_2Cl_2 is removed under vacuum to yield 3 as an orange analytically pure solid (49 mg, 0.102 mmol) in 34% yield.

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