Letter

First tungsten complexes with 2′-pyridyl alcoholate ligands: synthesis, structure, and application as novel epoxidation catalysts

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Novel tungsten(VI) complexes of the type $WOCl_3L$ and WO_2L_2 [L = 2′-pyridylalcoholate] are formed from $WOCl_4$ or WO_2Cl_2, respectively, and 2′-pyridyl alcohols; the dioxotungsten(VI) complexes (characterised by X-ray crystallography) can also be obtained from $WO_2(acac)_2$ by ligand exchange; they represent catalysts with remarkable activity and excellent product selectivity in olefin epoxidation.

Recently, we reported the synthesis of new dioxomolybdenum(VI) complexes with 2′-pyridyl alcoholate ligands as catalysts for olefin epoxidation.[1] The objective of further research was to develop an easy and straightforward synthesis of analogous dioxotungsten(VI) complexes starting from easily available materials. The stronger Lewis acidity and the greater thermodynamic barrier to the reduction of W^{VI} *vs.* Mo^{VI} should be beneficial in catalysis. Tungsten(VI) compounds are known for their catalytic activity in olefin oxidation reactions since Milas reported the metal-catalysed dihydroxylation of olefins with H_2O_2 and WO_3 in the 1930s.[2] In recent years, tungstates or tungsten-based heteropoly acids were employed as epoxidation catalysts.[3,4]

Several adducts and chlorine substitution products of $WOCl_4$ have been known since the 1960s.[5] Yamanouchi and Yamada reported six-coordinate trichlorooxotungsten(VI) complexes with bidentate Schiff-base ligands obtained from salicylaldehyde and various amines.[6] To open the field of tungsten complexes with 2′-pyridyl alcoholate ligands, $WOCl_4$ was reacted with either alkyl- or aryl-substituted pyridyl alcohols.† We applied 2-(2′-pyridyl)propan-2-ol as an example for an alkyl-substituted and 9-(2′-pyridyl)fluoren-9-ol for an aryl-substituted ligand. The experiment indicated that the polymeric structure of $WOCl_4$ is broken down easily by these pyridyl alcohols in methylene chloride under mild conditions. Using equimolar amounts of $WOCl_4$ and the respective pyridyl alcohol complexes of the type $WOCl_3L$ are formed in almost quantitative yields. The coloured compounds are moisture sensitive solids. The two complexes trichlorooxo[2-(2′-pyridyl)propan-2-olato-*N*,*O*]tungsten(VI) **1** (yellow) and trichlorooxo[9-(2′-pyridyl)fluoren-9-olato-*N*,*O*]tungsten(VI) **2** (red) were characterised by ^1H and ^{13}C NMR spectra. The chemical shift values of the NMR signals of the protons in *ortho* position to the pyridine nitrogen and the quaternary α-carbon atom related to the hydroxy function are useful indicators for the electronic characteristics of the ligand (Table 1). When the pyridyl alcohol is bound to the $WOCl_3$-unit, the signal of the *ortho* proton is shifted more than 0.5 ppm and the signal of the α-carbon atom is shifted up to 30 ppm to lower field. This effect can be explained by a shift of electron density towards the tungsten atom.

The substitution of further chlorine ligands by a two- or four-fold excess of pyridyl alcohol was not observed under these conditions, obviously due to the lack of a coordination site for an additional nitrogen ligand at the six-coordinate complex $WOCl_3L$. Besides the complexes of the type $WOCl_3L$ only the hydrochlorides of the corresponding pyridyl alcohols were formed due to the reaction with HCl.

The reason for the little number of known dioxotungsten(VI) complexes is the poor availability of suitable starting materials. Literature-known synthetic routes starting from WO_2Cl_2 usually include adducts or ligand exchange reactions.[7–11] McDonell *et al.* also reported the substitution of chlorine with *N*,*N*-dialkylhydroxylamines.[9] In our research we performed the *direct* synthesis of a dioxotungsten(VI) complex with two 2′-pyridyl alcoholate ligands using WO_2Cl_2 as starting material.‡ The reaction of WO_2Cl_2 with two equivalents of 2-(2′-pyridyl)propan-2-ol in refluxing THF afforded dioxobis[2-(2′-pyridyl)propan-2-olato-*N*,*O*]tungsten(VI) **3** in almost quantitative yield.

Since acetylacetonate complexes have proven to be useful in ligand exchange reactions,[1,9–13] we chose $WO_2(acac)_2$ as a moisture-resistant precursor for further complex synthesis with various pyridyl alcohols. The literature-known

Table 1 Representative NMR spectroscopic data

Ligand/complex	δ of (*ortho* H)	δ of (α-C)
Pyridylcarbinol	8.32	64.11
2-(2′-Pyridyl)propan-2-ol	8.50	71.64
Di[4″,4‴-di(methoxy)phenyl](2′-pyridyl)methanol	8.55	80.20
9-(2′-Pyridyl)fluoren-9-ol	8.59	82.68
5-(2′-Pyridyl)-10,11-dihydrodibenzo[*a*,*d*]cycloheptan-5-ol	8.51	80.03
Trichlorooxo[2-(2′-pyridyl)propan-2-olato-*N*,*O*]tungsten(VI) **1**	9.08	99.80
Trichlorooxo[9-(2′-pyridyl)fluoren-9-olato-*N*,*O*]tungsten(VI) **2**	9.26	100.32
Dioxobis[2-(2′-pyridyl)propan-2-olato-*N*,*O*]tungsten(VI) **3**	8.72	85.17
Dioxobis[(2′-pyridyl)methanolato-*N*,*O*]tungsten(VI) **4**	8.56	75.66
Dioxobis{di[4″,4‴-di(methoxy)phenyl](2′-pyridyl)methanolato-*N*,*O*}tungsten(VI) **5**	7.67	94.23
Dioxobis[9-(2′-pyridyl)fluoren-9-olato-*N*,*O*]tungsten(VI) **6**	9.15	96.76
Dioxobis[5-(2′-pyridyl)-10,11-dihydrodibenzo[*a*,*d*]cycloheptan-5-olato-*N*,*O*]tungsten(VI) **7**	7.57	96.55

synthesis[9,10] to obtain $WO_2(acac)_2$ from WO_2Cl_2 was improved by using toluene instead of benzene as solvent and filtering right out of the reaction flask with a drain tube while still refluxing. Thus, the yield reported by Yu and Holm[10] was increased from 44 to 77% and the reaction time was reduced from 48 to 9 h. We obtained dioxotungsten(VI) complexes of the type WO_2L_2 with pyridyl alcoholate ligands from $WO_2(acac)_2$ by ligand exchange with two equivalents of pyridyl alcohol in methanol.§ Depending on the ligand the products precipitate immediately or after reducing the volume of the solvent and yields between 70 and 99% were achieved. We have applied five different pyridyl alcohols and characterised the respective complexes: dioxobis[2-(2′-pyridyl)propan-2-olato-*N*,*O*]tungsten(VI) **3**, dioxobis[(2′-pyridyl)methanolato-*N*,*O*]tungsten(VI) **4**, dioxobis{di[4″, 4‴-di(methoxy)phenyl]-(2′-pyridyl)methanolato-*N*,*O*}tungsten(VI) **5**, dioxobis[9-(2′-pyridyl)fluoren-9-olato-*N*,*O*]tungsten(VI) **6**, dioxobis[5-(2′-pyridyl)-10,11-dihydrodibenzo[*a*,*d*]cycloheptan-5-olato-*N*,*O*]-tungsten(VI) **7**.

These complexes form stable five-membered ring chelates, which was confirmed by ^1H and ^{13}C NMR spectra (Table 1). The signals of the α-carbon atoms of the bound ligands are shifted about 14 ppm to lower field compared to the free pyridyl alcohols. The signals of the *ortho* protons are shifted to lower field in complexes **3**, **4** and **6** and to the opposite direction in complexes **5** and **7**, which might occur due to an electronic interaction between the pyridine ring and the aromatic substituent at the ligand bound to the dioxotungsten(VI) unit. The IR spectra of **3-7** show two peaks at *ca.* 900 and 935 cm^{-1}, reflecting the asymmetric *cis*-dioxo structure, which is described in the literature.[6–11,14] The other peaks correspond to the vibrational signals of the ligands.

Crystals of compound **3** suitable for X-ray diffraction were obtained by adding hexane to a saturated methanol solution. The coordination geometry around the metal centre is similar to analogous molybdenum complexes[1] and can be described best as a distorted octahedron (Fig. 1).¶ The two oxo ligands form a *cis*-dioxo unit whereas each nitrogen atom of the pyridine ring is positioned *trans* to the oxo ligand. The alkoxy functions of the ligands are placed perpendicular to the plane defined by the dioxotungsten(VI) core.

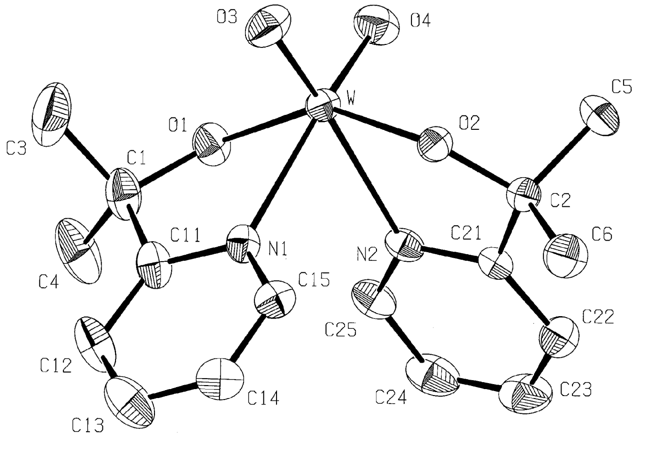

Fig. 1 Structure of **3** with key atoms labelled. Selected bond lengths (Å) and angles (°): W–O(1) 1.934(3), W–O(2) 1.924(2), W–O(3) 1.725(3), W–O(4) 1.740(3), W–N(1) 2.342(3), W–N(2) 2.361(3), O(1)–C(1) 1.426(4), O(2)–C(2) 1.423(4), N(1)–C(11) 1.342(5), N(2)–C(21) 1.338(4), C(1)–C(11) 1.515(6), C(2)–C(21) 1.519(5); O(1)–W–O(2) 149.4(1), O(1)–W–O(3) 103.1(1), 0(1)–W–O(4) 94.8(1), O(1)–W–N(1) 72.0(1), O(1)–W–N(2) 84.2(1), O(2)–W–O(3) 95.7(1), O(2)–W–O(4) 102.9(1), O(2)–W–N(1) 84.6(1), O(2)–W–N(2) 71.5(1), O(3)–W–O(4) 106.2(1), O(3)–W–N(1) 88.9(1), O(3)–W–N(2) 162.2(1), O(4)–W–N(1) 162.1(1), O(4)–W–N(2) 89.1(1), N(1)–W–N(2) 77.8(1), W–O(1)–C(1) 125.0(2), W–O(2)–C(2) 126.5(2), W–N(1)–C(11) 113.2(2), W–N(2)–C(21) 112.9(2), O(1)–C(1)–C(11) 107.4(3), O(2)–C(2)–C(21) 107.7(3), N(1)–C(11)–C(1) 114.4(3), N(2)–C(21)–C(2) 114.5(3).

We have selected complexes **3**, **5**, **6** and **7** and tested them as catalysts (1 mol%) in olefin epoxidation with *tert*-butyl hydroperoxide (oxidant) and *cis*-cyclooctene (substrate) at 70 °C without any addition of solvent. Compound **3** bearing methyl substituents on the ligand achieved the highest yield and quantitative conversion after 60 h whereas compounds **5–7** reached 50–65% conversion. Using 0.1 mol% of **3** 62% conversion was achieved. In all cases 100% selectivity towards the epoxide was obtained. Raising the temperature to 85 °C did not significantly increase the catalytic activities of the complexes. At 60 °C the yields were remarkably lower. We consider bulky ligands and a strong tungsten alkoxy bond in the complex to have a negative influence on the catalytic activity. The strength of the tungsten–alkoxy bond can be estimated by the NMR data of the quaternary α-carbon atom (Table 1). A series of NMR experiments with rising temperature confirms that the tungsten–alkoxy bond is broken during catalysis: **3** and *tert*-butyl hydroperoxide was added to a mixture of DMSO-d_6, C_6D_6 and $CDCl_3$ in an NMR tube. The tube was heated slowly and the ^1H NMR spectra showed both signals of the methylene protons starting to collapse at 70 °C, while the signals of the pyridine ring remain unchanged.

Further studies to optimise the catalytic conditions including the application of molecular oxygen as oxidant, which has successfully been demonstrated for analogous molybdenum complexes,[1] and the development of a synthetic route to dioxotungsten(VI) pyridyl alcoholate complexes from sodium tungstate are in progress.

Notes and references

† *General method* for preparation of complexes of the type $WOCl_3L$: $WOCl_4$ was prepared as reported by Gibson *et al.*[15] 0.73 mmol of the respective pyridyl alcohol were added to a suspension of $WOCl_4$ (0.25 g, 0.73 mmol) in 20 ml CH_2Cl_2 under nitrogen. The resulting coloured solution was heated carefully and stirred for a few minutes. Evaporating the solvent afforded a coloured moisture-sensitive solid, which was dried *in vacuo*. Yield: 0.32 g of **1** (98%), 0.41 g of **2** (98%). Satisfactory elemental analyses (C, H, N, W) were obtained.
Spectroscopic data for **1**: δ_H (CD_2Cl_2) 9.08 (d, 1H, $H^{6'}$, $^3J_{H6',H5'}$ 5.5 Hz), 8.15 (dd, 1H, $H^{4'}$, $^3J_{H4',H5'}$ 7.3 Hz, $^3J_{H4',H3'}$ 8.0 Hz), 7.63 (dd, 1H, $H^{5'}$, $^3J_{H5',H6'}$ 5.5 Hz, $^3J_{H5',H4'}$ 7.3 Hz), 7.52 (d, 1H, $H^{3'}$, $^3J_{H3',H4'}$ 8.0 Hz), 1.78 (s, 6H, $H^{1,3}$); δ_c (CD_2Cl_2) 166.30 ($C^{2'}$), 148.14 ($C^{6'}$), 141.67 ($C^{4'}$), 125.52 ($C^{5'}$), 121.11 ($C^{3'}$), 99.80 (C^2), 26.51 ($C^{1,3}$).
‡ *Preparation* of **3** from WO_2Cl_2 : 2.00 mmol (0.27 g) of 2-(2′-pyridyl) propan-2-ol were added to a suspension of 1.00 mmol (0.29 g) of WO_2Cl_2 in 20 ml THF under nitrogen. After refluxing for a few minutes **3** started to precipitate. The white solid was filtered off, washed with a small amount of cold MeOH and dried *in vacuo*. Yield: 0.44 g of **3** (91%). A satisfactory elemental anlaysis (C, H, N, W) was obtained.
§ *General method* for preparation of complexes of the type WO_2L_2 from $WO_2(acac)_2$: 2.00 mmol of the respective pyridyl alcohol were added to a solution of $WO_2(acac)_2$ (0.41 g, 1.00 mmol) in 25 ml MeOH. Reducing the volume of the solvent to 5 ml affords a white precipitate, which was filtered off, washed with a small amount of cold MeOH and dried *in vacuo*. Yield: 0.48 g of **3** (98%), 0.30 g of **4** (70%), 0.63 g of **5** (76%), 0.73 g of **6** (99%), 0.75 g of **7** (95%). Satisfactory elemental analyses (C, H, N, W) were obtained.
Spectroscopic data for **3**: δ_H ($CDCl_3$) 8.72 (d, 1H, $H^{6'}$, $^3J_{H6',H5'}$ 5.5 Hz), 7.81 (dd, 1H, $H^{4'}$, $^3J_{H4',H5'}$ 7.5 Hz, $^3J_{H4',H3'}$ 8.0 Hz), 7.32 (d, 1H, $H^{3'}$, $^3J_{H3',H4'}$ 8.0 Hz), 7.27 (dd, 1H, $H^{5'}$, $^3J_{H5',H6'}$ 5.5 Hz, $^3J_{H5',H4'}$ 7.5 Hz), 1.85 (s, 3H, $H^{1,3}$), 1.73 (s, 3H, $H^{1,3}$); δ_C ($CDCl_3$) 168.64 (s, $C^{2'}$), 146.35 (d, $C^{6'}$, J_{CH} 182.5 Hz), 139.88 (d, $C^{4'}$, J_{CH} 163.6 Hz), 123.22 (d, $C^{3'}$, J_{CH} 166.1 Hz), 120.39 (d, $C^{5'}$, J_{CH} 157.5 Hz), 85.17 (s, C^2), 30.62 (q, $C^{1,3}$, J_{CH} 126.4 Hz), 27.97 (q, $C^{1,3}$, J_{CH} 127.0 Hz); (KBr pellet): $\nu(WO_2)$ 932, 893 cm^{-1}; Mass spectrum (CI), *m*/*z* 488 ($[M]^+$), 472 ($[WO_3N_2C_{16}H_{20}]$).
Spectroscopic data for further compounds can be requested from the author.
¶ *Crystal data* for **3**: $C_{16}H_{20}N_2O_4W$, $M = 488.19$, orthorhombic, space group *Pbca*, $a = 14.6650(5)$, $b = 14.5373(7)$, $c = 17.1010(6)$ Å, $V = 3645.8(3)$ Å^3, $Z = 8$, $D_c = 1.779$ g cm^{-3}, μ(Mo-Kα) = 6.36 mm^{-1}, $F(000) = 1888$; all crystallographic measurements were made at 193(1) K using a STOE Image Plate Detecting System. A total of

24596 reflections were collected; 3410 independent reflections ($R_{int} = 0.054$) were used in structure refinement; $R_1 = 0.0328$, $wR_2 = 0.0539$, GOF = 0.954 for 3410 reflections and 288 parameters. The contribution of a disordered solvent molecule to the reflection data has been eliminated by the "calc squeeze" option (program: PLATON).[16–19] CCDC reference number 440/075. See http://www.rsc.org/suppdata/njc/1999/5 for crystallographic files in cif format.

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