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On the mechanism of carboxylate ligand scrambling at Mo_2^{4+} centers: evidence for a catalyzed mechanism

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The reaction between $Mo_2(O_2CBu^t)_4$ and $Mo_2(O_2CCF_3)_4$ has been studied by ^1H and ^{19}F NMR spectroscopy in the solvents C_6D_6, CD_2Cl_2, CD_3CN, pyridine-d$_5$ and THF-d$_8$. In each solvent ligand exchange is observed with the formation of $Mo_2(O_2CBu^t)_3(O_2CCF_3)$ **1**, *cis*- and *trans*-$Mo_2(O_2C^tBu)_2(O_2CCF_3)_2$ (*cis*-**2**, *trans*-**2**) and $Mo_2(O_2CBu^t)(O_2CCF_3)_3$ **3**. The approach to equilibrium is solvent dependent with the rate being $C_6D_6 \sim CD_2Cl_2 > CD_3CN$ and THF-d$_8$. Attempts to quench the ligand exchange by the addition of proton and carboxylate anion traps such as $BaCO_3$, Cs_2CO_3, proton sponge, 2,6-di-*tert*-butylpyridine (2,6-Bu$^t_2$-py) and $[Mo_2(O_2CBu^t)_2(CH_3CN)_4]^{2+}[BF_4^-]_2$ all failed. In the presence of $[Mo_2(PhNCHNPh)_2(CH_3CN)_4]^{2+}[BF_4^-]_2$ and 2,6-Bu$^t_2$-py the ligand exchange reaction is halted. These data are used to argue for a catalyzed ligand exchange reaction involving free carboxylate anion or carboxylic acid in the reaction between $Mo_2(O_2CBu^t)_4$ and $Mo_2(O_2CCF_3)_4$ to give $Mo_2O_2(CBu^t)_n(O_2CCF_3)_{4-n}$, where $n = 0$–4. Similarly, the reaction between $Mo_2(O_2CBu^t)_4$ and $[Mo_2(O_2CBu^t)_2(CH_3CN)_4]^{2+}[BF_4^-]_2$ to give $[Mo_2(O_2CBu^t)_3(CH_3CN)_2]^+[BF_4^-]$ is suppressed in the presence of 2,6-di-*tert*-butylpyridine.

Introduction

In our attempts to prepare parallel and perpendicularly linked polymers of M–M quadruply bonded complexes supported by carboxylate ligands[1] we have been thwarted by deleterious side reactions leading to polymer/oligomer degradation. The chief cause of this polymer degradation seems to be due to carboxylate group scrambling reactions. Such reactions have been noted before by Cotton[2] in studies of eqn. (1), where $n = 0$ to 4 and

$$Mo_2(O_2CH)_4 + Mo_2(O_2CCF_3)_4 \rightleftharpoons Mo_2(O_2CH)_n(O_2CCF_3)_{4-n} \quad (1)$$

by us in a similar reaction between $Mo_2(O_2CBu^t)_4$ and $Mo_2(O_2CH_2Bu^t)_4$.[3]

In the present work we describe studies of the closely related reaction shown in eqn. (2) as a function of various solvents and

$$Mo_2(O_2CBu^t)_4 + Mo_2(O_2CCF_3)_4 \rightleftharpoons Mo_2(O_2CBu^t)_n(O_2CCF_3)_{4-n} \quad (2)$$

additives aimed at elucidating the facility and mechanism of this ligand exchange process ($n = 0$–4).

Although it is known that certain compounds with M–M quadruple and triple bonds may associate to give tetranuclear species, *e.g.* $2W_2(O^iPr)_6 \rightleftharpoons W_4(OPr^i)_{12}$[4] and $2Mo_2Cl_4L_2(HOMe)_2 \longrightarrow Mo_4Cl_8L_4 + 4MeOH$,[5] it is hard to see how an associative mechanism leading to a $[Mo_4(O_2CR)_8]$ complex could achieve this facile exchange. We therefore suspected that the mechanism for ligand exchange might involve fortuitous RCO_2H which was present in the solution since we have previously studied the fluxionality of the $Mo_2(\mu\text{-}O_2CBu^t)_4(\eta^1\text{-}O_2CBu^t)^-$ anion[6] in benzene-d$_6$ and a well known route to $Mo_2(O_2CR)_4$ compounds involves the reaction shown in eqn. (3).[7]

$$Mo_2(O_2CMe)_4 + RCO_2H\ (\text{excess}) \xrightarrow[\text{solvent}]{\text{heat}} Mo_2(O_2CR)_4 + 4MeCO_2H \quad (3)$$

Results and discussion

Reaction (2) is readily followed by both ^1H and ^{19}F NMR spectroscopies. The compounds $Mo_2(O_2CBu^t)_3(O_2CCF_3)$ **1**, and $Mo_2(O_2CBu^t)(O_2CCF_3)_3$ **3**, are formed concurrently. Subsequently the formation of $Mo_2(O_2CBu^t)_2(O_2CCF_3)_2$ **2**, which exists in *cis* and *trans* isomers, is seen.

In a typical reaction *ca.* 5 mg of each of the pivalate and trifluoroacetate were mixed (in as close to a 1 : 1 mole ratio as possible, given the small quantities involved) and dissolved in the deuteriated NMR solvent *ca.* 0.7 mL. The results obtained by monitoring reaction (2) with ^{19}F NMR are qualitatively similar to those obtained using ^1H NMR. However, the interpretation of the ^{19}F NMR spectra was complicated by the presence of one or more overlapping resonances. In addition, chemical shift values in ^{19}F NMR spectra are highly sensitive to changes in temperature and solvent. Therefore, we report only the results based on the ^1H NMR spectra. The reactions were monitored at room temperature in a Varian Gemini-2000 spectrometer. Within 1 h in benzene-d$_6$ and CD_2Cl_2 there is essentially no evidence for the homoleptic carboxylates and after *ca.* 3 h an equilibrium mixture of **1**, **2**, and **3** is formed. Rather interestingly, we see that after 1 h the formation of **2** is in a 1 : 1 ratio of *cis* and *trans* isomers but with time the ratio of the *cis* isomer increases to *ca.* 2.5 : 1 in benzene-d$_6$. Thus the *trans* isomer of **2** must be formed kinetically at essentially the same rate as the *cis* even though the *cis* isomer is favored thermodynamically (statistics alone give a 2 : 1 *cis* : *trans* preference). A series of ^1H spectra showing the formation of **1** and **3** and **2** (*cis* + *trans*) are shown in Fig. 1.

Qualitatively the same results are seen in CD_2Cl_2 but in CD_3CN and THF-d$_8$, the formation of **1**, **3** and **2** are notably slower such that equilibrium is not attained until *ca.* 48 h. Also in the more polar CD_3CN the thermodynamic preference for *cis*-**2** : *trans*-**2** is *ca.* 5 : 1. The initial formation of **2**, however, has a smaller *cis* to *trans* ratio, once again indicating a kinetic preference for *trans* ligand exchange. Attempts to follow **2** in pyridine-d$_5$ are thwarted by a direct reaction between $Mo_2(O_2CCF_3)_4$ and pyridine which causes formation of $\eta^1\text{-}O_2CCF_3$ ligands.[8]

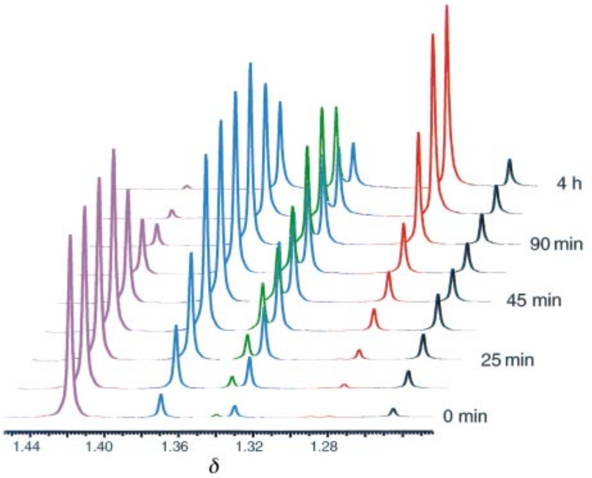

Fig. 1 ^{1}H NMR spectra of the carboxylate scrambling reaction involving $Mo_2(O_2C^tBu)_4$ and $Mo_2(O_2CCF_3)_4$ recorded in benzene-d_6, 500 MHz at 22 °C showing the disappearance of $Mo_2(O_2C^tBu)_4$ (purple) and the concomitant formation of $Mo_2(O_2C^tBu)_3(O_2CCF_3)$ **1** (blue) and $Mo_2(O_2CCF_3)_3(O_2C^tBu)$ **3** (black) followed by formation of $Mo_2(O_2C^tBu)_2(O_2CCF_3)_2$ **2**, which occurs in both *trans* (green) and *cis* (red) isomers. The formation of *trans*-**2** is seen to be kinetically favored.

The rate of ligand scrambling, which followed the order $C_6D_6 \approx CD_2Cl_2 > CD_3CN \approx$ THF-d_8, led us to question the role of axial ligation to the Mo_2^{4+} centers. We therefore investigated the scrambling in C_6D_6 in the presence of added PPh_3 (*ca.* 60 equiv). [This tertiary phosphine is known to bind axially to $Mo_2(O_2CCF_3)_4$ without displacing any Mo–O bonds.[8]] However, the added PPh_3 failed to yield any significant decrease in the rate of carboxylate group scrambling.

We also investigated the influence of dilution on the rate of carboxylate scrambling and found that with dilution the rate of scrambling was decreased. While this could be viewed as evidence for a bimolecular reaction pathway involving an $[Mo_2]_2$ species it could also result from a bimolecular pathway involving $[Mo_2]$ and an adventitious reagent. In order to investigate the possible role of adventitious carboxylic acid in promoting a catalyzed ligand exchange reaction we studied the reaction (2) in the presence of various additives intended to capture any mischevious free RCO_2H.

Finely divided $BaCO_3$ and Cs_2CO_3 were introduced since they could act as scavengers for carboxylic acids. However, these failed to suppress reaction (2). Since it is necessary to trap both a proton source and any free carboxylate anion, we studied reaction (2) in the presence of $[Mo_2(O_2CBu^t)_2(CH_3CN)_4]^{2+}[BF_4^-]_2$ and proton sponge [1,8-bis(dimethylamino)naphthalene]. However, here a reaction occurred between $[Mo_2(O_2CBu^t)_2(CH_3CN)_4]^{2+}[BF_4^-]$ and the added proton sponge. This led us to investigate reactions involving the use of 2,6-di-*tert*-butylpyridine (2,6-Bu^t_2-py) as a proton trap and $[Mo_2(O_2CBu^t)_2(CH_3CN)_4]^{2+}[BF_4^-]_2$ as a carboxylate anion trap. In these studies of reaction (2), we observed ligand scrambling to $[Mo_2(O_2CBu^t)_2(CH_3CN)_4]^{2+}[BF_4^-]_2$. [These reactions have to be carried out in CD_3CN because the $Mo_2(O_2CBu^t)_2^{2+}$ cationic complex is not soluble in benzene-d_6 or CD_2Cl_2.] Given the lability of the coordinated CH_3CN ligands in $[Mo_2(O_2CBu^t)_2(CH_3CN)_4]^{2+}$ it is possible that the Mo_2^{4+} center is sufficiently electrophilic to remove a carboxylate ligand from a $Mo_2(O_2CR)_4$ complex. In fact a reaction occurs between $[Mo_2(O_2CBu^t)_2(CH_3CN)_4]^{2+}[BF_4^-]_2$ and $Mo_2(O_2CCF_3)_4$ virtually instantaneously even in the presence of 2,6-di-*tert*-butylpyridine. Likewise, the fully solvated cationic complex $[Mo_2(CH_3CN)_{10}]^{4+}[BF_4^-]_4$[9] is capable of removing a pivalate ligand from $Mo_2(O_2CBu^t)_4$ in the presence of added 2,6-di-*tert*-butylpyridine. We have, however, noted that the pivalate exchange reaction between $[Mo_2(O_2CBu^t)_2(CD_3CN)_4]^{2+}[BF_4^-]_2$ and $Mo_2(O_2CBu^t)_4$ in CD_3CN to give $[Mo_2(O_2CBu^t)_3(CD_3CN)_2]^+[BF_4^-]$ is greatly suppressed by added 2,6-Bu^t_2-py. This suggested that a suitable protic trap such as 2,6-Bu^t_2-py in the presence of a more efficient carboxylate anion scavenger might completely suppress reaction (2). In this context we turned to the use of the $[Mo_2(PhNCHNPh)_2(CH_3CN)_4]^{2+}[BF_4^-]_2$ salt which we have found to have kinetically inert formamidinato ligands with respect to ligand exchange.[10]

$Mo_2(O_2CBu^t)_4$ and $Mo_2(O_2CCF_3)_4$ in CD_3CN showed no evidence for ligand exchange, reaction (2), after 12 h in the presence of 2,6-Bu^t_2-py and $[Mo_2(PhNCHNPh)_2(CH_3CN)_4]^{2+}[BF_4^-]$. The ability of $[Mo_2(PhNCHNPh)_2(CH_3CN)_4]^{2+}[BF_4^-]_2$ to function as a carboxylate trap was confirmed independently by reacting the dicationic complex with 2 equivalents of $Na(O_2CCBu^t)$ in CD_3CN.

From this we can conclude that carboxylate scrambling in reaction (2) is suppressed in the presence of appropriate protic and carboxylate traps. It is therefore unnecessary to invoke $[M_2]_2$ activated complexes in order to achieve carboxylate exchange and it would seem that carboxylate supported dimers of "dimers" and higher oligomers may be chemically persistent in the presence of appropriate traps such as 2,6-Bu^t_2-py and $[Mo_2(PhNCHNPh)_2(CH_3CN)_4]^{2+}[BF_4^-]$ which only need to be present in low concentrations.

Experimental

All manipulations were carried out by using standard Schlenk-line and glove-box techniques under an atmosphere of argon or nitrogen. The deuteriated solvents benzene-d_6, CD_2Cl_2, CD_3CN, THF-d_8 and pyridine-d_5 were degassed with argon and stored over molecular sieves (3 Å or 4 Å) prior to use. The ^{1}H and ^{19}F NMR spectra were recorded on a 300 Varian Gemini-2000 NMR spectrometer at 300 and 288.2 MHz, respectively. Higher resolution ^{1}H NMR spectra were recorded on a 500 Varian Inova NMR spectrometer. ^{1}H NMR spectra were referenced to residual protio impurities of the deuteriated solvents. ^{19}F NMR spectra were referenced externally relative to CF_3CO_2H. The dimolybdenum complexes $Mo_2(O_2CBu^t)_4$,[11] $Mo_2(O_2CCF_3)_4$,[12] $[Mo_2(O_2CBu^t)_2(CH_3CN)_4{}^{2+}][BF_4^-]_2$[1] and $[Mo_2(PhNCHNPh)_2(CH_3CN)_4]^{2+}[BF_4^-]_2$[10] were synthesized according to published procedures. Proton sponge®, Cs_2CO_3 and $BaCO_3$ were purchased from Aldrich and were dried under vacuum for 12 h. The 2,6-di-*tert*-butylpyridine was purchased from Aldrich, freeze–pump–thaw degassed and stored under Ar over 4 Å sieves prior to use.

The samples were prepared using Young® NMR tubes in a helium glove-box. The $Mo_2(O_2CR)_4$ complexes were weighed using an analytical balance accurate to 0.1 mg. A 1 : 1 solution of the $Mo_2(O_2CR)_4$ complexes was prepared by weighing out equimolar amounts of $Mo_2(O_2CBu^t)_4$ and $Mo_2(O_2CCF_3)_4$ and adding the deuteriated solvent.

^{1}H NMR (δ, C_6D_6): $Mo_2(O_2CBu^t)_4$ 1.42 (s); **1** 1.37 (s), 1.33 (s) (2H : 1H); *trans*-**2** 1.34 (s); *cis*-**2** 1.28 (s); **3** 1.24 (s). (δ, CD_3CN): $Mo_2(O_2CBu^t)_4$ 1.38 (s); **1** 1.39 (s), 1.42 (s) (2H : 1H); *cis*-**2** 1.43 (s); *trans*-**2** 1.47 (s); **3** 1.47 (s). (δ, THF-d_8): $Mo_2(O_2CBu^t)_4$ 1.41 (s); **1** 1.41 (s), 1.45 (s) (2H : 1H); *cis*-**2** 1.46 (s); *trans*-**2** 1.50 (s); **3** 1.50 (s).

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