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Rapid, Covalent Addition of Phosphine to Dithiolene in a Molybdenum Tris(dithiolene). A New Structural Model for Dimethyl Sulfoxide Reductase

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Supporting Information

ABSTRACT: Triphenylphosphine (PPh_3) rapidly and reversibly adds to the bdt ligand in the molybdenum tris(dithiolene) complex $Mo(tfd)_2(bdt)$ [tfd = $S_2C_2(CF_3)_2$; bdt = $S_2C_6H_4$], turning chelating bdt into the monodentate zwitterionic ligand $SC_6H_4SPPh_3$. A second PPh_3 molecule fills the newly created open site in the crystallographically characterized product $Mo(tfd)_2(SC_6H_4SPPh_3)(PPh_3)$, which is a structural model for dimethyl sulfoxide (DMSO) reductase. While the complex is only a precatalyst for reduction of DMSO by PPh_3 (the initially low catalytic rate increases with time), $Mo(tfd)_2(SMe_2)_2$ was found to be catalytically active without an induction period.

When transition-metal complexes undergo reactions, the supporting ligands are normally "spectator ligands". They control the geometry and electronic structure of the metal, whereas oxidation/reduction as well as bond-breaking and bond-making occur at the metal. In comparably rare cases, where frontier orbitals at the ligands are more accessible than metal orbitals, a "non-innocent" behavior of the ligand is observed.

Redox chemistry that involves electron transfer by reducing the ligand has been known for decades for dithiolene ($S_2C_2R_2$) complexes of transition metals.[1] Bond-making and bond-breaking reactivity at dithiolene ligands appears much less understood than electron transfer involving the ligands. While the sulfur centers of dithiolenes can be expected to be attacked by electrophiles (e.g., alkylating agents)[2] and nucleophiles have been reported to attack other ligands (for example, nitrides),[3] it is still very rare that a dithiolene ligand is attacked by a nucleophile other than an alkene.[4,5] Alkene additions to the ligand[6] have been reported for square-planar metal bis(dithiolene) complexes since the late 1960s for strained alkenes[7] and since 2001 for simple unstrained alkenes.[8] Then, in 2007 metal tris(dithiolene) complexes were also found to be reactive to simple unstrained alkenes.[9] However, alkenes are often considered amphiphilic and are not clear-cut examples of nucleophiles. We now report the addition of the nucleophile triphenylphosphine (PPh_3) to the bdt ligand in the molybdenum tris(dithiolene) $Mo(tfd)_2(bdt)$ [**1**; tfd = $S_2C_2(CF_3)_2$; bdt = $S_2C_6H_4$], creating the zwitterionic ligand $SC_6H_4SPPh_3$. The product complex is a structural dimethyl sulfoxide (DMSO) reductase model. It is also a precatalyst for DMSO reduction (discussed below).

When the known compound[9] **1** was treated with excess (4 equiv or more) PPh_3, we observed the formation of a new stable complex. As will be detailed below, an intermediate species (**2**) is involved in the formation of the stable product (**3**) from **1**. A sharp singlet in the ^{19}F NMR spectrum is observed for **3**, at −54.94 ppm, indicating that all CF_3 groups on the tfd ligands are equivalent either by symmetry or, as discussed below, by rapid pseudorotation. Two sharp ^{31}P singlet peaks are seen at very different shifts, at 54.14 and 43.54 ppm. Magenta crystals of **3** were obtained from two different solvents, benzene and chloroform, by directly reacting concentrated solutions of **1** with an excess (ca. 3.7 equiv) of PPh_3. Figure 1 shows the structure of **3**, where two phosphines have added in a very unusual way.

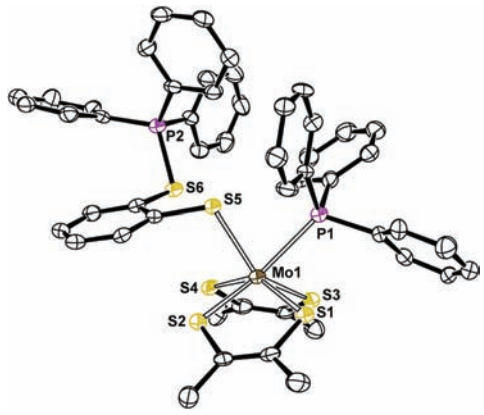

Figure 1. Molecular structure of **3**, from X-ray crystallography on the benzene solvate (30% probability ellipsoids). H and F atoms are omitted for clarity. Selected distances and angles: Mo1−S1, 2.358(3); Mo1−S2, 2.364(2); Mo1−S3, 2.335(2); Mo1−S4, 2.369(3); Mo1−S5, 2.416(2); Mo1−P1, 2.564(2); S5−Mo1−P1, 76.24(7); S1−Mo1−S2, 80.72(8); S3−Mo1−S4, 80.74(9). The structure of **3** in the chloroform solvate is similar (Supporting Information).

One has attacked the bdt ligand, whereas the other one coordinates to molybdenum, such that compound **3** is $Mo(tfd)_2(SC_6H_4SPPh_3)(PPh_3)$. Apart from the molybdenum-

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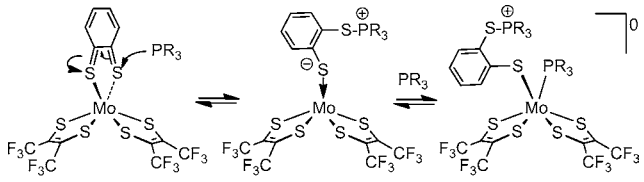
bound phosphine, which is labile (see below), the first coordination sphere of molybdenum in **3** (a thiolate ligand in conjunction with two dithiolenes) is very similar to what is seen for the DMSO reductase family of molybdenum oxotransferases[10,11] or for nitrate reductase from *desulfovibrio desulfuricans*[12] and also for a model complex for nitrate reductase from Sarkar's group, $[Et_4N][Mo^{IV}(PPh_3)(p\text{-MeSPh})(mnt)_2]$.[13] The Mo−thiolate and Mo−P bond lengths are virtually identical across the two complexes, at 2.416(2) versus 2.390(2) Å (this work versus Sarkar's complex) for Mo−thiolate and 2.564(2)/2.586(2) Å for Mo−P. The Mo−dithiolene bond distances are also very similar, with the average being 2.357(15) versus 2.364(13) Å. The same is true for thiolate−Mo−P angles, at 76.24(7)° versus 77.16(6)°.

The crystal structure shows no symmetry (C_1), but flexibility in the dangling $SC_6H_4SPPh_3$ will lead to at least C_s symmetry in solution. Furthermore, trigonal-prismatic molybdenum(IV) complexes have access to a low-barrier "twisting" process in which two distinct positions can rapidly exchange.[14] This leads to pseudo-C_{2v} symmetry in solution, as is observed in the NMR spectra of six-coordinate bis(dithiolene) complexes having two different non-ditholene ligands.[15,16] The positions occupied by $SC_6H_4SPPh_3$ and PPh_3 are thus expected to exchange, and one, averaged, CF_3 environment is indeed seen in the ^{19}F NMR spectrum of **3**, at −54.94 ppm. The connectivity of atoms is unchanged in solution: one phosphine is coordinated to the bdt ligand and the other one to molybdenum, as supported by ^{31}P NMR. The singlet at 43.54 ppm corresponds to the sulfur-bonded phosphorus, and its shift is very similar to the 44.1 ppm shift of sulfur-coordinated, monodentate $SC_6H_4SPPh_3$ in a gold dithiolene complex, reported as a synthetic byproduct in 11% yield.[5] While the formation of $SC_6H_4SPPh_3$ has precedence, its high-yielding and reversible formation is unprecedented. The second singlet at 54.14 ppm corresponds to the molybdenum-coordinated phosphorus, consistent with literature shifts (49.68 ppm).[13]

The formation of **3** might be expected to proceed via intermediate **2** (Scheme 1). When **1** was treated with between

Scheme 1



1 and 2 equiv of PPh_3, an additional species, **2**, is indeed observed, with a singlet in the ^{19}F NMR spectrum at −55.09 ppm and a singlet in the ^{31}P NMR spectrum at 47.58 ppm. The addition of excess PPh_3 (>2 equiv) leads to the disappearance of these signals and the appearance of the signals for **3**. Computational modeling suggests that **2** is a five-coordinate complex with square-pyramidal geometry (Supporting Information). More support for the equilibrium in Scheme 1 is obtained with a triarylphosphine having a methyl as a spectroscopic "handle": When tri-*p*-tolylphosphine is added to **1**, the products **2′** and **3′** (Scheme 1) can be clearly distinguished not only in their ^{31}P and ^{19}F NMR spectra but also in their ^1H NMR spectra. **2′** shows a single sharp singlet at 2.45 ppm (^1H), while **3′** shows a sharp singlet at 2.42 ppm and a broad singlet at 2.23 ppm. This is consistent with **2′** having only one attached triarylphosphine, while **3′** has two. The broad singlet at 2.23 ppm is assigned as the molybdenum-coordinated phosphine. K for $\mathbf{3} \rightleftarrows \mathbf{2} + PPh_3$ was determined to be $2(1) \times 10^{-5}$ M at 29 °C (UV−vis; Supporting Information). When a sufficiently diluted solution of **3** is equilibrated for ca. 30 min at room temperature, some **2** can be seen by NMR. Further dilution shifts the equilibrium more toward **2**. Similarly, we observe $\mathbf{3}' \rightleftarrows \mathbf{2}' + P(p\text{-tolyl})_3$, where $K = 6(5) \times 10^{-5}$ M (29 °C). **3** is stable for at least a few days in the presence of excess phosphine, while **2** slowly and irreversibly decays. Decay may be due to dimerization.[17] Inspired by the close structural similarity of **3** to oxotransferase enzymes, we tested for corresponding activity. In a stoichiometric oxotransfer reaction (without extra phosphine), the addition of 16 equiv of DMSO produced ∼1 equiv of dimethyl sulfide (DMS; relative to **3**), along with Ph_3PO (^1H and ^{31}P NMR). The complex decomposed slowly, as expected given the instability of **2**. However, the reaction was successfully made catalytic with the addition of extra phosphine before the addition of DMSO.

We typically observed at least 80 turnovers in the presence of 112 equiv of PPh_3 and 408 equiv of DMSO over the course of ∼2 days.

Preliminary kinetic studies using the *p*-tolyl system revealed the rate of oxygen transfer to *increase* with time rather than decrease. This induction period (see the Supporting Information) indicates that the catalytically active species might actually be a decomposition product of one of the phosphine adducts. A possible pathway is the loss of the bdt-derived ligand to give a $Mo(tfd)_2$ complex with two labile solvent molecules. Indeed, in a control experiment, the reaction of $Mo(tfd)_2(DMS)_2$ (where DMS is very labile) with 6.3 equiv of $P(p\text{-tolyl})_3$ and 59 equiv of DMSO yielded nearly quantitative conversion of $P(p\text{-tolyl})_3$ to $OP(p\text{-tolyl})_3$ with equivalent generation of DMS (see the Supporting Information), where the catalytic rate was high from the outset, without an induction period. It is unknown how exactly the bdt-derived ligand is lost and what mechanistic cycle $Mo(tfd)_2$ undergoes in catalyzing O-atom transfer. A full mechanistic study will be performed in the future.

We conclude that nucleophilic addition to a noninnocent ligand can open a coordinatively saturated complex and thus enhance reactivity. In **1**, phosphine can directly add to the bdt ligand, creating a zwitterionic $SC_6H_4SPPh_3$ monodentate ligand, giving a complex that is a structural DMSO reductase model and a precatalyst to a functional DMSO-reducing system. Future work will expand on the mechanism of the observed oxotransferase activity and the generality of the new, logical but initially counterintuitive, approach to make an open site: via the addition of a nucleophile but to the ligand.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and crystallographic information for compound **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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