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

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Abstract

Tricarbonylmolybdenum(II) complexes, $Mo(CO)_3L_2$ ($L = S_2CPh$ (**1**) and $S_2CC_5H_4FeC_5H_5$ (**2**)), have been prepared. The oxygen atom transfer reactions of complexes **1** and **2** as well as $Mo(CO)_2(S_2CNEt_2)_2$ (**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 ($L = S_2CPh$ and $S_2CC_5H_4FeC_5H_5$). 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, $MoOL_2$ ($L = S_2CPh$ and $S_2CC_5H_4FeC_5H_5$). Similarly, complex **3** reacts with O_2 to give $MoO(S_2CNEt_2)_2$, which is further oxidized to dioxomolybdenum species $MoO_2(S_2CNEt_2)_2$, whereas the reaction of **3** with Me_2SO affords $MoO(S_2CNEt_2)_2$. 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, $Mo_2(NO)L_4$ ($L = S_2CPh$ and $S_2CC_5H_4FeC_5H_5$) or $Mo_2(NO)_2(S_2CNEt_2)_4$.

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; $Mo(CO)_2(S_2CNEt_2)_2$ reacts with O_2 to afford $Mo_2O_3(S_2CNEt_2)_4$ in Me_2CO [12]. This letter reports the oxygen atom transfer reactions from oxygen containing donors O_2, Me_2SO, and NO_2^- to $Mo(CO)_3L_2$ ($L = S_2CPh$ (**1**), $S_2CC_5H_4FeC_5H_5$ (**2**)) and $Mo(CO)_2(S_2CNEt_2)_2$ (**3**), accompanied by decarbonylation reactions of the molybdenum complexes, where $S_2CC_5H_4FeC_5H_5$ is ferrocene carbodithioate.

Preparation of the Molybdenum Complexes

To an MeOH solution (10 cm^3) of $Mo(CO)_4Br_2$ [13] (2.87 g, 7.8 mmol) was added dropwise $[Et_2NH_2][L]$ ($L = S_2CPh$ [14] and $S_2CC_5H_4FeC_5H_5$ [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 cm^3 × 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 $C_{17}H_{10}MoO_3S_4$: C, 41.97; H, 2.07%. *Anal.* for **2**. Found: C, 42.50; H, 2.85. Calc. for $C_{25}H_{18}Fe_2MoO_3S_4$: C, 42.75; H, 2.58%. Complex **3** was prepared according to the literature [12]. The infrared spectra of **1** and **2** in the $\nu(C\equiv O)$ region are very similar to those of the dithiocarbamato analog, $Mo(CO)_3(S_2CNEt_2)_2$ [12] (Table I), which easily releases one molecule of CO in solution to give $Mo(CO)_2(S_2CNEt_2)_2$ [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 $\nu(C\equiv O)$ bands at 2040 and 1965 cm^{-1} immediately after dissolution (Table I). After 5 min, however, two new $\nu(C\equiv O)$ 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. $\nu(C{\equiv}O)$ Frequencies of the Carbonylmolybdenum Complexes

Complex	$\nu(C{\equiv}O)$ (cm^{-1})				
	in Nujol mull			in THF	
$Mo(CO)_3(S_2CPh)_2$	2046 1925	1963 1903	1953	2040	1965 br
$Mo(CO)_3(S_2CC_5H_4FeC_5H_5)_2$	2029 1912	1956 1881	1942	2030	1940 br
$Mo(CO)_3(S_2CNEt_2)_2$ [a]	2020 1915	1951 1898	1935		
$Mo(CO)_2(S_2CPh)_2$				1940	1880
$Mo(CO)_2(S_2CC_5H_4FeC_5H_5)_2$				1940	1880
$Mo(CO)_2(S_2CNEt_2)_2$ [a]	1925[a]	1842[a]		1930[b]	1850[b]

[a]Ref. 12. [b]This work.

and 1880 cm^{-1} bands attained the maximum intensities *ca.* 3 h after dissolution and then gradually decreased. Finally, all the $\nu(C{\equiv}O)$ bands had completely disappeared 24 h later. The resulting dark brown solution was evaporated to dryness under reduced pressure to give $Mo_2(S_2CPh)_4$, which was identified by elemental analysis and comparison of the infrared spectrum with that of the authentic sample [17], 68% yield. The transient $\nu(C{\equiv}O)$ bands appeared at 1940 and 1880 cm^{-1} and may reasonably be assigned to $Mo(CO)_2(S_2CPh)_2$ by comparison with the $\nu(C{\equiv}O)$ frequencies of $Mo(CO)_2(S_2CNEt_2)_2$ in THF [12] (Table I). Similarly, **2** undergoes a decarbonylation reaction in O_2-free THF to yield $Mo_2(S_2CC_5H_4FeC_5H_5)_4$ via $Mo(CO)_2(S_2CC_5H_4FeC_5H_5)_2$ ($\nu(C{\equiv}O)$ in Table I), in 50% yield. *Anal.* Found: C, 42.41; H, 2.90. Calc. for $C_{44}H_{36}Fe_4Mo_2S_8$: 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 $S_2CC_5H_4FeC_5H_5$) (Scheme 1). This reaction also proceeded with CH_2Cl_2.

$$Mo(CO)_3L_2 \xrightarrow{-CO} Mo(CO)_2L_2 \xrightarrow{-2CO} Mo_2L_4$$

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 $MoO(S_2CPh)_2$ ($\nu(Mo{=}O)$ 970 cm^{-1}) and $MoO(S_2CC_5H_4FeC_5H_5)_2$ ($\nu(Mo{=}O)$ 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 $MoO_2(S_2CNEt_2)_2$ 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 $Mo_2O_3(S_2CNEt_2)_4$ 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 $MoO(S_2CPh)_2$ and $MoO(S_2CC_5H_4FeC_5H_5)_2$ are stable to O_2, whereas the corresponding dithiocarbamate complex $MoO(S_2CNEt_2)_2$ is readily oxidized by O_2 to give $MoO_2(S_2CNEt_2)_2$ via $Mo_2O_3(S_2CNEt_2)_4$ [19].

$$Mo(CO)_3L_2 + \tfrac{1}{2}O_2 \longrightarrow MoOL_2 + 3CO \qquad (1)$$

$$Mo(CO)_2(S_2CNEt_2)_2 + O_2 \longrightarrow MoO_2(S_2CNEt_2)_2 + 2CO \qquad (2)$$

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 °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 $MoO(S_2CPh)_2$ and $Mo_2(S_2CPh)_4$ (56 and 35% yields, respectively), or a mixture of $MoO(S_2CC_5H_4FeC_5H_5)_2$ and $Mo_2(S_2CC_5H_4FeC_5H_5)_4$ (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

$$Mo(CO)_3L_2 + Me_2SO \longrightarrow MoOL_2 + Me_2S + 3CO \qquad (3)$$

dimerization reactions (Scheme 1). On the other hand, the reaction of **3** (0.25 mmol) with Me_2SO (0.28 mmol) in O_2-free CH_2Cl_2 (10 cm^3) selectively proceeded via oxygen atom transfer to afford MoO-$(S_2CNEt_2)_2$ in 90% yield.

Reactions of 1, 2, and 3 with NO_2^-

Complexes **1** and **2** (0.21 mmol) reacted rapidly with $[n\text{-}Bu_4N][NO_2]$, obtained by the literature method [20] (0.21 mmol), in CH_2Cl_2 (10 cm^3) at room temperature to evolve almost two equivalent amounts of CO (0.41 and 0.38 mmol, respectively), almost equivalent amounts of CO_2 (0.20 and 0.19 mmol, respectively) and small amounts of N_2O (0.044 and 0.035 mmol, respectively). This result indicates that two CO molecules are released as well as the oxygen atom transfer from NO_2^- to one CO molecule, followed by the evolution of CO_2. Such oxygen atom transfer has been reported to occur in the reactions of palladium nitrite complexes with CO in CH_2Cl_2, producing carbonylpalladium complexes with evolution of CO_2 and N_2O [21]. Evaporation of the solvent from the mixtures of **1** and **2** with $[n\text{-}Bu_4N][NO_2]$ in CH_2Cl_2 under reduced pressure gave oily residues, which were triturated with MeOH (30 cm^3) 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 $Mo(NO)(S_2CNEt_2)_3$ (1630 cm^{-1}) [22], suggesting the existence of a coordinated nitrosyl moiety in the products. The molecular weights of the products measured cryoscopically in C_6H_6 are consistent with the values calculated for the 1:1 adduct of NO with Mo_2L_4 (L = S_2CPh and $S_2CC_5H_4FeC_5H_5$) (eqn. (4))*. *Anal.* Found: 850 and 1130. Calc.: 837 and 1266%,

$$Mo(CO)_3L_2 + NO_2^- \longrightarrow \frac{1}{2}Mo_2(NO)L_4 + 2CO + CO_2 + \frac{1}{2}NO \quad (4)$$

respectively. The elemental analyses also support the formation of the 1:1 adduct. Yield: 55% for $Mo_2(NO)(S_2CPh)_4$. *Anal.* Found: C, 40.50; H, 2.63; N, 1.29. Calc. for $C_{28}H_{20}Mo_2NOS_8$: C, 40.28; H, 2.41; N, 1.68%. Yield 35% for $Mo_2(NO)(S_2CC_5H_4FeC_5H_5)_4$. *Anal.* Found: C, 42.20; H, 2.94; N, 1.51. Calc. for $C_{44}H_{36}Fe_4Mo_2NOS_8$: C, 41.72; H, 2.86; N, 1.11%.

The reaction of **3** (0.24 mmol) with $[n\text{-}Bu_4N][NO_2]$ (0.24 mmol) also proceeded rapidly in CH_2Cl_2 (10 cm^3) to evolve only CO_2 (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 $Mo(CO)(NO)(S_2CNEt_2)_2$. 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 $Mo_2(NO)_2(S_2CNEt_2)_4$ (ν(NO) 1650 cm^{-1}) (Scheme 2) in 40% yield. *Anal.* Found: C, 28.12; H, 4.68; N, 9.84. Calc. for $C_{20}H_{40}Mo_2N_6O_2S_8$: C, 28.43; H, 4.77; N, 9.95%. Molecular weight: 850 in C_6H_6 (Calc. 845).

$$Mo(CO)_2(S_2CNEt_2)_2 + NO_2^- \xrightarrow[CH_2Cl_2]{-CO_2} Mo(CO)(NO)(S_2CNEt_2)_2 \xrightarrow[MeOH]{-CO} \frac{1}{2}Mo_2(NO)_2(S_2CNEt_2)_4$$

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 Mo_2L_4 type (L = S_2CPh, $S_2CC_5H_4FeC_5H_5$). In the presence of oxygen-containing donors O_2 or Me_2SO, complex **3** as well as **1** and **2** effectively abstract oxygen atoms from the donor molecules to afford monomeric oxomolybdenum complexes, $MoOL_2$ (L = S_2CPh, $S_2CC_5H_4FeC_5H_5$, S_2CNEt_2) or $MoO_2(S_2CNEt_2)_2$. On the other hand, NO_2^- reacts with compounds **1**–**3** to transfer oxygen atoms to CO, resulting in the formation of nitrosylmolybdenum complexes, $Mo_2(NO)L_4$ (L = S_2CPh, $S_2CC_5H_4FeC_5H_5$) or $Mo_2(NO)_2(S_2CNEt_2)_4$.

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*The evolution of NO has been difficult to identify.

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