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Bridged bis(imido)molybdenum complexes: isolobal analogues of *ansa*-zirconocenes and bizirconocenes

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The first complexes containing chelating bis(imide) ligands and a novel dinuclear bis(imido) derivative have been synthesized and characterised by X-ray crystallography.

The isolobal relationship between the metal–ligand fragments $(cp)_2Zr$ (cp = η^5-C_5H_5) and $(RN)_2Mo$ has been firmly established by quantum-chemical calculations and by experimental studies.[1] As a modification of the zirconocene system, *ansa*-zirconocene derivatives have received much attention over the past few years owing to their special (stereo-) chemical properties, which have proved useful for catalytic processes such as α-olefin polymerisation.[2] Although of great intrinsic interest, no corresponding isolobal analogues containing a bridged chelating bis(imide) ligand attached to a metal centre have been reported to date. Here, we describe the first examples of such compounds together with a closely related dinuclear species which contains bridging (instead of chelating) bis(imide) ligands and corresponds to Group 4 bimetallocenes that have been developed only recently.[3]

Since the now well established one-pot method for converting sodium molybdate into bis(imido) complexes of the type $[Mo(NR)_2Cl_2(dme)]$ (dme = 1,2-dimethoxyethane) is known to tolerate a variety of R groups,[4] it seemed possible that, by judicious choice of a diamine, chelated bis(imido)molybdenum complexes should also be accessible. The reaction of Na_2MoO_4 with the diamines **Ia** and **Ib** under standard conditions did indeed give the corresponding mononuclear bis(imido) complexes **1a** and **1b** in high yields† (Scheme 1).

The molecular structures of both compounds were investigated by single-crystal X-ray diffraction studies‡ (Fig. 1). Their core geometry is best described as distorted octahedral with *cis*-chelating bis(imide) and dme ligands and a *trans* arrangement of the chloride ligands. Compound **1a** has a molecular (and crystallographic) mirror plane, which contains the molyb-

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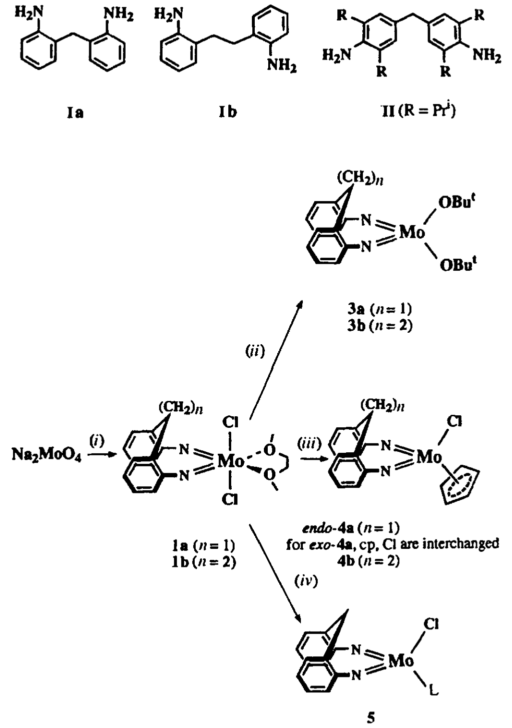
† Satisfactory elemental analyses have been obtained. Selected NMR spectroscopic data: compound **1a**, ^{1}H ($CDCl_3$) δ 3.55 (d, 1 H, CH_aH$_b$, ^2J = 13.0), 3.94 (br s, 10 H, dme), 5.40 (d, 1 H, CH$_a$$H_b$, ^2J = 13.0), 6.87–6.89 (m, 2 H, aryl H), 7.04–7.16 (m, 4 H, aryl H) and 7.47–7.50 (m, 2 H, aryl H); ^{13}C-{^{1}H} ($CDCl_3$) δ 34.7 (CH_2), 62.9 (OCH_3), 71.3 (OCH_2), 119.5, 126.4, 128.6, 129.7 (=CH), 150.0 (=*C*CH_2) and 154.9 (CN); **1b**, ^{1}H ($CDCl_3$) δ 3.14 (s, 4 H, aryl CH_2), 4.01 (br s, 4 H, OCH_2), 4.10 (br s, 6 H, OCH_3), 7.11–7.22 (m, 6 H, aryl H) and 7.34–7.37 (m, 2 H, aryl H); ^{13}C-{^{1}H} ($CDCl_3$) δ 34.8 [$(CH_2)_2$], 64.3 (OCH_3), 71.6 (OCH_2), 124.0, 126.0, 129.4 (=CH), 145.2 (=*C*CH_2) and 154.4 (=CN); **2**, ^{1}H ($CDCl_3$) δ 1.28 (d, 48 H, $^3J_{HH}$ 6.8, CH*Me*$_2$), 3.23 (br s, 4 H, OCH_2), 3.40 (br s, 6 H, OCH_3), 3.82 (s, 4 H, CH_2), 4.26 (2 × sept, 8 H, $^3J_{HH}$ = 6.8, C*H*CMe$_2$) and 6.92 (s, 8 H, aryl H); **3a**, ^{1}H (C_6D_6) 1.26, 1.37 [2 s, 2 × 9 H, $C(CH_3)_3$], 3.51 (d, 1 H, CH_aH$_b$, ^2J = 12.9), 4.76 (d, 1 H, ^2J = 12.9, CH$_a$$H_b$) and 6.78–7.28 (m, 8 H, aryl H); ^{13}C-{^{1}H} (C_6D_6) δ 31.3, 31.8 [C(*C*H$_3$)$_3$], 36.5 (CH_2), 80.0, 80.2 [*C*(CH$_3$)$_3$], 119.0, 125.7, 129.3, 129.6 (=CH), 142.8 (=*C*CH_2) and 155.0 (=CN); **3b**, ^{1}H ($CDCl_3$) δ 1.36 [s, 18 H, $C(CH_3)_3$], 2.89 [s, 4 H, $(CH_2)_2$], 7.04–7.09, 7.13–7.16, 7.20–7.25 and 7.35–7.38 (4 m, 4 × 2 H, aryl H); ^{13}C-{^{1}H} ($CDCl_3$) δ 31.8 [C(*C*H$_3$)$_3$], 34.2 [$(CH_2)_2$], 81.3 [*C*(CH$_3$)$_3$], 121.9, 125.0, 126.2, 129.0 (=CH), 138.8 (=*C*CH_2) and 154.2 (=CN); **4a**, ^{1}H ($CDCl_3$) δ 3.54 (m, 2 H, *exo-/endo*-CH_aH$_b$), 4.54, 5.16 (2 d, 2 × 1 H, *exo-/endo*-CH$_a$$H_b$, ^2J = 12.9), 6.47, 6.58 (2 s, 2 × 5 H, cp), 6.67–6.70, 6.83–6.86, 6.90–6.95 (3 m, 3 × 2 H, aryl H), 7.07–7.17 (m, 6 H, aryl H), 7.41–7.44 and 7.50–7.53 (2 m, 2 × 2 H, aryl H); ^{13}C-{^{1}H} (C_6D_6) δ 35.4, 36.2 (CH_2), 110.4, 110.6 (cp), 119.1, 120.3 (=CH), 147.3, 147.8 (=*C*CH_2), 155.9 and 157.5 (=CN); **4b**, ^{1}H ($CDCl_3$) δ 2.88 (d, 2 H, CH_aH$_b$, ^2J = 7.8), 3.22 (d, 2 H, CH$_a$$H_b$, ^2J = 7.8), 6.47 (s, 5 H, cp), 7.02–7.05, 7.09–7.14, 7.21–7.26 and 7.30–7.33 (4 m, 4 × 2 H, aryl H); ^{13}C-{^{1}H} ($CDCl_3$) δ 34.4 (CH_2), 109.9 (cp), 123.0, 126.5, 128.1, 129.2 (=CH), 141.0 (=*C*CH_2) and 155.4 (=CN); **5**, ^{1}H ($CDCl_3$) δ 1.45, 2.40 (2 s, 2 × 3 H, CH_3 of dmpz), 2.44, 2.70 (2 s, 2 × 6 H, CH_3 of dmpz), 3.63 (d, 1 H, ^2J = 12.8, CH_aH$_b$), 5.65 (s, 1 H, CH of dmpz), 5.87 (s, 2 H, CH of dmpz), 6.10 (d, 1 H, ^2J = 12.8 Hz, CH$_a$$H_b$), 6.70–6.72 (m, 2 H, aryl H), 7.03–7.12 (m, 4 H, aryl H) and 7.60–7.62 (m, 2 H, aryl); ^{13}C-{^{1}H} ($CDCl_3$), inequivalent pyrazolyl rings A and B (ratio 2:1), δ 12.5 (A)/13.3 (B) (5-CH_3), 13.4 (B)/14.8 (A) (3-CH_3), 35.2 (CH_2), 106.6 (A)/106.7 (B) (C^4), 120.5, 126.2, 127.7, 130.0 (aryl =CH), 143.3 (A)/145.6 (B) (C^3), 152.8 (A)/152.9 (B) (C^5), 153.0 (=*C*CH_2) and 156.1 (aryl =CN).

‡ For all three structures data were collected on a Siemens SMART CCD area-detector diffractometer with Mo-Kα radiation (λ = 0.710 73 Å) at 160 K (190 K for **1b**). Each data set was at least a hemisphere to 25° in θ, and semiempirical absorption corrections were applied, based on redundant and symmetry-equivalent reflections. The structures were solved by heavy-atom methods (direct methods for **2**) and refined by full-matrix least-squares techniques based on F^2 with statistical weights. Disorder in some ligands (especially dme) was refined with the assistance of geometrical and displacement parameter restraints; anisotropic displacement parameters were refined for non-hydrogen atoms, and isotropic H atoms were constrained with a riding model. Compound **1a**: $C_{17}H_{20}Cl_2MoN_2O_2$, $M = 451.2$, orthorhombic, space group *Pnma*, $a = 14.479(3)$, $b = 12.167(3)$, $c = 10.540(2)$ Å, $U = 1856.9(7)$ Å^3, $Z = 4$, $D_c = 1.614$ g cm^{-3}, $\mu = 1.006$ mm^{-1}, $F(000) = 912$; 4617 reflections measured, 1664 unique ($R_{int} = 0.106$), 133 refined parameters, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}} = 0.1608$, conventional $R = 0.0763$ for F values of 1096 reflections having $F_o^2 > 2\sigma(F_o^2)$, goodness of fit $S = 1.136$ on F^2, largest difference peak and hole 0.87 and −0.94 e Å^{-3}. Compound **1b**: $C_{18}H_{22}Cl_2MoN_2O_2$, $M = 465.2$, orthorhombic, space group $P2_12_12_1$, $a = 10.4222(7)$, $b = 13.6127(9)$, $c = 13.9744(9)$ Å, $U = 1982.6(2)$ Å^3, $Z = 4$, $D_c = 1.559$ g cm^{-3}, $\mu = 0.944$ mm^{-1}, $F(000) = 944$; 10 763 reflections measured, 3943 unique ($R_{int} = 0.023$), 238 refined parameters, $wR2 = 0.0429$, conventional $R = 0.0170$ for F values of 3863 reflections having $F_o^2 > 2\sigma(F_o^2)$, $S = 1.092$, largest difference peak and hole 0.21 and −0.26 e Å^{-3}. Compound **2**·3dme: $C_{70}H_{118}Cl_4Mo_2N_4O_{10}$, $M = 1509.4$, orthorhombic, space group *Pbcn*, $a = 10.7881(8)$, $b = 34.378(3)$, $c = 21.338(2)$ Å, $U = 7913.7(10)$ Å^3, $Z = 4$, $D_c = 1.267$ g cm^{-3}, $\mu = 0.505$ mm^{-1}, $F(000) = 3192$; 31 411 reflections measured, 6778 unique ($R_{int} = 0.054$), 463 refined parameters, $wR2 = 0.1843$, conventional $R = 0.0732$ for F values of 4907 reflections having $F_o^2 > 2\sigma(F_o^2)$, $S = 1.097$, largest difference peak and hole 0.71 and −0.51 e Å^{-3}. Programs:[5] Siemens SMART, SAINT and SHELXTL, and local programs. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/314.



Scheme 1 (*i*) NEt_3, $SiMe_3Cl$, dme, 90 °C, diamine (**Ia** or **Ib**), 12 h; (*ii*) $KOBu^t$, tetrahydrofuran (thf), −78 °C; (*iii*) Li(cp), thf, −78 °C; (*iv*) KL [L = $HB(dmpz)_3$, dmpz = 3,5-dimethylpyrazolyl], thf, reflux, 12 h

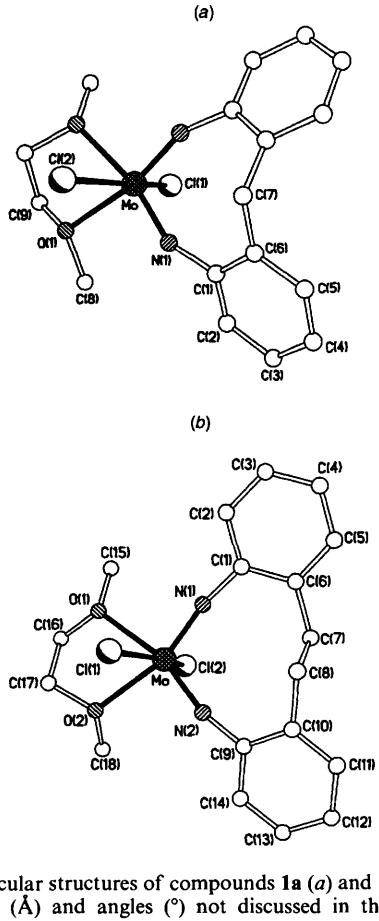


Fig. 1 Molecular structures of compounds **1a** (*a*) and **1b** (*b*). Selected bond lengths (Å) and angles (°) not discussed in the text: for **1a**, Mo–Cl(1) 2.412(3), Mo–Cl(2) 2.414(3), Mo–O(1) 2.331(7) and C(1)–N(1) 1.390(10); Cl(1)–Mo–Cl(2) 160.97(12), O(1)–Mo–O(1a) 70.8(4) and C(6)–C(7)–C(6a) 118.1(10); for **1b**, Mo–Cl(1) 2.3929(6), Mo–Cl(2) 2.4145(5), Mo–O(1) 2.359(2), Mo–O(2) 2.3387(13), C(1)–N(1) 1.385(2) and C(9)–N(2) 1.383(2); Cl(1)–Mo–Cl(2) 160.43(2) and O(1)–Mo–O(2) 69.93(5)

denum atom, the two chlorine atoms and also the methylene carbon atom of the bis(imide) ligand. Compound **1b** has molecular (but non-crystallographic) C_2 symmetry; the axis contains the Mo atom, the centre of the dme C–C bond and the centre of the ethanediyl bridge. The C–N–Mo angles in **1a** are both 155.4(7)°, which is at the low end of the range typical of 'linear' imide ligands;[*] the corresponding angles for **1b** are 168.02(14)° at N(1) and 165.04(14)° at N(2). The N–Mo–N 'bite angle' is 100.8(5)° for **1a** and 107.13(7)° for **1b**. The Mo–N bond lengths are 1.725(7) Å for **1a** and 1.747(2) [to N(1)] and 1.754(2) Å [to N(2)] for **1b**, respectively; these values are in accord with the expected formal bond order of 2.5 for the Mo–N bonds.

The structure of compound **1a** seems to be rigid in solution: in the ^1H NMR spectrum the two protons of the methylene bridge give rise to two doublets centred at δ 3.19 and 5.72 (^2J = 13.0 Hz) in [$^2H_8$]toluene (δ 3.55 and 5.40 respectively in $CDCl_3$), and the spectrum remains virtually unchanged up to 110 °C. This is in marked contrast to the behaviour of **1b**: owing to the flexibility of the ethanediyl bridge of the bis(imide) ligand, a single averaged signal is observed for the four protons of the bridge (δ 3.14) at room temperature (CD_2Cl_2 solvent). The underlying dynamic process is slowed at low temperature, however, to a rate comparable with the NMR time-scale: cooling the sample to −10 °C results in severe broadening of the singlet resonance which eventually collapses into two new broadened signals at −70 °C.

In contrast to the reaction of sodium molybdate with the *ortho*-bridged diamines **Ia** and **Ib**, reaction with the *para*-bridged diamine **II** yields the dinuclear complex **2**, the molecular structure of which was determined (Fig. 2). The molecule contains two Mo atoms, each in a pseudo-octahedral ligand environment. The Mo atoms are linked *via* two *cis*-bridging bis(imide) ligands and are each co-ordinated by a *cis*-chelating dme and two chloride ligands in a *trans* arrangement. In addition to the precise crystallographic C_2 axis passing through both Mo atoms, a non-crystallographic C_2 axis bisects the bridging ligands, passing through the two CH_2 groups, and another lies perpendicular to these two, containing no atoms; the molecule thus has approximate D_2 (222) symmetry. The bond parameters of compound **2** are unexceptional. The Mo–N bond lengths [1.736(4) for Mo(1) and 1.742(4) Å for Mo(2)] and C–N–Mo angles [161.7(4) for Mo(1) and 161.1(4)° for Mo(2)] are in the range typical of 'linear' imido complexes with a formal Mo–N bond order of 2.5.[7,8] The N–Mo–N 'bite angles' are 102.6(3) and 103.0(3)° for Mo(1) and Mo(2), respectively. Although quite a number of dinuclear complexes containing bridging bis(imide) ligands are known,[9] **2** constitutes the first example of a species containing two such groups, which renders the complex an isolobal analogue of a bizirconocene.

We have started to study the chemical reactivities of compounds **1a** and **1b** towards various nucleophiles (Scheme 1). Both react cleanly with $KOBu^t$ to give the corresponding four-co-ordinate species **3a** and **3b**. Their reaction with Li(cp) affords **4a** and **4b**. With this reagent a single isomer is obtained for the ethanediyl-bridged species **4b**, whereas an *exo* and an *endo* isomer are obtained in a 1 : 1 ratio for the methylene-bridged compound **4a**. With the much bulkier tris(3,5-dimethylpyrazol-1-yl)borate ligand L only the sterically more favourable *endo* isomer of **5** is isolated. These and related reactivity studies will be discussed more fully in a future publication.

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[*] Variations in the angle at nitrogen for 'linear' imide ligands between *ca.* 150 and 180° are primarily due to interligand interactions and crystal-packing forces.[6a] This is in accord with quantum-chemical calculations, which indicate a very shallow potential energy well for such ligands with respect to these variations.[6b,c]

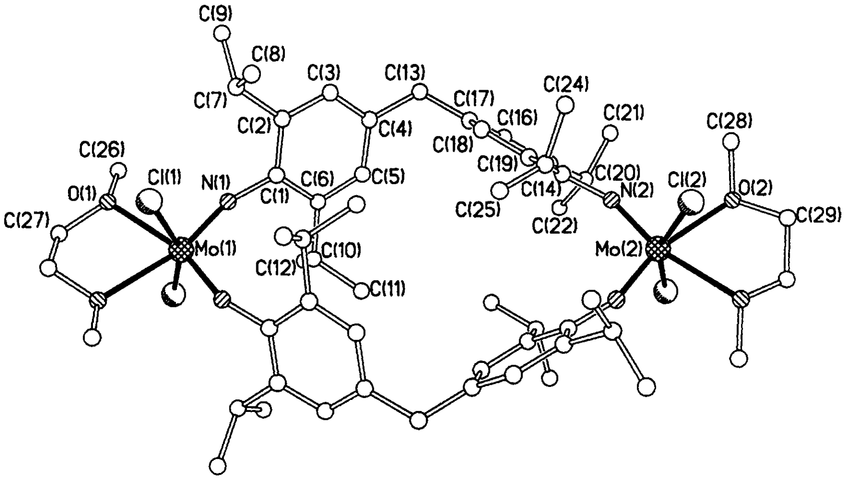

Fig. 2 Molecular structure of compound **2**. Selected bond lengths (Å) and angles (°) not discussed in the text: Mo(1)–Cl(1) 2.397(2), Mo(2)–Cl(2) 2.408(2), Mo(1)–O(1) 2.349(5), Mo(2)–O(2) 2.347(4), C(1)–N(1) 1.396(7) and C(14)–N(2) 1.406(7); Cl(1)–Mo(1)–Cl(1a) 157.33(9), O(1)–Mo(1)–O(1a) 71.0(3), Cl(2)–Mo(2)–Cl(2a) 157.01(9) and O(2)–Mo(2)–O(2a) 70.5(2)

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