

Oxygen Atom Transfer Reactions from Oxygen Containing Molecules to Carbonylmolybdenum(II) Complexes

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(Received December 18, 1986)

Abstract

Tricarbonylmolybdenum(II) complexes, $\text{Mo}(\text{CO})_3\text{-L}_2$ ($\text{L} = \text{S}_2\text{CPh}$ (1) and $\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5$ (2)), have been prepared. The oxygen atom transfer reactions of complexes 1 and 2 as well as $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNET}_2)_2$ (3) with oxygen containing molecules O_2 , Me_2SO , and NO_2^- have been performed. Complexes 1 and 2 slowly evolve CO in the absence of the oxygen containing donors, followed by the dimerization reaction to give dinuclear complexes of the Mo_2L_4 type ($\text{L} = \text{S}_2\text{CPh}$ and $\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5$). In the presence of an oxygen containing donor O_2 or Me_2SO , complexes 1 and 2 effectively abstract oxygen atoms from the donor molecule to afford monomeric oxomolybdenum complexes, MoOL_2 ($\text{L} = \text{S}_2\text{CPh}$ and $\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5$). Similarly, complex 3 reacts with O_2 to give $\text{MoO}(\text{S}_2\text{CNET}_2)_2$, which is further oxidized to dioxomolybdenum species $\text{MoO}_2(\text{S}_2\text{CNET}_2)_2$, whereas the reaction of 3 with Me_2SO affords $\text{MoO}(\text{S}_2\text{CNET}_2)_2$. On the other hand, NO_2^- reacts with 1–3 to transfer oxygen atoms to ligated CO rather than the molybdenum center, resulting in the evolution of CO_2 and the formation of nitrosylmolybdenum complexes, $\text{Mo}_2(\text{NO})\text{L}_4$ ($\text{L} = \text{S}_2\text{CPh}$ and $\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5$) or $\text{Mo}_2(\text{NO})_2\text{-(S}_2\text{CNET}_2)_4$.

Introduction

Molybdenum is an essential element for the activity of xanthine [1, 2], aldehyde [2] and sulfite oxidases [3], and nitrate reductase [4], all of which catalyze oxygen atom transfer reactions. Thus, the oxygen atom transfer reactions catalyzed by molybdenum complexes have been studied extensively [5–7]. Although most of these studies were carried out using oxomolybdenum complexes [8–11], a carbonyl molybdenum complex also has the ability to

abstract oxygen atoms from oxygen containing molecules; $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNET}_2)_2$ reacts with O_2 to afford $\text{Mo}_2\text{O}_3(\text{S}_2\text{CNET}_2)_4$ in Me_2CO [12]. This letter reports the oxygen atom transfer reactions from oxygen containing donors O_2 , Me_2SO , and NO_2^- to $\text{Mo}(\text{CO})_3\text{L}_2$ ($\text{L} = \text{S}_2\text{CPh}$ (1), $\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5$ (2)) and $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNET}_2)_2$ (3), accompanied by decarbonylation reactions of the molybdenum complexes, where $\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5$ is ferrocene carbodithioate.

Preparation of the Molybdenum Complexes

To an MeOH solution (10 cm^3) of $\text{Mo}(\text{CO})_4\text{Br}_2$ [13] (2.87 g, 7.8 mmol) was added dropwise $[\text{Et}_2\text{NH}_2][\text{L}]$ ($\text{L} = \text{S}_2\text{CPh}$ [14] and $\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5$ [15]) (15.6 mmol) in the same solvent (30 cm^3) at -40°C , and the solution was stirred for 30 min at that temperature. A precipitate formed and was collected by filtration, washed with CO -saturated MeOH ($10 \text{ cm}^3 \times 4$), and dried under a CO stream at room temperature to give reddish-brown and dark blue microcrystals of 1 and 2, in 54 and 51% yields, respectively. *Anal.* for 1. Found: C, 41.97; H, 2.19. Calc. for $\text{C}_{17}\text{H}_{10}\text{MoO}_3\text{S}_4$: C, 41.97; H, 2.07%. *Anal.* for 2. Found: C, 42.50; H, 2.85. Calc. for $\text{C}_{25}\text{H}_{18}\text{Fe}_2\text{MoO}_3\text{S}_4$: C, 42.75; H, 2.58%. Complex 3 was prepared according to the literature [12]. The infrared spectra of 1 and 2 in the $\nu(\text{C}=\text{O})$ region are very similar to those of the dithiocarbamate analog, $\text{Mo}(\text{CO})_3(\text{S}_2\text{CNET}_2)_2$ [12] (Table I), which easily releases one molecule of CO in solution to give $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNET}_2)_2$ [16].

Decarbonylation Reactions of 1 and 2

Both 1 and 2 are stable in the solid state, but they undergo a decarbonylation reaction in solution. The infrared spectrum of 1 in O_2 -free THF shows the $\nu(\text{C}=\text{O})$ bands at 2040 and 1965 cm^{-1} immediately after dissolution (Table I). After 5 min, however, two new $\nu(\text{C}=\text{O})$ bands appeared at 1940 and 1880 cm^{-1} , whose intensities strengthened with time at the expense of the 2040 and 1965 cm^{-1} bands. The 1940

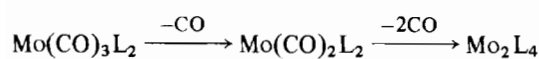
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TABLE I. $\nu(\text{C}\equiv\text{O})$ Frequencies of the Carbonylmolybdenum Complexes

Complex	$\nu(\text{C}\equiv\text{O})$ (cm^{-1})			
	in Nujol mull		in THF	
$\text{Mo}(\text{CO})_3(\text{S}_2\text{CPh})_2$	2046 1925	1963 1903	1953	2040 1965 br
$\text{Mo}(\text{CO})_3(\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2$	2029 1912	1956 1881	1942	2030 1940 br
$\text{Mo}(\text{CO})_3(\text{S}_2\text{CNEt}_2)_2^{\text{a}}$	2020 1915	1951 1898	1935	
$\text{Mo}(\text{CO})_2(\text{S}_2\text{CPh})_2$				1940 1880
$\text{Mo}(\text{CO})_2(\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2$				1940 1880
$\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)_2^{\text{a}}$	1925 ^a	1842 ^a		1930 ^b 1850 ^b

^aRef. 12. ^bThis work.

and 1880 cm^{-1} bands attained the maximum intensities ca. 3 h after dissolution and then gradually decreased. Finally, all the $\nu(\text{C}\equiv\text{O})$ bands had completely disappeared 24 h later. The resulting dark brown solution was evaporated to dryness under reduced pressure to give $\text{Mo}_2(\text{S}_2\text{CPh})_4$, which was identified by elemental analysis and comparison of the infrared spectrum with that of the authentic sample [17], 68% yield. The transient $\nu(\text{C}\equiv\text{O})$ bands appeared at 1940 and 1880 cm^{-1} and may reasonably be assigned to $\text{Mo}(\text{CO})_2(\text{S}_2\text{CPh})_2$ by comparison with the $\nu(\text{C}\equiv\text{O})$ frequencies of $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)_2$ in THF [12] (Table I). Similarly, **2** undergoes a decarbonylation reaction in O_2 -free THF to yield $\text{Mo}_2(\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)_4$ via $\text{Mo}(\text{CO})_2(\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2$ ($\nu(\text{C}\equiv\text{O})$ in Table I), in 50% yield. *Anal.* Found: C, 42.41; H, 2.90. Calc. for $\text{C}_{44}\text{H}_{36}\text{Fe}_4\text{Mo}_2\text{S}_8$: C, 42.73; H, 2.93%. Molecular weight: 1200 in C_6H_6 (calc. 1236). Thus, **1** and **2** release CO molecules stepwise in solution to afford dimeric Mo_2L_4 (L = S_2CPh and $\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5$) (Scheme 1). This reaction also proceeded with CH_2Cl_2 .



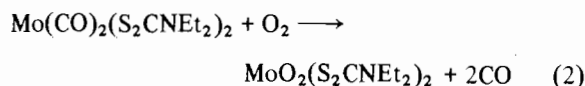
Scheme 1.

Reactions of **1**, **2**, and **3** with O_2

Dioxygen was bubbled into CH_2Cl_2 solutions of **1** and **2** for 3 h at room temperature, followed by removal of the solvent under reduced pressure to give $\text{MoO}(\text{S}_2\text{CPh})_2$ ($\nu(\text{Mo}=\text{O})$ 970 cm^{-1}) and $\text{MoO}(\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2$ ($\nu(\text{Mo}=\text{O})$ 960 cm^{-1}), respectively, in almost quantitative yields (eqn. (1)). These products were identified by elemental analyses and



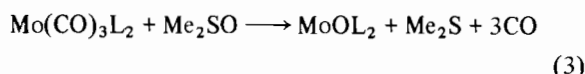
comparison of the infrared spectra with those of the authentic samples prepared by the literature methods [14, 15]. On the other hand, oxidation of **3** with O_2 in CH_2Cl_2 selectively afforded $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$ in almost quantitative yield, which was identified by comparison of the infrared spectrum with that of the authentic sample [18] (eqn. (2)), while the same reaction conducted in Me_2CO was reported to separate



out $\text{Mo}_2\text{O}_3(\text{S}_2\text{CNEt}_2)_4$ owing to its low solubility in this solvent [12]. The difference between **1** or **2** and **3** toward O_2 oxidation may be a result of the fact that both $\text{MoO}(\text{S}_2\text{CPh})_2$ and $\text{MoO}(\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2$ are stable to O_2 , whereas the corresponding dithiocarbamate complex $\text{MoO}(\text{S}_2\text{CNEt}_2)_2$ is readily oxidized by O_2 to give $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$ via $\text{Mo}_2\text{O}_3(\text{S}_2\text{CNEt}_2)_4$ [19].

Reactions of **1**, **2**, and **3** with Me_2SO

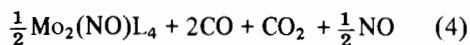
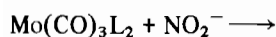
Upon mixing a CH_2Cl_2 (10 cm^3) solution of **1** or **2** (0.25 mmol) with Me_2SO (0.42 mmol) at 35 $^\circ\text{C}$, not only CO (0.70 or 0.65 mmol) but also Me_2S (0.15 or 0.058 mmol) were released over 15 h, suggesting that oxygen atom transfer from Me_2SO to the complex takes place to some extent. In fact, evaporation of the solvent gave a mixture of $\text{MoO}(\text{S}_2\text{CPh})_2$ and $\text{Mo}_2(\text{S}_2\text{CPh})_4$ (56 and 35% yields, respectively), or a mixture of $\text{MoO}(\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2$ and $\text{Mo}_2(\text{S}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)_4$ (18 and 68% yields, respectively). Thus, the reaction of **1** or **2** with Me_2SO results in oxygen atom transfer (eqn. (3)) as well as



dimerization reactions (Scheme 1). On the other hand, the reaction of **3** (0.25 mmol) with Me₂SO (0.28 mmol) in O₂-free CH₂Cl₂ (10 cm³) selectively proceeded via oxygen atom transfer to afford MoO(S₂CNEt₂)₂ in 90% yield.

Reactions of **1**, **2**, and **3** with NO₂⁻

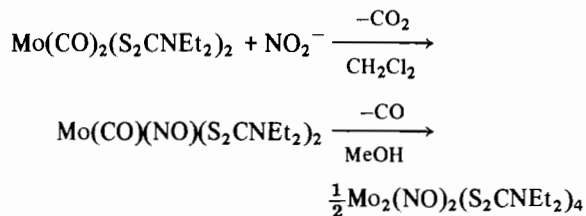
Complexes **1** and **2** (0.21 mmol) reacted rapidly with [*n*-Bu₄N][NO₂], obtained by the literature method [20] (0.21 mmol), in CH₂Cl₂ (10 cm³) at room temperature to evolve almost two equivalent amounts of CO (0.41 and 0.38 mmol, respectively), almost equivalent amounts of CO₂ (0.20 and 0.19 mmol, respectively) and small amounts of N₂O (0.044 and 0.035 mmol, respectively). This result indicates that two CO molecules are released as well as the oxygen atom transfer from NO₂⁻ to one CO molecule, followed by the evolution of CO₂. Such oxygen atom transfer has been reported to occur in the reactions of palladium nitrite complexes with CO in CH₂Cl₂, producing carbonylpalladium complexes with evolution of CO₂ and N₂O [21]. Evaporation of the solvent from the mixtures of **1** and **2** with [*n*-Bu₄N][NO₂] in CH₂Cl₂ under reduced pressure gave oily residues, which were triturated with MeOH (30 cm³) to afford brown and purple microcrystals, respectively. The infrared spectra of these products showed neither ν(Mo=O) nor ν(Mo—O—Mo) bands in the 1000–800 and 700–600 cm⁻¹ range; instead a strong absorption band appeared at 1660 cm⁻¹, which is close to the ν(NO) frequency of Mo(NO)(S₂CNEt₂)₃ (1630 cm⁻¹) [22], suggesting the existence of a coordinated nitrosyl moiety in the products. The molecular weights of the products measured cryoscopically in C₆H₆ are consistent with the values calculated for the 1:1 adduct of NO with Mo₂L₄ (L = S₂CPh and S₂CC₅H₄FeC₅H₅) (eqn. (4))*.



respectively. The elemental analyses also support the formation of the 1:1 adduct. Yield: 55% for Mo₂(NO)(S₂CPh)₄. *Anal.* Found: C, 40.50; H, 2.63; N, 1.29. Calc. for C₂₈H₂₀Mo₂NOS₈: C, 40.28; H, 2.41; N, 1.68%. Yield 35% for Mo₂(NO)(S₂CC₅H₄FeC₅H₅)₄. *Anal.* Found: C, 42.20; H, 2.94; N, 1.51. Calc. for C₄₄H₃₆Fe₄Mo₂NOS₈: C, 41.72; H, 2.86; N, 1.11%.

The reaction of **3** (0.24 mmol) with [*n*-Bu₄N][NO₂] (0.24 mmol) also proceeded rapidly in CH₂Cl₂ (10 cm³) to evolve only CO₂ (0.20 mmol) in contrast to the reactions of **1** and **2**. Removal of the solvent from the reaction mixture under reduced pressure gave a yellowish-brown oil, which exhibited strong ν(C≡O) and ν(NO) absorptions at 1845 and 1630

cm⁻¹, respectively, suggesting the formation of Mo(CO)(NO)(S₂CNEt₂)₂. Upon dissolving the oily product in MeOH, however, the ν(C≡O) band completely disappeared and the ν(NO) band was shifted to 1650 cm⁻¹. Moreover, evaporation of the MeOH solution under reduced pressure gave a dimeric nitrosylmolybdenum complex Mo₂(NO)₂(S₂CNEt₂)₄ (ν(NO) 1650 cm⁻¹) (Scheme 2) in 40% yield. *Anal.* Found: C, 28.12; H, 4.68; N, 9.84. Calc. for C₂₀H₄₀Mo₂N₆O₂S₈: C, 28.43; H, 4.77; N, 9.95%. Molecular weight: 850 in C₆H₆ (Calc. 845).



Scheme 2.

In conclusion, **1** and **2** slowly evolve CO in the absence of oxygen-containing donors, followed by the dimerization reaction to give dinuclear complexes of the Mo₂L₄ type (L = S₂CPh, S₂CC₅H₄FeC₅H₅). In the presence of oxygen-containing donors O₂ or Me₂SO, complex **3** as well as **1** and **2** effectively abstract oxygen atoms from the donor molecules to afford monomeric oxomolybdenum complexes, MoOL₂ (L = S₂CPh, S₂CC₅H₄FeC₅H₅, S₂CNEt₂) or MoO₂(S₂CNEt₂)₂. On the other hand, NO₂⁻ reacts with compounds **1–3** to transfer oxygen atoms to CO, resulting in the formation of nitrosylmolybdenum complexes, Mo₂(NO)L₄ (L = S₂CPh, S₂CC₅H₄FeC₅H₅) or Mo₂(NO)₂(S₂CNEt₂)₄.

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*The evolution of NO has been difficult to identify.

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