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Half-sandwich molybdenum complexes: molecular structure and catalyst precursors for olefin epoxidation with *tert*-butyl hydroperoxide

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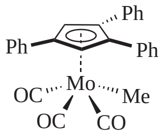
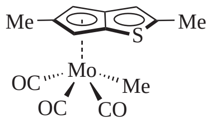
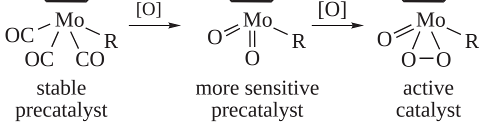
Half-sandwich carbonyl molybdenum complexes with bulky triphenylcyclopentadienyl and cyclopenta[*b*]thienyl ligands have been synthesized, analyzed by X-ray diffraction method and tested as precatalysts in α-olefin epoxidation with *tert*-butyl hydroperoxide.





The epoxidation of α-olefins is an important process from both industrial and academic perspective. The commercial catalytic epoxidation of propylene with *tert*-butyl hydroperoxide is based on various molybdenum precatalysts that are soluble in the reaction mixture.[1,2] Fundamental understanding of the mechanism of catalytic epoxidation of olefins is highly relevant direction of modern catalysis.[3–5]

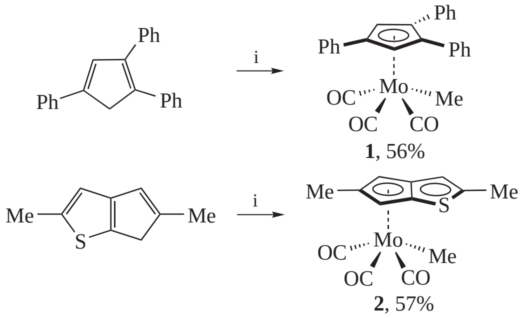
Among Mo complexes, half-sandwich carbonyl derivatives of composition $LMo(CO)_3R$ (L = η^5 cyclopentadienyl-type ligand, R = alkyl) have proven to be efficient olefin epoxidation precatalysts[3,6–11] which once oxidized *in situ* generate the dioxo and peroxo compounds as the actual catalytically active epoxidation species (Scheme 1). The mechanism and catalytic species have been previously described in detail for the olefin epoxidation with Bu^{t}OOH involving $LMo(CO)_3R$ precatalysts.[7,12,13]



Scheme 1

Catalytic activity and selectivity of complexes $LMo(CO)_3R$ are highly dependent on ligand environment at the molybdenum center. There are two feasible ways for $LMo(CO)_3R$ precatalyst design: modification of alkyl substituent R and variations in geometry and electron properties of the η^5-coordinated ligand (see Scheme 1). Efficiency of the first approach was demonstrated in a series of recent publications.[9,14–19] The second approach of the catalyst design by modification of η^5 ligand L is significantly less explored with only a few precatalysts $LMo(CO)_3R$ with L other than η^5-$C_5H_{5-n}R_n$ (R = alkyl) prepared, structurally characterized[20] and studied as epoxidation precatalysts.[6,21–23]

Herein we report on the synthesis and crystal structures of two novel carbonyl complexes $LMo(CO)_3Me$ (L = 1,2,4-triphenylcyclopentadienyl **1** and 2,5-dimethyl-4*H*-cyclopenta[*b*]thienyl **2**) as new olefin epoxidation precatalyst candidates. The orange crystalline complex **1** was obtained *via* a one-pot procedure based on metalation of 1,2,4-triphenylcyclopenta-1,3-diene[24] with BuLi followed by consequent reactions with $Mo(CO)_6$ and then with iodomethane in THF (Scheme 2). Complex **2** was prepared similarly from 2,5-dimethyl-4*H*-cyclopenta[*b*]thiophene[25] as the ligand precursor.



Scheme 2 *Reagents and conditions:* i, BuLi, THF; then $Mo(CO)_6$, MeI.

The molecular structures of compounds **1** and **2** were confirmed by X-ray diffraction analysis. The asymmetric unit of **1** contains one molecule of the complex (η^5-1,2,4-$Ph_3C_5H_2$)Mo(Me)$(CO)_3$ (Figure 1).† The molybdenum coordination number (CN_{Mo}) is 7, taken into account that the Cp ligand is η^5 coordinated and occupies three coordination sites. The C_{Cp}–C_{Cp} bond distances are in the range

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† *Crystal data for* **1**: $C_{27}H_{20}MoO_3$, M = 488.37, monoclinic, space group $P2_1/n$, a = 11.7825(6), b = 7.1720(3) and c = 26.9399(13) Å, β = 101.8255(7)°, V = 2228.21(18) Å^3, Z = 4, d_{calc} = 1.456 g cm^{-3}, $F(000)$ = = 992, μ(MoKα) = 0.986 mm^{-1}, T = 150 K, 2.61° < θ < 30.52°, 26784 reflections measured, 6819 independent reflections (R_{int} = 0.020), R_1 = = 0.027 for 6242 reflections with $I > 2\sigma(I)$, wR_2 = 0.065 for all data, GOF = 1.10, largest diff. peak/hole: 0.86/–0.62 e Å^{-3}.

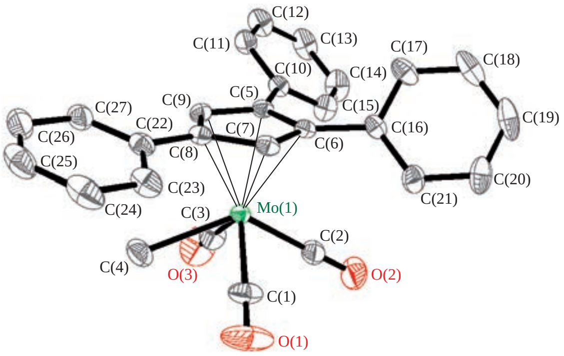


Figure 1 Molecular structure of compound **1** (hydrogen atoms are omitted for clarity, thermal ellipsoids are set to 50% probability level). Selected bond lengths (Å): Mo(1)–C(1) 1.9785(18), Mo(1)–C(2) 1.9842(18), Mo(1)–C(3) 1.9811(18), Mo(1)–C(4) 2.3119(18), Mo(1)–C(5) 2.3518(14), Mo(1)–C(6) 2.3660(14), Mo(1)–C(7) 2.3658(14), Mo(1)–C(8) 2.3696(15), Mo(1)–C(9) 2.3267(15), Mo–$C_{Cp(averaged)}$ 2.356, Mo–$Cp_{(centroid)}$ 2.018(1). Selected bond angles (°): O(1)–C(1)–Mo(1) 173.61(18), O(3)–C(3)–Mo(1) 178.9(2), O(2)–C(2)–Mo(1) 179.40(18); Cp denotes η^5-C_5 ring.

of 1.422(2) to 1.438(2) Å with the averaged value of 1.430 Å. The rotation angles between Cp and Ph planes for two neighbouring phenyl groups (see Online Supplementary Materials) indicates a partial loss of Cp–Ph conjugation, which is induced by non-valence steric interactions in the bulky 1,2,4-$Ph_3C_5H_2$ ligand.

The asymmetric unit of complex **2** consists of two independent molecules (η^5-2,5-$Me_3C_7H_3S$)Mo(Me)$(CO)_3$ (one of molecules is shown in Figure 2).[‡] The CH fragment and S atom are nearly equally disordered over two positions in the 2,5-$Me_3C_7H_3S$ ligand in both molecules (not shown in Figure 2, for details see Online Supplementary Materials). The coordination environment of Mo atom in **2** is very similar to that in **1**; folding angles between 5-membered rings in 2,5-$Me_3C_7H_3S$ ligands are rather small being of 4.6(3)° and 5.7(4)°.

Complexes **1** and **2** along with the benchmark structurally related (η^5-C_5H_5)Mo$(CO)_3$Me **3** and (η^5-C_9H_7)Mo$(CO)_3$Me **4** complexes were tested as catalyst precursors for epoxidation of model oct-1-ene with Bu^{t}OOH (Scheme 3). Preliminary evaluation of their performance shows a clear effect of the ligand on the catalytic activity (in terms of TOF for 2-hexyloxirane formation), while the reaction selectivity is less influenced by the structure of the complex (Table 1).

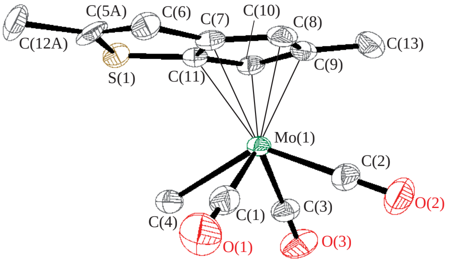
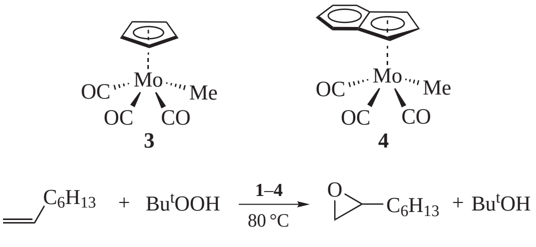


Figure 2 Molecular structure of compound **2** (hydrogen atoms are omitted for clarity, the 2,5-$Me_3C_7H_3S$ ligand disorder is not shown, thermal ellipsoids are set to 50% probability level). Selected bond lengths (Å): Mo(1)–C(1) 1.986(3), Mo(1)–C(2) 1.981(3), Mo(1)–C(3) 1.977(3), Mo(1)–C(4) 2.328(3), Mo(1)–C(7) 2.391(3), Mo(1)–C(8) 2.311(3), Mo(1)–C(9) 2.310(3), Mo(1)–C(10) 2.342(3), Mo(1)–C(11) 2.430(3), Mo–$C_{Cp(averaged)}$ 2.357, Mo–$Cp_{(centroid)}$ 2.022(1), Cp denotes η^5-C_5 ring.



Scheme 3

Table 1 Comparison of catalytic activity of complexes **1**–**4** in epoxidation of oct-1-ene and the main structural parameters for complexes **1**, **2** and previously synthesized **3**.[26,a]

Precatalyst	TOF[b]/h^{-1}	Selectivity towards epoxide[c] (%)	$d_{(Mo–Cp)}$[d]/Å	Angle OC–Mo–CO (average)/deg
1	386	80.5	2.018	88.9
2	617	80.9	2.022	87.6
3	508	80.2	2.007	88.1
4	501	78.8	–	–

[a] Reagents and conditions: oct-1-ene (40.3 g, 360 mmol), Bu^{t}OOH (1.8 g, 20 mmol), Bu^{t}OH (5 ml), nonane (2 ml as an internal standard), Mo precatalyst **1**–**4** (0.01 mmol), 80 °C, 2 h. [b] Estimation, calculated using data for 2 h reaction. [c] GC data shows oct-1-ene-3-ol, oct-3-ene-1-ol and 2,3-epoxyoctene as minor by-products along with other trace compounds; iodometric titration of the reaction mixture shows residual Bu^{t}OOH. [d] Cp is centroid of η^5-ring.

We expected that the strength of η^5-bonding and bulkness of cyclopentadienyl ligand L would affect catalytic activity of LMo$(CO)_3$Me complexes. However, the values of Mo–$L_{(centroid)}$ distances and OC–Mo–CO angles (see Table 1) do not correlate with catalytic activity. We can only note that the distance between the η^5-ligand and the molybdenum atom is maximal in complex **2**. This may be explained by the electron-donor properties of the η^5-ligand in **2** due to the presence of the fused thiophene fragment. We assume that structural data for the true catalytically active molybdenum peroxo species (see Scheme 1) should be used to establish structure–activity relationships for Cp–Mo epoxidation catalysts.

In summary, two half-sandwich molybdenum(II) complexes with 1,2,4-$Ph_3C_5H_2$ and 2,5-$Me_3C_7H_3S$ ligands have been obtained *via* a simple one-pot procedure and their crystal structures have been studied. The complex (η^5-2,5-$Me_3C_7H_3S$)Mo(Me)$(CO)_3$ shows enhanced performance in oct-1-ene epoxidation test over the structurally related (η^5-C_5H_5)Mo$(CO)_3$Me complex reported earlier to be the most productive representative in the series of LMo$(CO)_3$Me precatalysts.[26] This result demonstrates that structural modification of cyclopentadienyl ligand is promising to develop new epoxidation catalysts.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.09.019.

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[‡] *Crystal data for* **2**: $C_{13}H_{12}MoO_3S$, M = 344.23, triclinic, space group $P\bar{1}$, a = 7.9519(8), b = 10.8202(11) and c = 16.6515(17) Å, α = 107.765(1), β = 92.593(2) and γ = 91.198(2)°, V = 1362.1(2) Å^3, Z = 4, d_{calc} = 1.679 g cm^{-3}, $F(000)$ = 688, μ(MoKα) = 0.986 mm^{-1}, T = 150 K, 1.98° < θ < 29.00°, 14771 reflections measured, 7167 independent reflections (R_{int} = 0.022), R_1 = 0.033 for 5623 reflections with $I > 2\sigma(I)$; wR_2 = 0.083 for all data; GOF = 1.05, largest diff. peak/hole: 1.40/–0.69 eÅ^{-3}.

CCDC 1833970 and 1833971 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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