The first chiral diimido chelate complexes of molybdenum and tungsten: transition metal diimido complexes on the way to asymmetric catalysis

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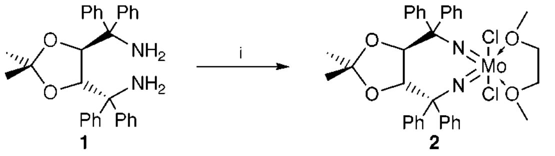
The first complexes [M(TADDAMINat)Cl_2(dme)] (M = Mo (2), W (4)) containing a chiral diimido ligand regime have been synthesized; 2 has been structurally characterized and used as catalyst for C–C and C–N bond formation reactions.

Transition metal imido complexes [$M^{VI}(NR)_2X_2$] have attracted considerable attention as isolobal analogues of group 4 metallocene complexes [$cp_2M^{IV}X_2$].[1] This may well make these diimido complexes, chelating ones in particular, promising alternatives to the well known,[2] highly efficient *ansa*-metallocenes for olefin polymerisation and other C–C or C–N coupling reactions.Although few applications of diimido complexes in catalysis are known,[3] no successful use in enantioselective transformations has been described so far.

Gibson *et al.* first reported chelating bis(arylimido) complexes, one of them revealing a solid state structure of C_2-symmetry.[4] However, this compound was found to be configurationally unstable in solution at room temperature. Here, we present the synthesis of the first chiral C_2-symmetric diimido complexes of molybdenum **2** and tungsten **4** derived from the enantiomerically pure chiral diamine **1**.

Our efforts towards the synthesis of chiral five-membered as well as seven-membered chelate complexes containing sp^2 carbon atoms in the ligand backbone failed, in accordance with the work of Siemeling *et al.*[5] In order to render the system more flexible we decided to use an entirely aliphatic backbone containing only sp^3 carbons in our chelate. The ligand TADDAMIN {(4*S*,5*S*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolan-4,5-dimethanamine} **1** reported by Seebach *et al.*[6] the amine derivative of the TADDOL family, which has proven its high efficiency in asymmetric synthesis,[7] looked very promising to us. Following the well established route for the synthesis of diimido complexes of the type [$Mo(NR)_2Cl_2$(dme)] from Na_2MoO_4 in the presence of $Me_3SiCl–Et_3N$,[3] we obtained [Mo(TADDAMINat)Cl_2(dme)] **2** in 95% yield (Scheme 1).†



Scheme 1 Synthesis of molybdenum complex **2**. *Reagents and conditions*: i, Na_2MoO_4, **1**, Me_3SiCl, Et_3N, dme (Mo : **1** : Me_3SiCl : Et_3N = 1 : 1 : 20 : 20), 12 h, 85 °C.

Crystals of **2** suitable for X-ray structure determination‡ were grown from a saturated toluene solution. Each unit cell contains one solvent molecule (Fig. 1).

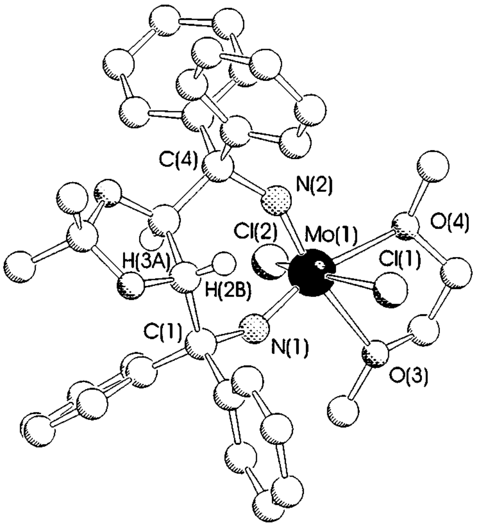
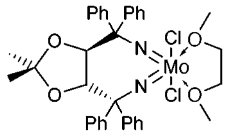
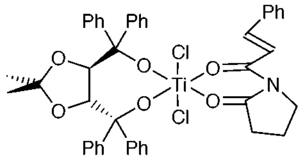


Fig. 1 The molecular structure of [Mo(TADDAMINat)Cl_2(dme)] **2** (toluene omitted for clarity). Selected bond lengths (pm) and angles (°): Mo–N(1) 173.7(2), Mo–N(2) 173.9(3), Mo–Cl(1) 240.7(1), Mo–Cl(2) 240.0(1), Mo–O(3) 236.6(2), Mo–O(4) 238.0(2), C(1)–N(1) 145.8(4), C(4)–N(2) 145.6(5); N(1)–Mo–N(2) 99.52(13), C(1)–N(1)–Mo 148.7(2), C(4)–N(2)–Mo 148.7(2), Cl(1)–Mo–Cl(2) 158.23(4), O(3)–Mo–O(4) 68.91(9).

Group 6 metal complexes of the constraint-geometry [TADDAMINat]$^{4-}$ ligand type are isoelectronically related to the well known [TADDOLat]$^{2-}$ complexes of group 4 metals described by Seebach in ref. 9. Table 1 compares the most important structural features of the structurally characterized titanium TADDOLato complex **3**[10] with its isoelectronic TADDAMINato molybdenum counterpart **2**. Similar bonding distances and bond angles indicate comparable metal ligand π-bonding interactions and similar constraints within the isoelectronic TiO_2 and MoN_2 structural units.

Table 1 Comparison of bond lengths (Å) and angles (°) in the molybdenum complex **2** and the titanium complex **3**

 **2**		 **3**	
Mo≡N	1.74/1.74	Ti≡O	1.76/1.79
Mo—N—C	148.7/148.7	Ti—O—C	147.1/145.2
N—Mo—N	99.5	O—Ti—O	97.2

The analogous tungsten complex [W(TADDAMINat)-Cl_2(dme)] **4** was synthesized following a route used before in our group.[11] Reaction of WO_2Cl_2(dme), prepared *in situ* from $WOCl_4$,[12] with TADDAMIN **1** in the presence of Et_3N and TMSCl gave complex **4** as an off-white solid in 90% yield (Scheme 2).†

Since d^0 imido complexes are excellent Lewis acids, we were interested in the potential of enantiomerically pure **2** in various stereoselective reactions. Recently Leung *et al.* described the successful application of achiral group 6 organoimido com-

$$WOCl_4 \xrightarrow{i} WO_2Cl_2(dme) \xrightarrow{ii} \underset{\mathbf{4}}{[W(TADDAMINat)Cl_2(dme)]}$$

Scheme 2 Synthesis of tungsten complex **4**. *Reagents and conditions*: i, $WOCl_4$ (1 equiv.), $(Me_3Si)_2O$ (1 equiv.), dme, 0 °C followed by 3 h at 40 °C; ii, TMSCl (8 equiv.), Et_3N (5.6 equiv.), **1** (1 equiv.), dme, 6 d, 85 °C.

plexes in the ring opening of epoxides with $TMSN_3$.[13] Here we disclose our first results under non-optimized conditions,[§] using **2** as catalyst for the kinetic resolution of racemic styrene oxide with $TMSN_3$ and the enantioselective trimethylsilylcyanation of benzaldehyde with TMSCN. Whereas the transformation of styrene oxide resulted in up to 30% ee at 100% conversion based on consumed $TMSN_3$ for the reaction of benzaldehyde with TMSCN 20% ee at 100% conversion could be obtained.[14]

As C_2-symmetric complexes of this type are of high interest for the stereoselective polymerisation of α-olefins, we currently are investigating their catalytic potential in this respect.

In conclusion, we present here the first chiral diimido complexes of molybdenum **2** and tungsten **4** and the application of **2** as a catalyst for enantioselective transformations using C–N and C–C bond forming reactions. Currently we are investigating modified ligand systems with sterically more demanding aryl substituents in order to further improve the stereodifferentiation using these complexes as a promising new class of chiral Lewis acid catalysts.

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Notes and references

[†] *Selected spectroscopic data*. For **2**: ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.76 (s, 6H, CH_3), 3.72 and 3.89 (br s, 10H, CH_3, CH_2 dme),[a] 5.21 (s, 2H, CH), 7.20–7.54 (m, 20H, Ar-/Ar′-H). [a]Resolution at 223 K (400 MHz): δ 3.72 (d, 2H, CH_2), 3.81 (s, 6H, CH_3), 3.99 (d, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 27.1 (q, CH_3), 62.6 (q, CH_3 dme), 71.0 (t, CH_2 dme), 80.0 (d, CH), 94.9, 107.7 (s, *C*Ph_2 and *C*Me_2), 127.4, 128.0, 128.2, 128.3, 130.7 (d, Ar-/Ar′-C), 141.7 (s, Ar-C_{ipso}), 142.7 (s, Ar-C'_{ipso}). MS (APCI positive, MeCN): 719 (M + 1). $\alpha_{298} = -207.2$($CHCl_3$, c = 1 g 100 ml^{-1}, T = 298 K).

For **4**: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 0.69 (s, 6H, CH_3), 3.82 and 3.91 (br s, 10H, CH_2, CH_3 (dme)),[a] 5.05 (s, 2H, CH), 7.20–7.53 (m, 20H, aryl-H). [a]Resolution at 223 K (400 MHz): δ 3.79 (d, 2H, CH_2), 3.97 (s, 6H, CH_3), 4.03 (d, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 27.1 (q, CH_3), 55.8 (q, CH_3 dme), 71.3 (t, CH_2 dme), 81.4 (d, CH), 90.3, 107.6 (s, *C*Ph_2 and *C*Me_2), 127.0, 127.1, 127.7, 128.1, 130.7 (d, Ar-/Ar′-C), 144.1 (s, Ar-C_{ipso}), 144.5 (s, Ar-C'_{ipso}).

[‡] *Crystal data* for $C_{42}H_{46}Cl_2MoN_2O_4$ **2**: M = 809.65, monoclinic, space group $P2_1$ (no. 4), a = 1057.2(1), b = 1489.2(1), c = 1251.9(1) pm, β = 91.504(10), $U = 1970.2(4) \times 10^{-30}$ m^3, T = 223(2) K, Z = 2, μ(Mo-Kα) = 0.511 mm^{-1}, F(000) = 840, 6389 reflections measured, 6027 unique (R_{int} = 0.0205) which were used in all calculations. The final $wR(F_2)$ was 0.0838 and $R1$ = 0.0319 (all data). A colorless, irregular quadertype single crystal of **2** (dimensions 0.35 × 0.30 × 0.25 mm), recrystallized from toluene, was used. The structure was solved using direct methods and refined by full matrix least squares on F^2. CCDC 182/1455. See http://www.rsc.org/suppdata/cc/1999/2381/ for crystallographic files in .cif format.

[§] *Conditions for catalytic epoxide ring opening reactions*: styrene oxide: $TMSN_3$: **2** = 2 : 1 : 0.01, 3 d room temp; *regioselectivity*: 1-trimethylsilyloxy-2-azido-2-phenyl ethane : 1-azido-2-phenyl-2-trimethylsiloxy ethane = 85 : 15 [c(**2**) = 6 mM]. *Conditions for catalytic trimethylsilylcyanation reaction*: benzaldehyde: TMSCN: **2** = 1 : 1 : 0.05, 3 d, −25 °C. Enantiomeric excess determined by chiral capillary GLC (CP-Chirasil-Dex CB).

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