Chiral Schiff base ligated dioxomolybdenum (VI) complexes and their asymmetric catalytic properties in the epoxidation of styrene

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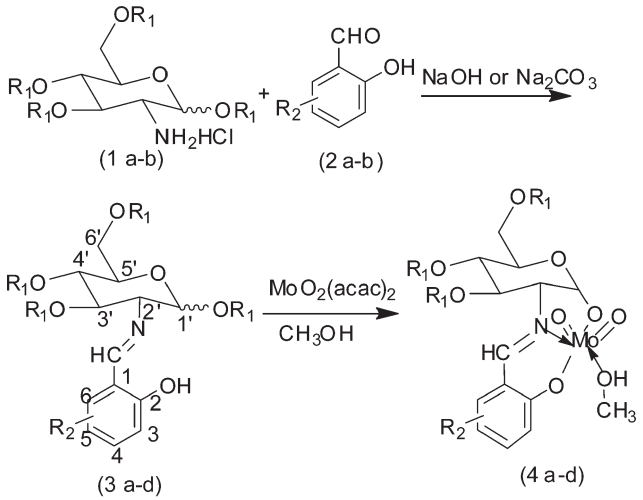
Two series of Schiff base dioxomolybdenum (VI) complexes of the general formula [MoO_2(L)(MeOH)] (L = D-glucosamine-derived Schiff base) have been synthesised, characterised and their asymmetric catalytic activities evaluated through the epoxidation of styrene. The molybdenum complexes with acetyl-protected D-glucosamine Schiff base ligands exhibited higher enanatioselectivity than those with unprotected sugar ligands. Protecting D-glucosamine by acetyl groups is an effective way to improve asymmetric catalytic epoxidation activities.

Keywords: D-Glucosamine, Schiff bases, molybdenum (VI) complex, asymmetric catalysis, epoxidation

During the past few decades, increasing attention has been paid to chiral catalysts for enantioselective epoxidation of olefins for the many applications of chiral epoxides.[1,2] Although a variety of carbon–carbon double bonds such as allylic alcohols and α- and β-unsaturated esters can be catalytically epoxidised with several metal complex catalysts,[3–6] the asmmmetric epoxidation of non-functionalised olefins is still a challenge despite the success of Mn–salen and metalloporphyrin complexes.[7–9]

As a cheap and naturally occurring chiral compound, D-glucosamine has been used to synthesise stable Schiff bases complexes with transition-metal ions such as Fe(III), Co(II), Ni(II), Cu(II) and Mo(VI).[10] Metal complexes derived from carbohydrates are of interest in metal-assisted or metal-catalysed enantioselective synthesis such as cyclopropanation,[11] hydroformylation,[12] hydrogenation[13] and allylic alkylation[14] but the potential of this class of complexes as catalysts for enantioselective epoxidation of olefins still remains sparse.[15,16] We now report four kinds of dioxomolybdenum(VI) complexes with Schiff base ligands derived from D-glucosamine and their catalytic activities for asymmetric epoxidation of styrene. The synthetic routine is shown in Scheme 1.



1a R_1=H; 1b R_1=CH_3CO-;
2a R_2=5-NO_2; 2b R_2=5, 6-benzo;
3a R_1=H, R_2=5-NO_2; 3b R_1=H, R_2=5, 6-benzo;
3c R_1= CH_3CO-, R_2=5-NO_2; 3d R_1= CH_3CO-, R_2=5, 6-benzo;
4a R_1=H, R_2=5-NO_2; 4b R_1=H, R_2=5, 6-benzo;
4c R_1= CH_3CO-, R_2=5-NO_2; 4d R_1= CH_3CO-, R_2=5, 6-benzo.

Scheme 1 Synthetic route to D-glucosamine Schiff base dioxomolybdenum (VI) complexes.

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Results and discussion

The Mo-complexes **4a**–**d** were obtained by the reaction of $MoO_2(acac)_2$ and the corresponding chiral Schiff base ligands **3a**–**d** in methanol. In the IR spectra of **4a**–**d**, the imino (CH=N) bands are shifted compared to the free ligands due to the coordination of the metal to the imine nitrogen.[17] The two bands in the region *ca* 900–920 cm^{-1} and *ca* 920–940 cm^{-1} can be assigned to the symmetric and asymmetric stretching modes of Mo=O double bonds, respectively, indicating the presence of oxo–molybdenum centres[18–20] which is also validated by their Raman spectra. In addition, the values of ν (Mo–N_{imino}) at *ca* 320–370 cm^{-1}, ν (Mo-O_{sugar}) at about 420–480 cm^{-1} and ν (Mo–$O_{phenolic}$) around 286 cm^{-1} were observed in their Raman spectra and gave hint of are consistent with Mo coordination. In the case of the sugar–OH groups being protected by acetyl groups, one of them is selectively deacetylated and coordinated to the metal centre during the reaction process. The possible structures of the complexes are shown in Scheme 1. Analytical data including IR, Raman, NMR, and elemental analysis are in accord with their descriptions as monometallic compounds with one ligand L and a coordinated solvent molecule MeOH.

The enol-imine–keto-amine and the anomeric equilibria of **3a** and **3b** may occur in solution. The ^{1}H NMR spectra of ligands **3a** and **3b** showed two sets of signals (5.0–5.5 and 4.6–4.8 ppm) for H-1 representing α and β-configurations of sugar rings, respectively. In a low field, the signals assigned to the imino-proton (CH=N) appeared as two singlets due to the sugar residue in the α–β equilibrium,[21] and the vinyl proton of the keto-amine tautomer (C=CHN) gave two signals due to the anomeric equilibrium. But these equilibria were not detected in the acetyl protected D-glucosamine ligands (**3c** and **3d**) and complexes **4a**–**d**, which were found to be pure α-configurated compounds.

Catalytic asymmetric epoxidation of styrene

Complexes **4a**–**d** were examined as catalysts in the asymmetric epoxidation of styrene. Blank runs were performed and, as expected, without catalyst, no significant epoxide formation was observed under the applied conditions. The results were listed in Table 1.

As shown in Table 1, the enantiomeric excess (ee) value of **4b** is a little higher than **4a**, the reason may be related to the larger steric hindrance of naphthalene ring, which could increase the rigidity of ligand. Complexes **4c** and **4d** exhibited higher enantioselectivity than those with unprotected sugar ligands **4a** and **4b**, **4d** gave the highest ee value (about 67%). Molybdenum complexes with acetyl protected D-glucosamine Schiff base ligands exhibited higher enantioselectivity than those with unprotected sugar ligands. Although the reason was not very clear, we think that it might be related to the partial

Table 1 The results of catalytic asymmetric epoxidation of styrene by D-glucosamine Schiff base dioxomolybdenum (VI) complexes

Catalyst	Temperature/°C	Time/h	Yield/%	ee/%
4a	30	4	41.2	22.0
	0	6	27.3	23.8
4b	30	4	58.7	28.7
	0	6	42.6	32.1
4c	50	3	74.9	37.2
	30	4	53.3	62.0
	0	6	36.8	62.3
4d	50	3	92.2	47.6
	30	4	79.5	66.5
	0	6	54.0	67.2

dissociation of the complexes in solutions. After partial dissociation, the enol-imine–keto-amine and the anomeric equilibria of ligands **3a** and **3b** could decrease the asymmetric induction, but there were no such side effects for **3c** and **3d** because these equilibria did not exist in the acetyl protected D-glucosamine ligands. In addition, in all the test reactions, ee values gradually increased and yields gradually decreased with decrease of reaction temperature.

Experimental

D-Glucosamine hydrochloride, 5-nitrosalicylaldehyde, and 2-hydroxy-1-napthaldehyde were purchased from Alfa Aesar. Other reagents were analytic grade and used as received. $MoO_2(acac)_2$ was synthesised according to the literature.[22]

C, H and N elemental analysis were carried out on a Perkin-Elmer 2400 elemental instrument. IR spectra were recorded on Spectrum GX using polystyrene as a standard (KBr pellets). FT-Raman spectra were undertaken with a Bruker RFS100/S apparatus using a laser source of Nd/YAG λ=1064 nm of 200 mW and a Ge detector at 77 K. ^{1}H NMR spectra were recorded using a Bruker AV-300 spectrometer. GC analysis was obtained with an HP 6890 gas chromatograph equipped with a capillary column (50.0 m × 320 μm × 1.05 μm nominal) and a FID detector.

Synthesis of Schiff bases

The compound **1b** was obtained from **1a** according to the literature method.[23]

To an aqueous solution of **1a** (or **1b**) (0.1 mol) in NaOH (100 mL, 1.0 mol mL^{-1}) or Na_2CO_3 (100 mL, 0.5 mol mL^{-1}) was added slowly the aromatic aldehyde **2a** (or **2b**) (0.1 mol) in methanol (50 mL) at ice-water bath temperature, and the mixture was then stirred at room temperature overnight. The bright yellow precipitate was filtered and washed with methanol and diethyl ether respectively, recrystallised in methanol and dried *in vacuo*.

3a. Yield, 82.3%. Anal. Calcd for $C_{13}H_{16}N_2O_8$: C, 47.6; H, 4.9; N, 8.5. Found: C, 47.7; H, 5.0; N, 8.7%. ^{1}H NMR (DMSO-d_6) δ (ppm): 8.71 (s, HC=N), 8.55 (d, HC=N), 8.15–7.10 (m, 3H, ArH), 6.82 (s, C=CHN), 6.79 (s, C=CHN), 5.47 (d, H-1´α), 5.22 (d, H-1´α), 4.86 (d, H-1´β), 4.67 (s, H-1´β), 3.75–2.74 (m, sugar ring). IR (KBr matrix, in cm^{-1}) 3521, 3352 (–OH), 1654 (CH=N).

3b. Yield, 80.7%. Anal. Calcd for $C_{17}H_{19}NO_6$: C, 61.2; H, 5.8; N, 4.2. Found: C, 61.5; H, 5.6; N, 4.4%. ^{1}H NMR (DMSO-d_6) δ (ppm): 9.06 (s, HC=N), 8.96 (d, HC=N), 8.12–7.17 (m, 8H, ArH), 7.01 (s, C=CHN), 6.83 (d, C=CHN), 5.37 (s, H-1´α), 5.19 (d, H-1´α), 4.77 (d, H-1´β), 3.75–2.73 (m, sugar ring). IR (KBr matrix, in cm^{-1}) 3477, 3231 (–OH), 1636 (CH=N).

3c. Yield, 88.6%. Anal. Calcd for $C_{21}H_{24}N_2O_{12}$: C, 50.8; H, 4.9; N, 5.6. Found: C, 50.9; H, 5.0; N, 5.8%. ^{1}H NMR (DMSO-d_6) δ (ppm): 8.78 (s, 1H, CH=N), 8.56–7.05 (m, 3H, ArH), 6.23 (d, 1H, $J_{1,2}$ = 9.17 Hz, sugar H-1), 5.66 (t, 1H, J = 9.63 Hz, sugar H-3), 5.01 (t, 1H, J = 9.6 Hz, sugar H-4), 4.30–4.20 (m, 2H, sugar H-6), 4.04 (d, 1H, $J_{1,2}$ = 11.36 Hz, sugar H-5), 3.65 (t, 1H, sugar H-2), 2.03 (s, 9H, acetyl-1, 3, 4), 1.89 (s, 3H, acetyl-6). IR (KBr matrix, in cm^{-1}) 1755 (C=O), 1635 (vs).

3d. Yield, 76.9%. Anal. Calcd for $C_{25}H_{27}NO_{10}$: C, 59.9; H, 5.4; N, 2.8. Found: C, 59.7; H, 5.6; N, 2.9%. ^{1}H NMR (DMSO-d_6) δ (ppm): 12.40 (s, 1H, OH), 8.95 (s, 1H, CH=N), 8.12–7.06 (m, 8H, ArH), 6.20 (d, 1H, $J_{1,2}$=8.37 Hz, sugar H-1), 5.63 (t, 1H, J = 9.25 Hz, sugar H-3), 5.00 (t, 1H, J = 9.6 Hz, sugar H-4), 4.31–4.20 (m, 2H, sugar H-6), 4.05 (d, 1H, $J_{1,2}$ = 10.28 Hz, sugar H-5), 3.60 (t, 1H, sugar H-2), 2.04 (s, 9H, acetyl-1,3,4), 1.85 (s, 3H, acetyl-6). IR (KBr matrix, in cm^{-1}) 1749 (C=O), 1629 (CH=N).

Synthesis of D-glucosamine Schiff base dioxomolybdenum (VI) complexes

4a–**d** were prepared according to the following procedure. One of the Schiff base ligands **3a**–**d** (5 mmol) was dissolved in methanol (80 mL). After complete dissolution, $MoO_2(acac)_2$ (1.64 g, 5 mmol) was added to the yellow solution. The mixture was allowed to react for 4 h at room temperature, and then the volume was reduced to *ca* 10 mL and diethyl ether (20 mL) was added to precipitate the compound as a yellow solid. The solid was washed twice with diethyl ether and dried *in vacuo*.

4a. Yield, 82.7%. Anal. Calcd for $C_{14}H_{18}MoN_2O_{11}$: C, 34.6; H, 3.7; N, 5.8. Found: C, 34.5; H, 3.5; N, 6.3%. ^{1}H NMR (DMSO-d_6) δ (ppm): 8.77 (s, 1H, HC=N), 8.67–7.07 (m, 3H, ArH), 5.65 (d, 1H, J = 3.52 Hz, sugar H-1), 5.62–3.58 (m, 6H, sugar ring H), 1.11 (m, 3H, methanol). IR (KBr matrix, in cm^{-1}) 3373 (–OH), 1637 (CH=N), 946 (Mo=O), 918 (Mo=O).

4b. Yield, 80.5%. Anal. Calcd for $C_{18}H_{21}MoNO_9$: C, 44.0; H, 4.3; N, 2.9. Found: C, 44.6; H, 3.9; N, 3.8%. ^{1}H NMR (DMSO-d_6) δ (ppm): 9.46 (s, 1H, HC=N), 8.34–7.13 (m, 8H, ArH), 5.61 (d, 1H, J = 3.67 Hz, sugar H-1), 4.28–2.72 (m, 6H, sugar ring H), 1.11 (m, 3H, methanol). IR (KBr matrix, in cm^{-1}) 3385 (–OH), 1626 (CH=N), 930 (Mo=O), 905 (Mo=O).

4c. Yield, 76.6%. Anal. Calcd for $C_{20}H_{24}MoN_2O_{14}$: C, 39.2; H, 4.0; N, 4.6. Found: C, 39.5; H, 3.5; N, 4.3%. ^{1}H NMR (DMSO-d_6) δ (ppm): 8.55 (s, 1H, CH=N), 8.34–7.05 (m, 3H, ArH), 6.18 (m, 1H, sugar H-1), 5.77 (d, 1H, J = 8.44 Hz, sugar H-3), 4.93 (m, 1H, sugar H-4), 4.21 (m, 2H, sugar H-6), 4.00 (m, 1H, sugar H-5), 3.68 (m, 1H, sugar H-2), 2.21 (s, 6H, acetyl-3,4), 1.88 (s, 3H, acetyl-6), 1.08 (m, 3H, methanol). IR (KBr matrix, in cm^{-1}) 3468 (–OH), 1753 (C=O), 1630 (CH=N), 944 (Mo=O), 908 (Mo=O).

4d. Yield, 79.8%. Anal. Calcd for $C_{24}H_{27}MoNO_{12}$: C, 46.7; H, 4.4; N, 2.3. Found: C, 46.8; H, 4.6; N, 2.4%. ^{1}H NMR (DMSO-d_6) δ (ppm): 8.77 (s, 1H, CH=N), 8.26–6.98 (m, 8H, ArH), 6.16 (d, 1H, $J_{1,2}$ = 3.61 Hz, sugar H-1), 5.59 (m, 1H, sugar H-3), 4.90 (t, 1H, sugar H-4), 4.30–4.19 (m, 2H, sugar H-6), 3.98 (d, 1H, sugar H-5), 3.65 (t, 1H, sugar H-2), 2.12 (s, 6H, acetyl-3,4), 1.89 (s, 3H, acetyl-6), 1.11 (m, 3H, methanol). IR (KBr matrix, in cm^{-1}) 3447 (–OH), 1748 (C=O), 1631 (CH=N), 942 (Mo=O), 909 (Mo=O).

Catalytic asymmetric epoxidations with Mo-complexes **4a–d**

Epoxidations of styrene by D-glucosamine Schiff base dioxomolybdenum(VI) complexes with cumene hydroperoxide (CHP) as oxidant were carried out according to the following general procedure: a mixture of catalyst (0.003 mmol), styrene (0.08 mol) and 1,2-dichloroethane (5 mL) was placed in a three-necked round-bottomed flask equipped with a condenser and a magnetic stirrer. The mixture was stirred for 5 min at room temperature and then with the addition of CHP (2 mL, *ca* 0.02 mol), the reaction was started. The course of the reactions was monitored by quantitative GC analysis at certain time intervals.

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