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Selective Oxidation of Nonrefractory and Refractory Sulfides by Cyclopentadienyl Molybdenum Acetylide Complexes as Efficient Catalysts

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Abstract The synthesis and catalytic properties of molybdenum acetylide complexes $CpMo(CO)_3(–C{\equiv}CR)$, R = Ph(**1**), C_6H_4–*p*-CF_3 (**2**) and C_6H_4–*p*-CH_3 (**3**) has been studied. The molybdenum acetylide complexes were synthesized from $CpMo(CO)_3Cl$ and aryl acetylenes via Stephens–Castro coupling reaction. These complexes were characterized by single crystal X-ray diffraction analysis, FTIR and ^{1}H NMR spectroscopy. These complexes on treatment with hydrogen peroxide, formed corresponding molybdenum oxo-peroxo species. These in situ formed oxo-peroxo species were found very active (up to 100 % conversion) and selective (up to 100 %) oxidation catalysts for various refractory and nonrefractory sulfides. Interestingly, even though the molybdenum acetylide complexes are homogeneous, they could be recycled very efficiently by extracting the catalytically active molybdenum oxo-peroxo species in aqueous phase.

Keywords Homogeneous catalysis · Molybdenum acetylide · Refractory sulfide oxidation · Oxo-peroxo species

1 Introduction

Sulfur (S) is an essential element in the life processes of all living things including micro-organisms, higher plants, animals, and humans. Sulfur plays a major role in the formation of the proteins that are essential to sustain life in all biological organisms [1]. However, it is one of the major problems in fuel that causes air pollution leading to acid rains. Moreover, it poisons the catalyst in catalytic convertor [2]. In order to control the pollution, Environmental Protection Agency (EPA) has enforced stringent regulation for substantial reduction in the total sulfur content of gasoline and diesel fuel [3, 4]. Hence it is of great importance to develop effective ways to remove sulphur impurities from the fuel [5]. Commercially, these impurities are removed by hydrodesulfurization (HDS), which is a highly efficient process till date for removing nonrefractory sulfides, although not very effective for refractory sulfides [6]. An alternative route for removing refractory sulfides is oxidative desulfurization (ODS) process [7, 8]. Researchers worldwide have shown the use of heterogeneous Co–Mo or Co–Ni catalysts for HDS [9]. The refractory sulfides include dibenzothiophene (DBT) and especially 4,6-dimethyldibenzothiophene (DMDBT), which are difficult to remove by hydrodesulfurisation (HDS) process, owing to the steric hindrance of methyl groups of DMDBT that do not allow close contact with the catalyst surface [10]. In ODS process the organosulfur compounds are oxidized to their corresponding sulfones, and these products are removed by extraction, adsorption, distillation or decomposition [11, 12]. Though sulfur compounds in fuel are poison for catalytic converter, many sulphoxides and sulphones are used as intermediates in chemically and biologically active compounds, including therapeutic agents such as anti-ulcer (proton pump

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inhibitors) [13], antibacterial, antifungal, anti-atherosclerotic [14, 15], and cardiotonic agents [16] as well as psychotropic [17] and vasodilators [18]. Sulfoxides are important in organic synthesis as an activating group and have been utilized extensively in carbon bond formation reactions [19]. Conventionally this is achieved by using stoichiometric amount of *t*-butyl hypochlorite, *N*-halosuccinimides, *m*-chloroperbenzoic acid, sodium metaperiodate, nitrogen tetroxide, cerium ammonium nitrate (CAN), tetrabutylammonium peroxydisulfate, 2,6-dicarboxy pyridinium chlorochromate as oxidizing reagents [20] as well as large number of soluble metal complexes of Ti, V, Re, Mn, Cr, and W have been used [11, 21–23]. Apart from this, enzymatic methods have also been explored to remove these sulfides [24]. However the major drawbacks of these methods are their low operational stability and high cost of operation.

Sheldon and Van Doorn et al. [25] proposed that in oxidation reactions, the main function of the metal catalyst is to form co-ordinated peroxide complex that acts as a Lewis acid and removes electron density from the peroxidic oxygen. To prove these assumptions several molybdenum compounds with different ligands have been explored for oxidation of sulfides such as molybdyldiacetylacetonate [$MoO_2(acac)_2$] [26], molybdenum hexacarbonyl [$Mo(CO)_6$], and molybdenum oxoperoxide [$MoO(O_2)_2$] [27, 28]. More recently Gamelas et al. [29] have reported the selective oxidation of dialkyl, aryl–alkyl, benzylic, and benzothiophenic sulfides to either sulfoxides or sulfones, with stoichiometric amounts of aqueous H_2O_2 or TBHP, in the presence of complexes like $CpMo(CO)_3Cl$, $CpMoO_2Cl$. However the catalytic species (oxo-peroxo or dioxo) which perform actual catalysis is still unknown in these complexes.

Shiu et al. [30] have reported the formation of oxo-peroxo complexes $(C_5Me_5)W(O)(O_2)(C\equiv CR)$ after treatment of pentamethylcyclopentadienyl tungsten carbonyl acetylide complexes $(C_5Me_5)W(CO)_3(C\equiv CR)$, R=Ph, CH_2OMe, Pr^n and $C(Me)=CH_2$, with an acidic solution of hydrogen peroxide at room temperature. Facile formation of oxo-peroxo species after reaction with H_2O_2 makes this complex a very good catalyst for oxidation reactions.

In continuation to our efforts on development of molybdenum acetylide complex $CpMo(CO)_3(C\equiv CPh)$ as a precatalyst for oxidation reactions using green oxidant [31–33], herein we report the synthesis of molybdenum acetylide complexes having electron withdrawing as well as electron donating substituents on the phenyl ring of the acetylide moiety and their effect on oxidation of various sulfides including refractory sulfides.

2 Experimental

2.1 General

All preparations and manipulations were performed using standard Schlenk techniques under argon atmosphere. All reagents of commercial grade (Aldrich, SD fine) were used as received unless stated otherwise. 30 % aqueous hydrogen peroxide was used for oxidation reactions. Tetrahydrofuran was dried over sodium wires and refluxed after addition of benzophenone till appearance of blue color (ketyl formation) under argon and freshly distilled prior to use. Cyclopentadiene was obtained by freshly cracking dicyclopentadiene (Aldrich) by distillation prior to use. The complex, $CpMo(CO)_3Cl$ was prepared according to the reported procedure [34].

2.2 Preparation of $CpMo(CO)_3(–C\equiv CPh)$ (**1**)

A mixture of $CpMo(CO)_3Cl$ (2.0 g, 0.0071 mol), $H–C\equiv CPh$ (1.05 g, 0.010 mol) and catalytic amount of freshly prepared CuI (5 mg) was stirred at room temperature in diethyl amine (50 mL) for 15 min. The reaction was monitored by TLC using hexane/dichloromethane (80/20 v/v) as a mobile phase. After completion of the reaction, solvent was removed in vacuum. The product was separated by column chromatography using silica gel as stationary phase and hexane/dichloromethane (80/20 v/v) as eluent. The yield of complex **1** ($CpMo(CO)_3(–C\equiv CPh)$) = 1.5 g, 68.1 % based on $CpMo(CO)_3Cl$. Elemental analysis: found (calculated) for $CpMo(CO)_3(–C\equiv CPh)$: C 55.53 (55.49), H 3.05 (2.89). Further, the product was analyzed by FT-IR, ^{1}HNMR and ^{13}CNMR. FT-IR (KBr) $\nu_{(CO)}$, 1941, 1960, 2035 cm^{-1}, $\nu_{(C\equiv C)}$, 2103.1 cm^{-1} NMR in $CDCl_3$: δ (^{1}H); 5.5 (s, 5H, Cp), 7.15–7.38 (m, 5H, Ph) ^{13}C in $CDCl_3$: δ (^{13}C); 92.93 (Cp), 109.51 ($C\equiv \underline{C}Ph$); 108.21 ($C\equiv \underline{C}Ph$); 127.0, 129.39, 130.8, 130.87 ($C\equiv C\underline{C}_6H_5$) and 222.4, 238.78 (CO).

2.3 Preparation of $CpMo(CO)_3(–C\equiv C–C_6H_4–p\text{-}CF_3)$ (**2**) and $CpMo(CO)_3(–C\equiv C–C_6H_4–p\text{-}CH_3)$ (**3**)

The same synthetic procedure as for complex **1** was followed except addition of ($H–C\equiv C–C_6H_4–p\text{-}CF_3$) (0.010 mol) for preparation of **2** and ($H–C\equiv C–C_6H_4–p\text{-}CH_3$) (0.010 mol) for preparation of **3** instead of $HC\equiv CPh$ for **1**. Yield of $CpMo(CO)_3(–C\equiv C–C_6H_4–p\text{-}CF_3)$ = 2.15 g, 65.8 % based on $CpMo(CO)_3Cl$. Elemental analysis: found (calculated) for $CpMo(CO)_3(–C\equiv CPh)$: C 50.03 (49.27), H 2.32 (2.17). The compound was confirmed using FTIR spectroscopy. $\nu_{(CO)}$, 1938, 1966, 2037 cm^{-1}; $\nu_{(C\equiv C)}$, 2103.7 cm^{-1}. NMR in $CDCl_3$: δ (^{1}H); 5.58 (s, 5H, Cp), 7.35–7.49 (m, 4H, C_6H_4); δ (^{13}C); 93.3 (Cp), 113.6 ($C\equiv \underline{C}Ph$), 108.18 ($–\underline{C}\equiv CC_6H_4–p\text{-}CF_3$), 125.22, 128.12, 131.23, 132.4 ($C{\equiv}C\underline{C}_6H_4$); 124.2 ($-C{\equiv}C-C_6H_4-p-\underline{C}F_3$), 222.4 and 238.78 (CO).

Yield of $CpMo(CO)_3(-C{\equiv}C-C_6H_4-p-CH_3)$ = 1.82 g, 71.2 % based on $CpMo(CO)_3Cl$. Elemental analysis: found (calculated) for $CpMo(CO)_3(-C{\equiv}CPh)$: C 56.92 (56.67), H 3.46 (3.33). The compound was confirmed using FTIR spectroscopy. $\nu_{(CO)}$, 1936, 1963, 2036 cm^{-1}; $\nu_{(C{\equiv}C)}$, 2098.4 cm^{-1}. NMR in $CDCl_3$: δ (^1H); 2.23 (s, 3H, $C\mathit{H}_3$), 5.56 (s, 5H, *Cp*), 7.0–7.23 (m, 4H, $C_6\mathit{H}_4$); δ (^{13}C); 21.2 ($\mathit{C}H_3$); 93.3 (*Cp*); 108.0 ($\underline{C}{\equiv}CC_6H_4$); 109.32 ($C{\equiv}C\underline{C}_6H_4$); 129.1, 129.91, 131.23, 134.2 ($C{\equiv}C\underline{\mathit{C}}_6H_4$) and 222.0, 238.8 (*C*O).

2.4 Single Crystal X-Ray Diffraction Analysis

Single crystals of the complex **1** and **2** were grown by slow evaporation of the solution of complex in acetonitrile. The single crystal X-ray diffraction data for **1** and **2** were collected on a SMART APEX CCD single crystal X-ray diffractometer with ω and Φ scan mode and different number of scans and exposure times for both the crystals using λ MoK_α = 0.71073 Å radiation, crystal to detector distance 6.05 cm, 512 × 512 pixels/frame at room temperature. All the data was corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs. The crystal structures were solved by direct method using SHELXS-97 and the refinement was performed by full matrix least squares of F^2 using SHELXL-97 [35].

2.4.1 Single Crystal Data

*2.4.1.1 Compound **1*** Pale yellow rectangular crystal of approximate size 0.32 × 0.24 × 0.18 mm was used for data collection. Total scans = 3, total frames = 1818, exposure/frame = 10.0 s/frame, θ range = 2.09–25.0°, completeness to θ of 25.0° is 95.0 %, $C_{16}H_{10}MoO_3$, $M = 346.18$. Crystals belong to monoclinic, space group $P2_1/c$, $a = 6.7308(4)$, $b = 11.6071(6)$, $c = 17.949(1)$ Å, $\beta = 93.046(1)°$, $V =$ 1400.3 (14) $Å^3$, $Z = 4$, $D_c = 1.642$ g cc^{-1}, μ (Mo Kα) = 0.939 mm^{-1}, 9,068 reflections measured, 2324 unique [$I > 2\sigma(I)$], R value 0.0342, wR2 = 0.1075.

*2.4.1.2 Compound **2*** Brown plate of approximate size 0.44 × 0.36 × 0.12 mm was used for data collection. Total scans = 3, total frames = 1271, exposure/frame = 5.0 s/frame, θ range = 2.52–24.99°, completeness to θ of 24.99° is 99.6 %, $C_{17}H_9F_3MoO_3$, $M = 414.18$. Crystals belong to Monoclinic, space group $P2_1/c$, $a = 11.9333(7)$, $b = 12.8247(8)$, $c = 21.023(1)$ Å, $\beta = 90.413(1)°$, $V =$ 3217.3(3) $Å^3$, $Z = 8$, $D_c = 1.710$ g cc^{-1}, μ (Mo Kα) = 0.859 mm^{-1}, 15543 reflections measured, 5636 unique [$I > 2\sigma(I)$], R value 0.0504, wR2 = 0.1398. There are two molecules in the asymmetric unit with change of conformation for the phenyl ring and $-CF_3$ group in one of the molecule is disordered. Anisotropic refinement was carried out however the disordered atoms were refined isotropically.

3 Typical Catalytic Reaction Procedure

In a 50 mL two necked round-bottom flask equipped with a magnetic stirrer and oil bath with controlled heating, a solution of desired sulfide, solvent, 30 % aqueous H_2O_2 and Mo-acetylide complex was stirred magnetically at desired temperature. Reaction was monitored by withdrawing the aliquots of samples at regular intervals of time and analyzed by using gas chromatograph (Agilent 6890 Gas Chromatograph equipped with a HP-5 dimethyl polysiloxane capillary column, 60 m length, 0.25 mm internal diameter, 0.25 μm film thickness). Products were also confirmed by GC–MS (GC Agilent 6890N with HP-5 MS 30 m capillary column, MS Agilent 5973 Network MSD) and ^1H and ^{13}C NMR spectra on Bruker AC 200 (200 MHz) spectrometer. Chemical shifts were denoted relative to the solvent residual peak. (^1H: $CDCl_3$-7.27 ppm, TMS 0.0 ppm).

3.1 Catalyst Recycle Study

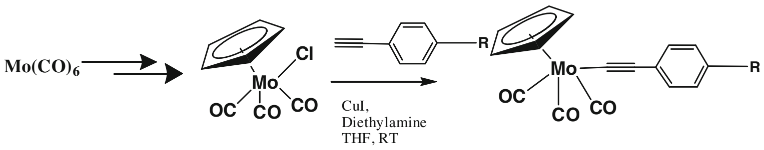
In a typical catalyst recycle experiment, a two necked 50 mL round-bottom flask was charged with thioanisole (1 mmol), 30 % hydrogen peroxide (2 mmol), 10 g solvent and catalyst precursor **1**, **2** or **3** (0.02 mmol). The reaction mixture was stirred at desired temperature till the completion of the reaction. After completion of the reaction, solvent was removed in vacuum. Organic products and unreacted sulfides were extracted in ethyl acetate and further organic phase was treated with sodium sulphate and products were recovered by evaporation of solvent. Catalytically active species ($CpMo(O_2)O(-C{\equiv}CR)$ which are soluble in aqueous phase were separated, concentrated and used for further recycle studies.

CAUTION: Please note that "The molybdenum oxo-peroxo species were found to be pyrophoric if completely dried".

4 Result and Discussion

The complexes $CpMo(CO)_3(-C{\equiv}CPh)$ (**1**), $CpMo(CO)_3(-C{\equiv}C-C_6H_4-p-CF_3)$ (**2**) and $CpMo(CO)_3(-C{\equiv}C-C_6H_4-p-CH_3)$ (**3**) were prepared in two steps as illustrated in Scheme 1. First, $CpMo(CO)_3Cl$ was synthesized from $Mo(CO)_6$ by following the literature procedure [34]. Initially the molybdenum hexacarbonyl [$Mo(CO)_6$] was reacted with the preformed cyclopentadienyl anion to produce the

Scheme 1 General scheme for preparation of molybdenum acetylide complex



where R= H (**1**), CF_3 (**2**), CH_3 (**3**)

intermediate, $CpMo(CO)_3^-Na^+$, which was acidified using acetic acid and the hydride complex thus formed was further treated with CCl_4 (without isolation) to form molybdenum chloride complex $CpMo(CO)_3Cl$. In the second step, the complexes $CpMo(CO)_3(–C{\equiv}CR)$ (R=Ph **1**, C_6H_4–*p*-CF_3 **2**, C_6H_4–*p*-CH_3 **3**) were prepared by Stephens–Castro coupling reaction with corresponding acetylenes in presence of CuI [36]. In brief, the previously synthesized molybdenum chloride complex was treated with phenyl acetylenes in presence of catalytic amount of freshly prepared copper iodide and excess of diethylamine which acts as a solvent as well as base to abstract proton from the acetylene at room temperature. The yield of the complexes varied from 65 to 72 %. The complexes were characterized by various spectroscopic methods. The FTIR peaks showed carbonyl stretching at 1941, 1959, 2035 cm^{-1} for complex **1,** 1938, 1966, 2037 cm^{-1} for complex **2** and at 1936, 1963, 2036 cm^{-1} for complex **3** confirming the presence of metal carbonyls. The FTIR peak at 2103.1, 2103.7 and 2098.4 cm^{-1} respectively for complex **1**, **2** and **3** confirmed the presence of $C{\equiv}C$. The ^{1}HNMR chemical shift at 5.5 ppm (s, 5H) for C*H* proton of cyclopentadienyl group was also present in all the complexes. In addition to this aromatic CH coupling peaks were observed at 7.15–7.38 ppm for complex **1,** at 5.58 (s, 5H, Cp), 7.35–7.49 (m, 4H, C_6H_4) for complex **2** and at δ (^{1}H); 2.23(s, 3H, CH_3), 5.56 (s, 5H, *Cp*), 7.0–7.23 (m, 4H, C_6H_4) for complex **3**. The complexes were also characterized by ^{13}C NMR where characteristic peaks for *Cp* were observed in the range of 92.9–93.3 ppm, acetylene carbons were observed in the range of 108.2–113.6 ppm, phenylic carbons where observed in the range of 124.2–134.2 ppm and carbonyl carbons were observed in the range of 222–238.8 ppm.

The molecular structure of complexes **1** and **2** were unambiguously determined by single crystal X-ray diffraction analysis. Crystals were grown by slow evaporation of acetonitrile at 298 K. ORTEP diagram of complex **1** and **2** is represented in Figs. 1 and 2 respectively. Crystals of **1** belong to monoclinic crystal system, space group $P2_1/c$. Two inverted molecules of compound **1**, come closer with C–H···C (distance being 2.849 Å) bonding and intramolecular C–H···H bonding in the packing of the molecules when viewed down a-axis (see Fig. S1). Two molecules packed in a zigzag manner via a-axis.

Bond lengths (Å): Mo(1)–C(3) 1.980(6), Mo(1)–C(4) 2.292(5), O(2)–C(2) 1.127(6), C(4)–C(5) 1.387(7), C(4)–C(8) 1.393(7), C(5)–C(6) 1.401(7); Bond angles [°]: C(3)–Mo(1)–C(9) 129.1(2), C(9)–C(10)–C(11) 176.9(5), C(3)–Mo(1)–C(5) 96.4(2), C(9)–Mo(1)–C(5) 130.9(2), C(9)–Mo(1)–C(4) 95.78(19).

Crystals of **2** crystallized in monoclinic crystal system with two molecules in asymmetric unit and CF_3 group of one of the molecule is disordered and hence this group is refined isotropically and rest of the molecule is refined anisotropically. The cyclopentadienyl moiety of two symmetry related molecules face opposite to each other when viewed along a-axis. The two symmetry related molecules are packed alternatively in a zigzag manner when viewed down b-axis (see Fig. S2). The overlap of Mo–C–C in two symmetry related molecules of complex **2** shows that the phenyl rings are oriented at 45^o (Fig. 3).

Bond lengths (Å): Mo(1)–C(3) 2.007(6), Mo(1)–C(4) 2.344(7), O(2)–C(2) 1.129(7), C(4)–C(5) 1.376(11), C(4)–C(8) 1.385(10), C(5)–C(6) 1.386(11); Bond angles [°]: C(3)–Mo(1)–C(9) 72.2(2), C(3)–Mo(1)–C(5) 122.5(3), C(9)–Mo(1)–C(5) 82.3(3), C(9)–Mo(1)–C(4) 104.6(3), C(9)–C(10)–C(11) 177.7(6).

Attempts were also made to grow a single crystal of complex **3** by varying the conditions. However the crystals suitable for X-ray study could not be obtained.

To determine the structure of catalytically active species, H_2O_2 was added to alcoholic solution of complexes **1**, **2** and **3** respectively. Within few minutes after the initiation of the reaction, effervescence was observed which could be the liberation of carbonyl ligand as carbon monoxide gas from catalysts [37]. When the effervescence ceased the alcoholic solution was concentrated and the FTIR spectrum of the yellow solid obtained was recorded immediately. The formation of oxo-peroxo complex of molybdenum acetytlide **(1, 2** and **3)** is represented in scheme 2. It was observed that when the completely dried sample was exposed to the atmosphere, it caught fire and due to the pyrophoric nature of the dried sample, the extensive characterization of these intermediates was not possible.

The FTIR spectrum of **1** after addition of H_2O_2 confirmed the formation of oxo-peroxo species. The IR band at 934 cm^{-1} confirmed the presence of Mo=O terminal bond. The band at 854 cm^{-1} corresponds to the O–O stretching vibration of peroxo species. The weak bands at 672 and 574 cm^{-1} can be assigned to the Mo–O_2 (peroxo) asymmetric and symmetric stretching vibrations, respectively. The IR positions for molybdenum oxo and peroxo moieties are in good agreement with the literature reports for various

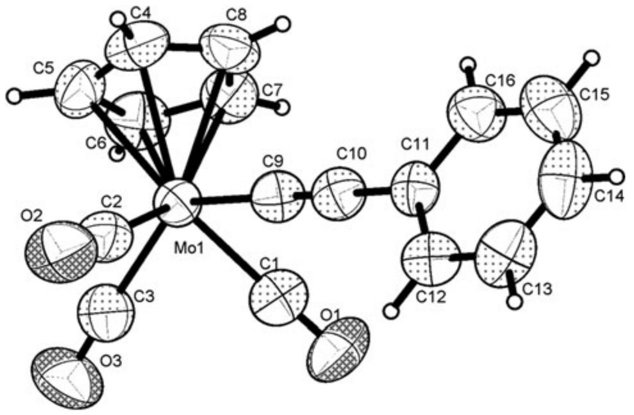


Fig. 1 ORTEP diagram of the complex **1** (Ellipsoids are drawn at 40 % probability)

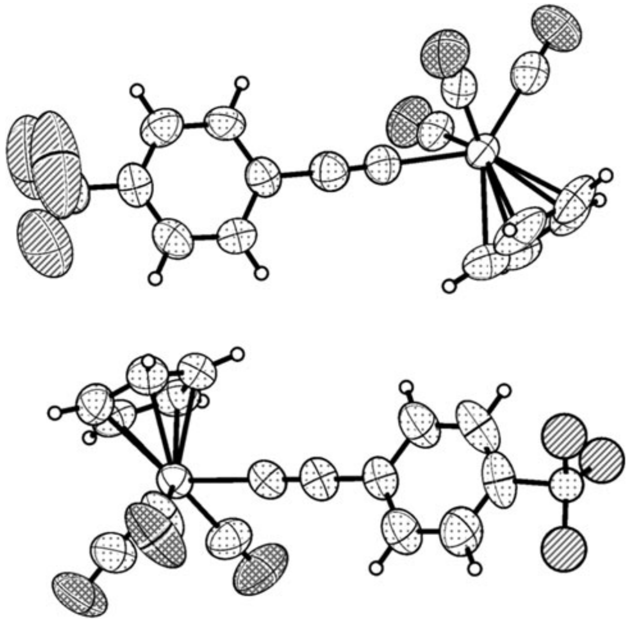


Fig. 2 ORTEP diagram of the compound **2** (Ellipsoids are drawn at 40 % probability)

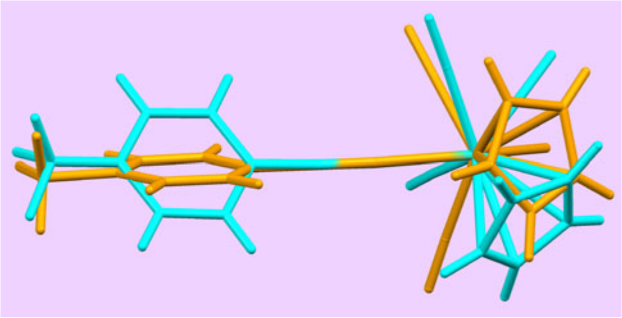
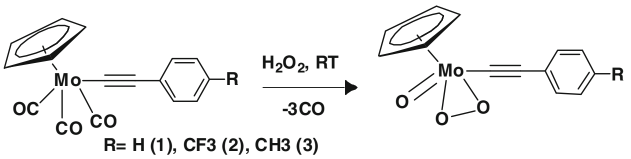


Fig. 3 Overlap of two molecules of complex **2**

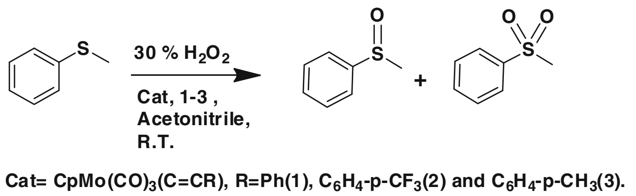


Scheme 2 In situ generation of oxo-peroxo Mo(VI) acetylide complex

molybdenum oxo-peroxo complexes [38, 39]. In all the three cases, the acetylide moiety remained intact even after addition of H_2O_2. However, a marginal shift in IR frequency of the acetylide band was obsvered. The IR frequency of acetylide group in **1** remained unchanged. However, the IR frequency of acetylide band in **2** and **3** shifted to 2112 and 2100 cm^{-1} from 2103 and 2096 cm^{-1}, respectively. The bands due to C–H stretching vibrations of phenyl ring are observed in the range 2854–2955 cm^{-1} and the C=C stretching vibrations of the ring are observed at 1464 and 1377 cm^{-1}. The bands due to carbonyl stretching vibrations in the range of 1935–2035 cm^{-1} disappeared after addition of H_2O_2. This clearly indicates elimination of all the CO ligands after addition of hydrogen peroxide forming higher oxidation state Mo(VI) complex with retention of acetylide moiety attached to Mo centre. Whereas the FTIR band at 930 cm^{-1} confirmes the presence of Mo=O terminal bond in the complex **2** and **3** both. The band at 843 and 849 cm^{-1} corresponds to the O–O stretching vibration of peroxo species and weak bands at 652, 578 and 655, 568 cm^{-1} respectively can be assigned to the Mo–O_2 (peroxo) asymmetric and symmetric stretching vibrations, for **2** and **3** respectively. Thus the structure of the active species formed after addition of H_2O_2 to the acetylide complexes **1–3** was confirmed by FTIR which proved the presence of acetylide moiety, Cp ligand as well as formation of oxo-peroxo species.

4.1 Catalytic Activity

Initially, the catalytic activity of the three complexes **1–3** was compared (Scheme 3) for sulfide oxidation particularly choosing the easily available thioanisole as a model substrate and hydrogen peroxide as an oxidant. When complex **1** was used as catalyst, 56 % thioanisole conversion was obtained with 92 % selectivity for sulfoxide within 2 h of reaction time at room temperature (Fig. 4a). Furthermore, thioanisole was completely (~100 %) consumed in 10 h giving 72 % selectivity for sulfoxide and 28 % for sulfone (Fig. 4a). These results suggest this reaction to be two step; initial oxidation to sulfoxide and in second step further oxidation of sulfoxide to sulfone. Hydrogen peroxide being an electrophilic oxidant, the initial oxidation of the highly nucleophilic sulfide to sulfoxide is an easier process than



Scheme 3 Molybdenum acetylide complexes catalyzed oxidation of thioanisole

the second oxidation of the resulting much less nucleophilic sulfoxide to sulfone which is the rate determining step [40, 41].

When catalyst precursor **2** was used for oxidation of thioanisole with H_2O_2 as oxidant, 64 % conversion was obtained after 2 h with 71 % selectivity for sulfone and the reaction was complete (~100 % conversion) in 7 h with 85 % selectivity for sulfone (Fig. 4b). However, when complex **3** was used as catalyst precursor under identical conditions (Fig. 4c) 100 % conversion of thioanisole was obtained only in 1.5 h; with very high selectivity for sulfone (90 %). When catalyst precursor **1** was used, the rate of reaction was found to be the slowest compared to **2** and **3**.

The reactivity order of the catalysts was found to be **3** > **2** > **1** but the selectivity order for the sulfoxide formation was found to be **1** > **2** > **3** at the complete conversion, which can be related to the substituent on the aryl acetylide. The substituent on phenyl ring of acetylide moiety can lead to the activation of phenyl ring which in turn may affect the catalytic activity of the complexes **2** and **3**. Presently there is no evidence to support the reason for enhancement in the catalytic activity of complex **2** and **3** with electron withdrawing and donating groups respectively compared to **1**.

4.2 Effect of Loading of Catalyst Precursor 1

Oxidation of thioanisole using H_2O_2 without catalyst gave 9 % conversion with 100 % selectivity for sulfoxide. When the catalyst precursor loading was varied gradually from 0.1 to 1 mol % with respect to substrate, the conversion increased gradually from 21 to 100 % in 2 h (Table 1). At lower catalyst precursor loading the selectivity for sulfoxide was higher whereas at high catalyst precursor loading the selectivity for sulfone was maximum (100 % at 0.01 and 0.004 mmol catalyst precursor loading).

4.3 Effect of Hydrogen Peroxide Molar Concentration

The effect of amount of H_2O_2 used on the conversion and the product selectivity was studied at various substrate/H_2O_2 molar ratios in the range of 1:0.5–1:3 (Table 2) for oxidation of thioanisole using complex **1**. Significant difference in the rate of reaction and selectivity pattern was observed with varying amount of H_2O_2. When amount of H_2O_2 was increased, the rate of the reaction was found to increase with decrease in the selectivity for sulfoxide. When one equivalent H_2O_2 was used the reaction was complete in 6 h with 84 % selectivity for sulfoxide (Table 2 entry 2). However when 3 equivalent H_2O_2 was used the reaction was complete in 1 h with only 15 % selectivity for sulfoxide (Table 2 entry 4). Thus the results clearly prove the fact that higher concentration of H_2O_2 enhances the rate of the reaction leading to over oxidation to sulfone as the major product.

4.4 Effect of Type of Solvents on Conversion and Selectivity

The effect of different solvents on thioanisole conversion and product selectivity was studied and the results are given in Table 3.

The use of aprotic solvents like acetonitrile or toluene (Table 3, entries 1 and 4) lead to higher selectivity for sulfone at 100 % conversion. On the other hand, the use of protic solvents like methanol or *tert*-butanol (Table 3, entries 3 and 5) gave sulfoxide as major product. Moreover, dichloromethane (Table 3, entry 2), led to the formation of sulfoxide with high selectivity of 97.5 % at 60 % conversion of sulfide. The choice of solvent was indeed very important as it allowed the tuning of selectivity towards the desired products.

4.5 Scope of Substrate

Wider applicability of the acetylide complex **1** was studied for the oxidation of a range of sulfides containing various functionalities (Table 4). For simple sulfides maximum conversion was achieved in short period of time at room temperature (Table 4, entries 1–4). However for bulky sulfides the maximum conversion was obtained at slightly higher temperature (60 °C or more) (Table 4 entries 5–10). In most of the cases very high selectivity for sulfoxide was obtained under mild reaction conditions. In case of thioanisole electron donating or withdrawing substituents on phenyl ring did not have any adverse effect on conversion as well as sulfoxide selectivity (Table 4, entries 5 and 6 respectively). Tetrahydrothiophene could be oxidized with 100 % conversion at 60 °C in only 2 h (entry 8).

Interestingly, refractory sulfides such as DBT and DMDBT (Table 4 entries 9 and 10 respectively) which are very difficult to remove by HDS, could also be oxidized efficiently using complex **1** and hydrogen peroxide as oxidant. At 100 °C, 100 % DBT conversion was achieved with 80 % selectivity for sulfoxide whereas 75 % conversion with 100 % selectivity for sulfone was achieved for

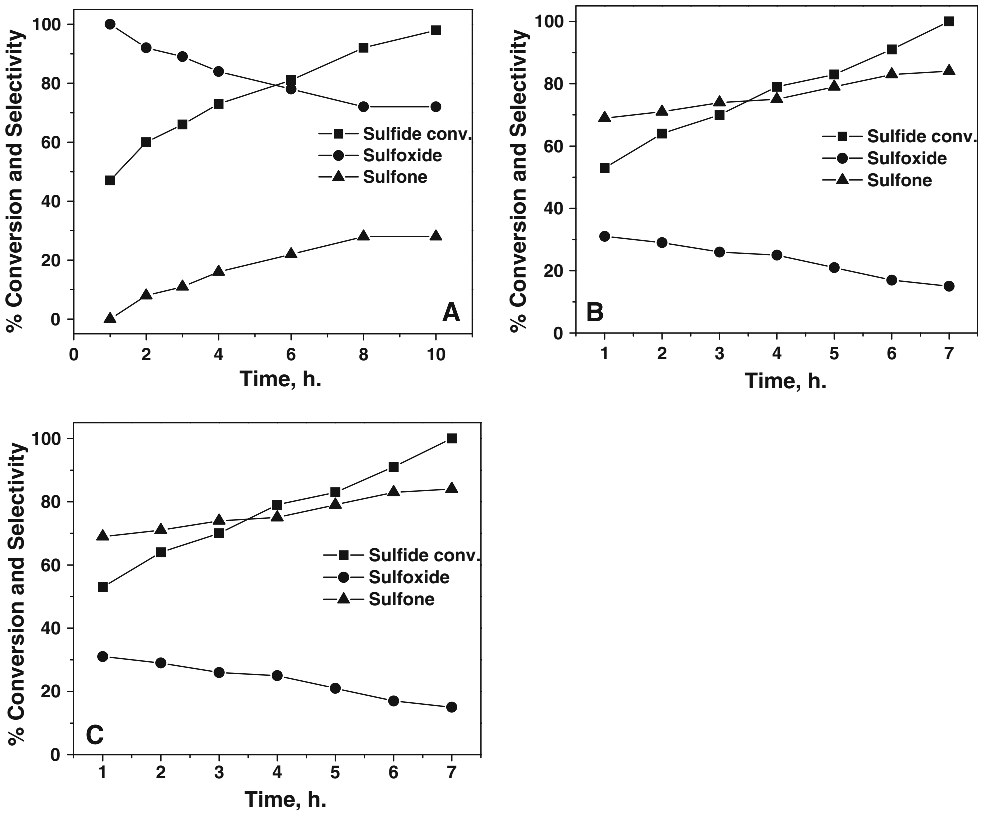


Fig. 4 Thioanisole oxidation with H_2O_2 using catalyst precursors **a 1, b 2, c 3** (reaction conditions: thioanisole: 1 mmol, H_2O_2 (30 %): 2 mmol, catalyst: 0.002 mmol, acetonitrile: 10 g, temperature: RT)

Table 1 Effect of catalyst loading on thioanisole oxidation using precursor **1**

Entry	Catalyst loading, mmol (mol%)	Conversion (%)	Selectivity (%)	
			Sulfoxide	Sulfone
1	Blank	9	100	00
2	0.001 (0.1)	21	100	00
3	0.002 (0.2)	56	92	08
4	0.004 (0.4)	100	47	53
5	0.01 (1)	100	0	100

Reaction conditions Thioanisole: 1 mmol, H_2O_2: 2 mmol, Acetonitrile:10 g, Time: 2 h, Temperature: RT

Table 2 Effect of varying H_2O_2 amount on oxidation of thioanisole using **1**

Entry	H_2O_2 used (mmol)	Time (h)	Conversion (%)	Selectivity (%)	
				Sulfoxide	Sulfone
1	0.5	15	48	93	07
2	1	6	100	84	16
3	2	2	100	47	53
4	3	1	100	15	85

Reaction conditions Thioanisole: 1 mmol, Catalyst precursor: 0.004 mmol, Acetonitrile: 10 g, Temperature: RT

Table 3 Effect of solvents on oxidation of thioanisole using **1**

Entry	Solvent	Conversion (%)	Selectivity (%)	
			Sulfoxide	Sulfone
1	Acetonitrile	100	47	53
2	Dichloromethane	60	97.5	2.5
3	*tert*-Butanol	84	70.5	29.5
4	Toluene	100	0	100
5	Methanol	83	86	14

Reaction conditions Thioanisole: 1 mmol, H_2O_2: 2 mmol, Catalyst precursor: 0.004 mmol, Temperature: RT, Time: 2 h

DMDBT. In case of 4,6-DMDBT, formation of sulfone is desired as the solubility of this sulfone is very low in petroleum feedstock and hence removal from petroleum feedstock becomes easier.

One important aspect of catalyst precursors **1–3** is that even though the complexes are homogeneous in nature, the catalytically active species could be recycled and reused. The recyclability of the catalyst precursors **1–3** was tested for 5 cycles after extracting the catalytically active species in aqueous phase (Table 5) which proves the stability of these catalysts. As the quantity of catalyst precursors used

Table 4 Oxidation of various sulfides with H_2O_2 using complex 1

Entry	Substrate	Time (h)	Conversion (%)	Selectivity (%)	
				Sulfoxide	Sulfone
1	Me_2S	2	100	92	8
2	Et_2S	2	76	68	32
	Et_2S	6	89	70	30
3	Ph_2S	2	64	87	13
		4	86	87	13
4	Methyl *p*-tolyl sulfide[a]	2	62	79	21
		6	100	74	26
5	*p*-Chloro thioanisole[a]	2	55	100	0
		8	100	81	19
6	Benzyl phenyl sulfide[a]	2	65	79	21
		8	100	75	25
7	Tetrahydrothiophene	2	94	7	93
9	DBT[b,c]	10	100	80	20
10	4,6-DMDBT[b,c]	8	75	0	100

Reaction conditions Substrate: 1 mmol; H_2O_2: 2 mmol; Catalyst precursor: 0.002 mmol; Acetonitrile: 10 g; Temperature: RT, [a]60 °C, [b]100 °C; DBT[c]: Dibenzothiophene, DMDBT[c]: 4, 6-dimethyldibenzothiophene

Table 5 Catalysts recycle studies for catalyst precursors **1**–**3**

Cycle	Catalyst **1**[a]			Catalyst **2**[b]			Catalyst **3**[c]		
	Conversion (%)	Selectivity (%)		Conversion (%)	Selectivity (%)		Conversion (%)	Selectivity (%)	
		SO	SO_2		SO	SO_2		SO	SO_2
0	100	0	100	100	0	100	100	0	100
1	100	0	100	99	0	100	99	0	100
2	99	0	100	99	0	100	99	0	100
3	99	0	100	99	0	100	98	0	100
4	99	0	100	98	0	100	98	0	100
5	98	0	100	98	0	100	98	0	100

Reaction conditions Thioanisole: 1 mmol, H_2O_2: 2 mmol, Catalyst: 0.01 mmol, Acetonitrile: 10 g, Temperature: RT, Reaction time for each cycle [a]2 h; [b]1 h; [c]0.5 h, SO: sulfoxide, SO_2: sulfone

in all previous experiments was very less (0.002 mmol), handling of such small quantities of catalyst is difficult during extraction and concentration, hence slightly higher catalyst precursor concentration (0.01 mmol) was used for recycle studies in case of all three acetylide complexes. Due to the higher catalyst concentration used 100 % selectivity for sulfone was obtained with all the three catalysts with difference in the time for completion of the reaction. In case of catalyst precursor **1**, time required for complete conversion was 2 h, in case of **2** it was 1 h whereas with **3** it was only 0.5 h showing the highest catalytic activity of **3**. The difference in product selectivity was prominent only at lower catalyst concentration. In case of all the catalysts precursors the conversion and the product selectivity did not decrease significantly even after five recycles. Hence recycling of these highly efficient homogeneous catalysts is the major achievement of this work.

5 Conclusion

Molybdenum acetylide complexes have been proved to be very efficient catalyst precursors for selective oxidation of various sulfides to sulfoxide or sulfone using H_2O_2 as an oxidant under very mild reaction conditions. The selectivity could be tuned to either sulfoxide or sulfone effectively. Sulfides with various functional groups could be oxidized with high efficiency. The refractory sulfides like DBT and DMDBT were also oxidized to corresponding sulfone. Even though complexes **1–3** are homogeneous; they were successfully recycled for five cycles without appreciable loss in the conversion and selectivity.

6 Supporting Information Available

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 719072 and 719073 for complex **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

1. Greenwood NN, Earnshaw A (1997) Chemistry of the Elements, 2nd edn. Butterworth-Heinemann, Oxford
2. Gorden D (1991) Steering a new course: transportation, energy, and the environment. Island, Washington DC, p 64
3. Venner SF (2000) Int Ed 79:51
4. A study performed for the alliance of automobile manufacturers by MathPro, Inc., October 18, 1999
5. Bharadwaj SK, Sharma SN, Hussain S, Chaudhuri MK (2009) Tetrahedron Lett 50:3767
6. Farhat Ali M, Al-Malki A, El-Ali B, Martinie G, Siddiqui MN (2006) Fuel 85:1354
7. Schulz H, Bohringer W, Ousmanov F, Waller P (1999) Fuel Process Technol 61:5
8. Schulz H, Bohringer W, Waller P, Ousmanov F (1999) Catal Today 49:87
9. Dong K, Ma X, Zang H, Lin G (2006) J Nat G Chem 15:28
10. Song C, Ma X (2003) Appl Catal B Environ 41:207
11. Collins FM, Lucy AR, Sharp C (1997) J Mol Catal A 117:397
12. Wang Y, Lente G, Espenson JH (2002) Inorg Chem 41:1272
13. Lai SKC, Lam KK, Chu M, Wong BC, Hui WM, Hu WH, Lau GK, Wong WM, Yuen MF, Chan AO, Lai CL, Wong JN (2002) Eng J Med 346:2033
14. Sovova M, Sova P (2003) Ces Slov Farm 52:82
15. Kotelanski B, Grozmann RJ, Cohn JNC (1973) Pharmacol Ther 14:427
16. Schmied R, Wang GX, Korth M (1991) Circ Res 68:597
17. Nieves AV, Lang AE (2002) Clin Neuropharmacol 25:111
18. Padmanabhan S, Lavin RC, Durant GJ (2000) Tetra Asym 11:3455
19. Patei S, Rappoport Z (1995) Chemistry of sulfoxides and sulfones. Wiley, New York, p 1357
20. Backvall JE (2004) Modern oxidation methods. Wiley, Weinheim
21. Adam W, Malisch W, Roschmann KJC, Saha-Möller R, Schenk WA (2002) J Organomet Chem 661:3
22. Legtenbarg AGJ, Hage R, Feringa BL (2003) Coord Chem Rev 237:89
23. Bolm C (2003) Coord Chem Rev 237:245
24. Velde FV, Könemann L, Rantwijk FV, Sheldon RA (1998) Chem Commun. 1891
25. Sheldon RA, Van Doorn JA (1973) J Catal 31:427
26. Vinas B (1995) Chem Abstr 123:228183f
27. Madesclaire M (1986) Tetrahedron 42:5459
28. Bonchio M, Carofiglio T, Di Furia F, Fornasier R (1995) J Org Chem 60:5986
29. Gamelas CA, Lourenço TA, Da Costa P, Simplício AL, Royo B, Romão CC (2008) Tetrahedron Lett 49:4708
30. Shiu CW, Su CJ, Pin CW, Chi Y, Peng PSM, Lee GH (1997) J Organomet Chem 151:545
31. Biradar AV, Sathe BR, Dongare MK, Umbarkar SB (2008) J Mol Catal A 285:111
32. Biradar AV, Kotbagi TV, Dongare MK, Umbarkar SB (2008) Tetrahedron Lett 49:3616
33. Biradar AV, Dongare MK, Umbarkar SB (2009) Tetrahedron Lett 50:2885
34. White C, Mawby R (1970) J Inorg Chim Acta 4:261
35. Sheldrick GM (1997) SHELX-97 program for crystal structure solution and refinement. University of Göttingen, Göttingen
36. Stephens RD, Castro CE (1963) J Org Chem 28:3313
37. Abrantes M, Santos AM, Mink J, Kuhn FE, Romao CC (2003) Organometallics 22:2112
38. Fujihara T, Hoshiba K, Sasaki Y, Imamura T (2000) Bull Chem Soc Jpn 73:383
39. Bianchi CL, Porta F (1996) Vacuum 47:179
40. Bonchio M, Conti V, De Conciliis MA, Di Furia F, Ballistreri FP, Tomaselli GA, Toscano RM (1995) J Org Chem 60:4475
41. Adam W, Haas W, Lohray BB (1991) J Am Chem Soc 113:6202