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The first bis(imido) transition metal Schiff-base complexes

Majid Motevalli, Bernadeta C. Parkin,* Ramkrishna Ramnauth and Alice C. Sullivan*

*Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London,
UK E1 4NS. E-mail: b.c.parkin@qmw.ac.uk; a.c.sullivan@qmw.ac.uk*

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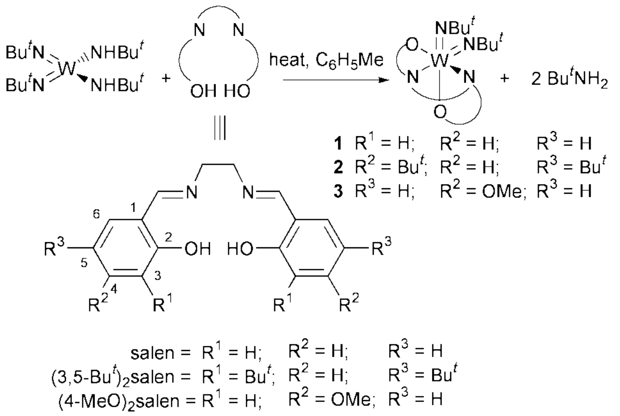
The first bis(imido) transition metal Schiff-base complexes [(Bu^tN)$_2$WL], where L = salen 1, (3,5-Bu^t_2)$_2$salen 2 or (4-MeO)$_2$ salen 3 [salen = dianion of *N*,*N*′-bis(salicylidene)ethane-1,2-diamine, (3,5-Bu^t_2)$_2$salen = dianion of *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)ethane-1,2-diamine and (4-MeO)$_2$salen = dianion of *N*,*N*′-bis(4-methoxysalicylidene)ethane-1,2-diamine] were synthesised by alcoholysis of [W(NBu^t)$_2$($NHBu^t$)$_2$] using the diprotonated Schiff-bases, LH_2, and characterised by ^{1}H and ^{13}C-{^{1}H} NMR for 1–3, and mass spectrometry, elemental analysis, cyclic voltammetry and X-ray crystallography for 2.

Schiff-base complexes are once again topical in connection with a diverse range of applications such as, in organic synthesis,[1–4] as liquid crystals[5] and as heterogeneous catalysts.[6] A variety of geometries are seen in octahedral complexes of the type LMX_2 where L is a tetradentate N_2O_2 donor Schiff base ligand.[7] Specific configurations are particularly influenced by the nature of the backbone between the two imine nitrogens,[8] but also by the substituents on the imine carbons[9] and the phenyl rings[8–10] and the nature of the metal.[11–13] In octahedral complexes of the type LMX_2, where L is the salen ligand, and X is a unidentate ligand, the Schiff-base generally adopts a *trans*-planar geometry[14] (see Fig. 1). The compound [Co(salen)(acac)]·0.7H_2O,[15] however, is a rare example of a structurally characterised β-*cis* salen complex, Fig. 1, and the only one we are aware of. In this case β-*cis* geometry is adopted to accommodate the acac ligand. Recently Moore showed that the presence of a cyclohexyl group in place of ethylene in the backbone, resulted in isolation of the dichlorotitanium complex, $LTiCl_2$, with folded β-*cis* Schiff-base ligand geometry.[7] The *trans*-planar geometry is commonly found for salen complexes of the type LMX_2 with a wide range of σ-donor, weak π-donor and some relatively strong π-donor ligands X.[10–13]

We were interested to learn whether the favoured *trans*-planar geometry for salen complexes would prevail in the presence of two strongly π-donating imido ligands X which generally adopt a mutually *cis*-configuration.[16] The imido ligands in known d^0 Group 6 six-coordinate complexes [(RN)$_2$MX_2L′$_2$] (where L′ is a neutral monodentate donor ligand and X monoanionic monodentate) generally adopt a *cis*-relationship to one another;[16] we note that the *trans*-geometry is found in d^4 *trans*-[Os($NC_6H_3Pr^i_2$-2,6)$_2$(PMe_2Ph)$_2$].[17] The *cis*-configuration in d^0 complexes [(RN)$_2$MX_2L′$_2$] maximises the imido to metal π-interaction. Treatment of [W(NBu^t)$_2$($NHBu^t$)$_2$] in toluene with the diprotonated Schiff-bases LH_2 as shown in Scheme 1 gave complexes, [(Bu^tN)$_2$WL] **1**–**3**.† These were found to adopt the rare β-*cis* geometry. Compounds **1**–**3** are the first examples of bis(imido)transition metal Schiff-base complexes. The folded β-*cis* geometry of the Schiff-base in **2** is almost certainly due to the electronically preferred *cis*-orientation of the imido ligands. Previous experimental and theoretical work indicated that backbones longer than C2 would be required for β-*cis* geometry in compounds of the type LMX_2.[14] The β-*cis* geometry is maintained in toluene solutions even after prolonged heating at 90 °C (monitored by ^{1}H NMR) and the observation of molecular ions in the mass spectrum shows that the molecular structure is present in the gas phase.



Scheme 1

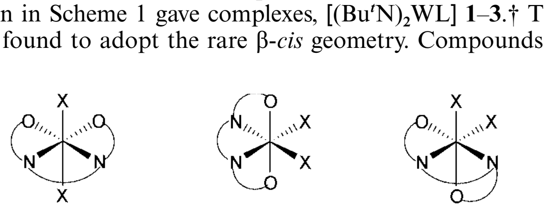

trans isomer α–*cis* isomer β–*cis* isomer

Fig. 1 Possible geometries adopted by metal salen complexes, LMX_2.

An interesting feature of the tungsten compounds **1**–**3** and other six-coordinate bis(imido) complexes [(RN)$_2$MX_2L′$_2$] is their high (20e) formal valence electron count where one electron pair resides on an imido N-centred orbital.[17,18] The electrochemistry of these species appears not to have been investigated. Mayer has recently reported on the electrochemistry of a series of d^2 rhenium–oxo and rhenium–imido complexes containing hydridotris(pyrazol-1-yl)borate ligands where oxidation is from a metal centred orbital.[19] We have observed that d^0 compound **2** readily undergoes a reversible one-electron oxidation process, see Fig. 2.‡ Further studies on this unusual oxidised product will be reported in future papers. To our knowledge similar studies have not been carried out on other 20e bis(imido) complexes [(RN)$_2$MX_2L′$_2$] and this is also part of our current programme.

Solution phase NMR spectroscopy indicates that the folded geometry of the Schiff-base ligand in **2** is also found for the salen complex **1** and the bis(4-methoxy)salen complex **3**. We are currently investigating similar bis(imido) complexes of chromium and molybdenum and in addition similar complexes of Schiff-bases with sterically rigid backbones. The structure of **2**§ is shown in Fig. 3 along with some selected bond lengths and angles, and depicts the distorted octahedral geometry at tungsten in addition to the overall β-*cis* configuration. Angles subtended by mutually *cis*-ligating groups are in the range 72.3(4)–105.8(4)°. The tungsten–imido-nitrogen distances and the approximately linear tungsten–imido units C(1)–N(1)–W(1), 161.9(9)°, C(5)–N(2)–W(1) 175.8(9)° indicate that the imido ligands may be considered to be 6e donors.

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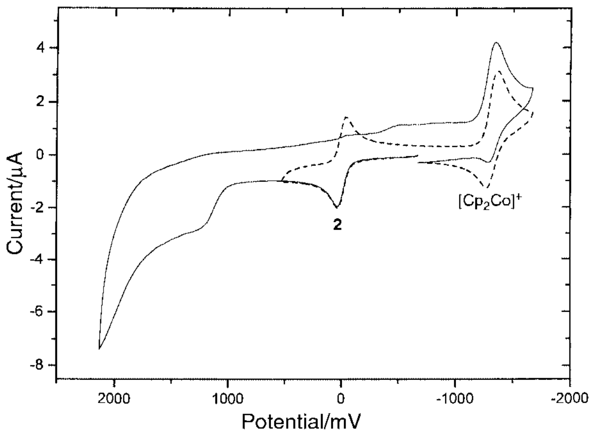

Fig. 2 Cyclic voltammograms of compound **2** in acetonitrile containing 0.05 M $[Bu^t_4N][PF_6]$. Sweep-rate 5000 mV sec^{-1}.

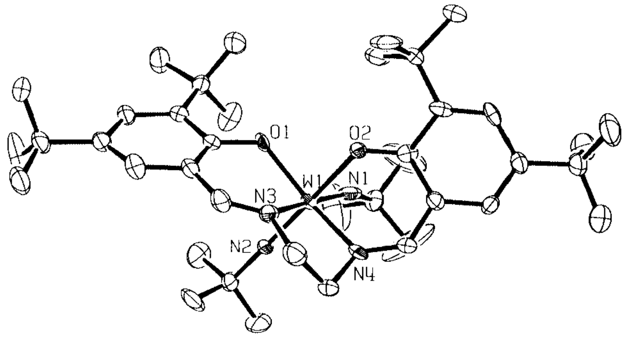

Fig. 3 Molecular structure of **2**, thermal ellipsoids at the 50% probability, hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): W(1)–N(1) 1.750(11), W(1)–N(2) 1.768(9), W(1)–O(1) 1.998(7), W(1)–N(4) 2.140(10), W(1)–O(2) 2.162(7), W(1)–N(3) 2.308(11), N(3)–C(26) 1.266(15), N(3)–C(9) 1.481(15), N(4)–C(11) 1.278(14), N(4)–C(10) 1.465(14), C(9)–C(10) 1.526(18), C(11)–C(12) 1.434(15); N(1)–W(1)–N(2) 105.2(5), N(1)–W(1)–O(1) 105.8(4), N(2)–W(1)–O(1) 98.9(3), N(1)–W(1)–N(4) 98.2(4), N(2)–W(1)–N(4) 96.1(4), O(1)–W(1)–N(4) 147.0(4), N(1)–W(1)–O(2) 88.7(4), N(2)–W(1)–O(2) 165.3(4), O(1)–W(1)–O(2) 81.4(3), N(4)–W(1)–O(2) 77.0(3), N(1)–W(1)–N(3) 168.3(4), N(2)–W(1)–N(3) 83.1(4), O(1)–W(1)–N(3) 80.5(3), N(4)–W(1)–N(3) 72.3(4), O(2)–W(1)–N(3) 82.5(3), C(26)–N(3)–C(9) 119.8(11), C(26)–N(3)–W(1) 122.8(8), C(9)–N(3)–W(1) 114.1(8), C(11)–N(4)–C(10) 118.8(10), C(11)–N(4)–W(1) 125.0(8), C(10)–N(4)–W(1)–113.4(7), C(1)–N(1)–W(1) 161.9(9), C(5)–N(2)–W(1) 175.8(9).

Examination of the bond distances between tungsten and the ligating atoms of the Schiff-base, shows that the *trans*-influence underpins the differences between the two tungsten–oxygen bond distances 1.998(7) Å (*trans*-imine), 2.162(7) Å (*trans*-imido) and the two tungsten–nitrogen bond distances 2.140(10) Å (*trans*-phenoxy), 2.308(11) Å (*trans*-imido).

Spectroscopic evidence (both ^1H and ^{13}C-{^1H} NMR) clearly indicates the folded nature of the salen ligand in solution. The ^1H NMR spectrum of **2** consists of six distinct *tert*-butyl resonances (two from the imido ligands and four from the substituents on the two phenoxide rings) as well as two distinct imine resonances. The most striking features, however, are the three multiplets due to the two methylene groups of the ethylene diamine backbone which display an AA′BB′ pattern. All NMR assignments were confirmed by appropriate 2D-studies and DEPT experiments.

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Notes and references

† Typical procedure: standard Schlenk techniques were employed in the synthesis of $[W(NBu^t_2)_2\{(3,5\text{-}Bu^t)_2salen\}]$ **2**. $H_2(3,5\text{-}Bu^t_2)_2salen$ (0.70 g, 1.42 mmol) in toluene (20 ml) was added dropwise to a solution of $[W(NBu^t)_2(NHBu^t)_2]$ (0.67 g, 1.42 mmol) in toluene (20 ml) and refluxed under nitrogen for 16 hours. The orange reaction mixture was then allowed to cool to room temperature, before the solvent was removed and the crude product dried *in vacuo*. The orange solid was then recrystallised from toluene at 25 °C to produce dark orange crystals of $[W(NBu^t)_2\{(3,5\text{-}Bu^t_2)_2salen\}]$ **2**. 0.68 g, 59% (mp: 209–219 °C) (Found C, 58.54; H, 7.85; N, 6.95. $C_{40}H_{64}N_4O_2W$ requires C, 58.82; H, 7.90; N, 6.86%). ^1H NMR (270 MHz, d_6-benzene): δ 7.61 (d, $^4J_{H\text{-}H} = 2.8$ Hz, 1H, H_6), 7.61 (d, $^4J_{H\text{-}H} = 2.8$ Hz, 1H, H_6), 7.32 (s, 1H, imine-*H*), 6.97 (s, 1H, imine-*H*), 6.84 (s, 2H, H_4), 3.93–3.80 (m, 1H, CH_2), 3.07–2.93 (m, 2H, CH_2), 2.65–2.50 (m, 1H, CH_2), 1.60 (s, 9H, NBu^t), 1.51 (s, 9H, NBu^t), 1.20 (s, 9H, 3-Bu^t), 1.20 (s, 9H, 3-Bu^t), 1.04 (s, 9H, 5-Bu^t), 0.94 (s, 9H, 5-Bu^t). ^{13}C-{^1H} NMR (67.88 MHz, d_6-benzene): δ 169.71 (C_2), 165.71 (*C*=N), 162.94 (C_2), 161.81 (*C*=N), 140.50 (C_1), 139.48 (C_1), 138.01 (C_6), 135.46 (C_6), 129.63 (C_3), 128.12 (C_3), 127.69 (C_5), 125.15 (C_5), 123.74 (C_4), 121.63 (C_4), 65.79 (Me_3CN=), 65.39 (Me_3CN=), 64.83 (CH_2), 60.97 (CH_2), 35.29 (Me_3C), 35.06 (Me_3C), 33.28 (Me_3C), 33.22 (Me_3C), 31.94 (CH_3), 31.39 (CH_3), 30.92 (CH_3), 30.82 (CH_3), 29.74 (CH_3), 29.66 (CH_3). MS (LSIMS) *m*/*z* 817.4615 [M^+]; *m*/*z* calculated for $C_{40}H_{64}N_4O_2W$ 817.4617 [M^+].

Compounds **1** and **3** were prepared in a similar manner by reactions of $[W(NBu^t)_2(NHBu^t)_2]$ with H_2salen or $H_2(4\text{-}OMe)_2salen$ respectively. **1** ^1H NMR (270 MHz, $CDCl_3$): δ 8.27 (s, 1H, imine-*H*), 8.14 (s, 1H, imine-*H*), 7.4–6.6 (six multiplets, 8H, C_6H_4), 4.46 (m, 1H, CH_2), 4.23 (m, 1H, CH_2), 4.01 (m, 1H, CH_2), 3.53 (m, 1H, CH_2) 1.04 (s, 9H, NBu^t), 0.96 (s, 9H, NBu^t). MS (LSIMS) *m*/*z* 593.2122 [M^+]; *m*/*z* calculated for $C_{24}H_{32}N_4O_2W$ 593.2113 [M^+]. **3** ^1H NMR (270 MHz, $CDCl_3$): δ 8.13 (s, 1H, imine-*H*), 8.02 (s, 1H, imine-*H*), 7.16–6.2 (five multiplets, 6H, C_6H_3), 4.36 (m, 1H, CH_2), 4.16 (m, 1H, CH_2), 3.93 (m, 1H, CH_2), 3.83 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.46 (m, 1H, CH_2), 1.06 (s, 9H, NBu^t), 1.01 (s, 9H, NBu^t). MS (LSIMS) *m*/*z* 653.2324 [M^+]; *m*/*z* calculated for $C_{26}H_{36}N_4O_4W$ 653.2302 [M^+].

‡ Compound **2** $E_{1/2} = -0.01$V *vs.* ferrocene–ferrocenium (internal reference $[Cp_2Co]PF_6$, $E_{1/2} = -1.33$V *vs.* ferrocene–ferrocenium).

§ X-Ray data for $C_{40}H_{64}N_4O_2W$, $M = 816.8$, $T = 180(2)$ K, triclinic, space group $P\bar{1}$, $a = 10.760(4)$, $b = 14.371(8)$, $c = 14.981(9)$ Å, $\alpha = 114.95(5)°$, $\beta = 84.79(5)$, $\gamma = 98.11(5)°$, $U = 2078.1(19)$ Å^3, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 2.814$ mm^{-1}, reflections collected 7290, independent reflections 7290 [$R(\text{int}) = 0.0268$], final R indices [$I > 2\sigma(I)$], $R1 = 0.0659$, $wR2 = 0.2139$, R indices (all data) $R1 = 0.0752$, $wR2 = 0.2232$. CCDC reference number 186/2077. See http://www.rsc.org/suppdata/dt/b0/b005043l/ for crystallographic files in .cif format.

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