Bent *versus* linear imido ligands in five-co-ordinate molybdenum complexes†

Vernon C. Gibson,*,*a* Edward L. Marshall,*a* Carl Redshaw,*a* William Clegg*b* and Mark R. J. Elsegood*b*

a Department of Chemistry, Imperial College, London SW7 2AY, UK
b Department of Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, UK

A comparison of the molecular structures of the five-co-ordinate bis(imido) and imido alkylidene molybdenum complexes [Mo(NC₆H₃Pr^i₂-2,6)(L)(L')], where L is a tridentate pyridinediolato ligand and L' is either NC₆H₃Pr^i₂-2,6 or CHCMe₂Ph, strongly supports the notion that the nitrogen of the bent imido ligand in the bis(imido) complex is sp²-hybridised.

The bonding of terminal imido (NR) ligands at transition-metal centres is usually viewed in terms of the valence-bond descriptions **I** and **II** in which the formally sp²- or sp-hybridised imido nitrogens give rise to bent or linear imido arrangements respectively. An additional linear form **III** is also recognised in which symmetry restrictions (and/or a severe energetic mismatch with the available metal dπ symmetry orbitals) do not allow for lone-pair donation and result in a linear imido group with a formal M–N double bond. In practice, the angle associated with the 'linear' imido ligand is quite soft and may occur anywhere in the range 150–180°,[1] largely as a result of interligand steric interactions and crystal-packing forces. This creates some difficulty in identifying *bona fide* examples of the bent imido-ligand situation, *i.e.*, where the imido nitrogen is truly sp²-hybridised. To our knowledge, the only clear example of a complex containing a bent terminal imido ligand is [Mo(NPh)₂(S₂CNEt₂)₂];[2] a recent structural study on the closely related derivative [Mo(NC₆H₃Pr^i₂-2,6)₂(S₂CNEt₂)₂][3] revealed linear imido groups, an observation attributed to unfavourable steric interactions within the crowded metal co-ordination sphere.

With a view to gaining further insight into the bonding of imido ligands at high-valent metal centres, we decided to investigate the effect of a five-co-ordinate geometry on the bonding of two imido ligands at molybdenum. We targeted a bis(imido) complex containing the tridentate pyridinediolate ligand (L) which we envisaged, in combination with the 2,6-diisopropylphenylimido ligands, would be of sufficient size to maintain a mononuclear formulation.

Results and Discussion

The five-co-ordinate complex [Mo(NC₆H₃Pr^i₂-2,6)₂(L)] **1** can be prepared *via* treatment of [Mo(NC₆H₃Pr^i₂-2,6)₂(OBu^t)₂] with H₂L according to equation (1). Crystals suitable for an

$$[Mo(NC_6H_3Pr^i_2\text{-}2,6)_2(OBu^t)_2] + H_2L \longrightarrow$$
$$[Mo(NC_6H_3Pr^i_2\text{-}2,6)_2(L)] + 2Bu^tOH \quad (1)$$
$$\mathbf{1}$$
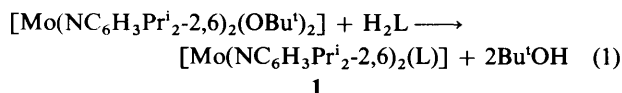
X-ray structure determination were obtained from a saturated CH₂Cl₂ solution upon standing at room temperature. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are collected in Table 1. The molecular geometry of complex **1** is best described as a distorted trigonal bipyramid with the pyridine of the diolate and an imido ligand occupying axial sites. A crystallographic mirror plane bisects the O–Mo–O angle and contains the aryl ring of the axial imido whilst
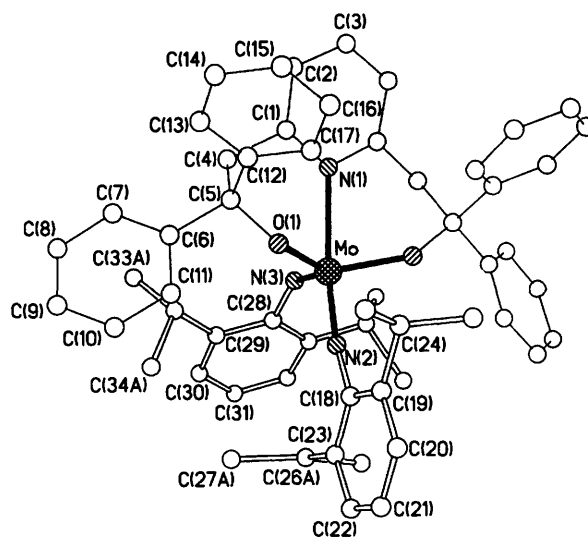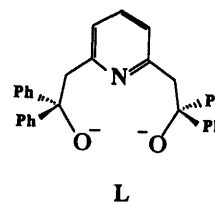
† Dedicated to the memory of Professor Sir Geoffrey Wilkinson.

Fig. 1 Molecular structure of [Mo(NC₆H₃Pr^i₂-2,6)₂(L)] **1**; only one disorder component is shown and H atoms are omitted for clarity

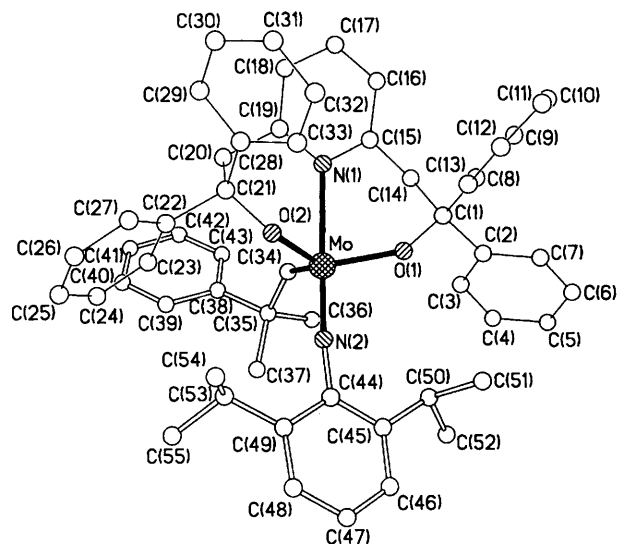

I   **II**   **III**

L

bisecting the ring of the equatorial imido group and the pyridine ring. The 'facial' arrangement of the pyridinediolate is similar to its co-ordination mode in the five-co-ordinate osmium nitrido complex [Os(≡N)Cl(L)][4] and contrasts with the meridional donor-atom arrangement found in the six-co-ordinate dioxo complexes [Mo(O)₂(L)(Me₂SO)][5] and [Os(O)₂(L)(H₂N-Bu^t)].[4]

The bond parameters associated with the imido ligands are of particular interest to us here. Whereas the Mo–N distances are identical within the precision of the structure determination, the angles at the imido nitrogens are substantially different,

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Mo–O(1)	1.940(2)	Mo–N(1)	2.390(4)
Mo–N(2)	1.760(4)	Mo–N(3)	1.771(4)
O(1)–C(5)	1.410(4)	N(2)–C(18)	1.360(7)
N(3)–C(28)	1.422(6)		
N(2)–Mo–N(3)	105.0(3)	N(2)–Mo–O(1)	93.10(11)
N(3)–Mo–O(1)	118.29(8)	O(1)–Mo–O(1')	118.93(14)
N(2)–Mo–N(1)	165.1(2)	N(3)–Mo–N(1)	89.9(2)
O(1)–Mo–N(1)	79.51(9)	C(5)–O(1)–Mo	139.0(2)
C(18)–N(2)–Mo	164.7(4)	C(28)–N(3)–Mo	144.8(5)

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Mo–O(1)	1.934(2)	Mo–O(2)	1.943(2)
Mo–N(1)	2.468(3)	Mo–N(2)	1.745(3)
Mo–C(34)	1.914(3)	O(1)–C(1)	1.412(4)
O(2)–C(21)	1.416(4)	N(2)–C(44)	1.389(4)
C(34)–C(35)	1.523(5)		
N(2)–Mo–C(34)	98.73(13)	N(2)–Mo–O(1)	99.53(11)
C(34)–Mo–O(1)	114.32(12)	N(2)–Mo–O(2)	101.45(11)
C(34)–Mo–O(2)	115.67(12)	O(1)–Mo–O(2)	121.25(10)
N(2)–Mo–N(1)	178.32(10)	C(34)–Mo–N(1)	82.82(12)
O(1)–Mo–N(1)	79.21(10)	O(2)–Mo–N(1)	78.38(10)
C(1)–O(1)–Mo	141.8(2)	C(21)–O(2)–Mo	139.0(2)
C(44)–N(2)–Mo	172.5(2)	C(35)–C(34)–Mo	141.0(2)

Fig. 2 Molecular structure of [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)(=CHCMe$_2$-Ph)(L)] **2** with unique atoms labelled and H atoms omitted

Fig. 3 Views of complexes **1** and **2** illustrating the imido and alkylidene ligand orientations (only key atoms are included for clarity)

164.7(4)° for the axial imide and 144.8(5)° for the equatorial imido ligand, values comparable to those found in [Mo(NPh)$_2$-(S$_2$CNEt$_2$)$_2$] [169.4(4) and 139.4(4)°]. There is no evidence for the bending arising as a consequence of steric interactions, there being ample space for the imido to adopt a linear orientation if so desired. Significantly, the direction of bending of the imido substituent is reminiscent of the orientation adopted by alkylidenes when lying *cis* to an imido group, *i.e.*, with the alkylidene substituent lying in the N–M–C (alkylidene) plane; this particular alignment allows the metal to accommodate two π bonds to the imido group and a single π bond to the sp^2-hybridised carbon of the alkylidene. Therefore, we thought it would be informative to compare the bond parameters of complex **1** with its imido alkylidene analogue, [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)(CHCMe$_2$Ph)(L)] **2**. This complex was prepared *via* treatment of [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)(CHCMe$_2$Ph)-(OBu^t)$_2$] [6] with H$_2$L using a procedure analogous to the synthesis of complex **1** and crystals were grown from a saturated acetonitrile solution at room temperature.

The molecular structure is shown in Fig. 2 and selected bond lengths and angles are collected in Table 2. Complex **2** possesses a similar distorted trigonal-bipyramidal geometry to that observed for **1**, with facially ligated L, the imido ligand occupying an axial site and the alkylidene positioned equatorially. Significantly, the CMe$_2$Ph substituent of the alkylidene bends towards the axial imido group, in much the same way as the substituent of the equatorial imido ligand in complex **1** (the orientations and angles are shown in Fig. 3 for comparison). The angle at the alkylidene carbon of 141.0(2)° is in line with values found in related molybdenum and tungsten imido alkylidene complexes {*e.g.* 141° in [Mo(CHCMe$_3$)-(NC$_6$H$_3$Pr$^i_2$-2,6)(OSO$_2$CF$_3$)$_2$(MeOCH$_2$CH$_2$OMe)] [6] and 145° (av.) in [W(CHCMe$_3$)(NC$_6$H$_3$Pr$^i_2$-2,6)(OCMe$_3$)$_2$] [7]} and is also comparable with the imido bend angle of 144.8(5)° in **1**.

These observations lend strong support to the imido ligand in complex **1** being sp^2-hybridised and thereby a *bona fide* example of the bent imido-ligand bonding mode.

Experimental

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by Medac Ltd., NMR spectra were recorded on a Varian VXR 400S spectrometer at 400.0 (^{1}H) or 100.6 MHz (^{13}C), chemical shifts are referenced to the residual protio impurity of the deuterated solvent, and IR spectra (Nujol mulls, CsI windows) on Perkin-Elmer 577 and 457 grating spectrophotometers. The compounds [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)$_2$(OBu^t)$_2$], [8] [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)(CHC-Me$_2$Ph)(OBu^t)$_2$] [6] and H$_2$L [5] were synthesised by the literature methods. All other chemicals were obtained commercially and used as received unless stated otherwise.

Synthesis of [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)$_2$(L)] 1

The compounds [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)$_2$(OBu^t)$_2$] (0.75 g, 1.27 mmol) and H$_2$L (0.6 g, 1.27 mmol) in pentane (30 cm^3) were refluxed for 12 h. On cooling, the volatiles were removed under reduced pressure and the residue was taken up in CH$_2$Cl$_2$ (20 cm^3). Orange-yellow prisms of the product were deposited upon standing at room temperature (2–3 d). Yield 0.34 g, 29% (Found: C, 74.0; H, 6.9; N, 4.5. C$_{57}$H$_{61}$MoN$_3$O$_2$ requires C, 74.7; H, 6.7; N, 4.6%). NMR (CD$_2$Cl$_2$, 298 K): ^{1}H (400 MHz), δ 0.91 (d, 24 H, $^3J_{HH}$ 6.8, CH*Me*$_2$), 3.74 (spt, 4 H, $^3J_{HH}$ 6.8 Hz, C*H*Me$_2$), 4.04 (s, 4 H, CH$_2$) and 6.84–7.42 (overlapping multiplets, aryl H); ^{13}C (100.6 MHz), δ 156.8, 154.1, 147.6, 141.4, 137.2, 127.1, 125.4, 123.8, 121.4, 82.1, 48.4, 27.2 and 22.7.

Synthesis of [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)(=CHCMe$_2$Ph)(L)] 2

The compounds [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)(CHCMe$_2$Ph)(OBu^t)$_2$] (0.5 g, 0.91 mmol) and H$_2$L (0.43 g, 0.91 mmol) were stirred in

Table 3 Crystallographic data

Compound	1	2
Formula	$C_{57}H_{61}MoN_3O_2$	$C_{55}H_{56}MoN_2O_2$
M	916.0	874.0
Crystal system	Orthorhombic	Triclinic
Space group	$Pmn2_1$	$P\bar{1}$
$a/\text{Å}$	17.684(4)	10.887(7)
$b/\text{Å}$	12.923(4)	11.847(7)
$c/\text{Å}$	10.439(3)	18.126(11)
$\alpha/°$		83.81(7)
$\beta/°$		88.10(6)
$\gamma/°$		74.62(5)
$U/\text{Å}^3$	2385.6(11)	2241(2)
Z	2	2
$D_c/\text{g cm}^{-3}$	1.275	1.295
μ/mm^{-1}	0.32	0.34
$F(000)$	964	918
Crystal size/mm	0.49 × 0.25 × 0.14	0.39 × 0.09 × 0.07
$\theta_{max}/°$	25.0	23.1
Maximum indices h,k,l	21, 15, 12	12, 13, 19
Reflections measured	3602	7679
Unique reflections	3198	6153
R_{int}	0.0172	0.0563
Transmission	0.921–0.941	0.754–0.778
Weighting parameters a, b	0.03, 0.1262	0, 1.3195
Number of refined parameters	343	547
$wR2$ (all data)	0.0814	0.1385
$R1$ ('observed' data)	0.0293 (2662)	0.0347 (5216)
Goodness of fit	1.069	1.091
Maximum, minimum electron density/e Å^{-3}	0.365, −0.306	0.741, −0.812

pentane (30 cm^3) for 10 min. The volatiles were removed *in vacuo* and toluene (30 cm^3) was added. After refluxing for 12 h, the volatiles were removed under reduced pressure and the residue was taken up in hot MeCN (20 cm^3). Red prisms of the product were deposited on standing at room temperature. Yield 0.58 g, 73% (Found: C, 75.8; H, 6.5; N, 3.1. $C_{55}H_{56}MoN_2O_2$ requires C, 75.7; H, 6.5; N, 3.2%). NMR (298 K): ^{1}H (CD$_2$Cl$_2$, 400 MHz), δ 0.64 (d, 12 H, $^3J_{HH}$ 6.8, CHMe_2), 1.66 (s, 6 H, CHCMe_2Ph), 3.50 (spt, 2 H, $^3J_{HH}$ 6.8, CHMe$_2$), 3.58 (d, 2 H, $^3J_{HH}$ 13.2, CH$_2$), 4.27 (d, 2 H, $^3J_{HH}$ 13.2 Hz, CH$_2$), 6.62 (d, 2 H, aryl H), 6.98–7.37 (overlapping multiplets, aryl H), 7.25 (d, 2 H, aryl H) and 11.32 (s, 1 H, CHCMe$_2$Ph); ^{13}C (C$_6$D$_6$, 100.6 MHz), δ 268.6, 157.4, 153.6, 152.3, 149.5, 148.9, 145.7, 137.4, 125.7, 123.8, 123.1, 81.8, 55.9, 50.4, 32.3, 28.3 and 24.2.

X-Ray crystallography

Crystal data for complexes **1** and **2** are summarised in Table 3, together with information on the structure determinations. The crystals were examined at 160 K with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) on a Stoe-Siemens diffractometer with a Cryostream cooler.[9] The cell parameters were refined from 2θ values of *ca.* 30 reflections measured at

±ω to minimise systematic errors. Intensities were collected by ω–θ scans with an on-line profile-fitting procedure.[10] Corrections were made for absorption (semiempirically,[11] based on azimuthal scan measurements) and for the slight decay of standard reflection intensities in each case. The structures were solved by heavy-atom techniques[11] and refined using full-matrix least-squares methods[11] based on F^2 with the weighting scheme $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$. Extinction effects were negligible. Disorder was resolved and refined for two isopropyl groups in complex **1**, with essentially equal occupancies. Hydrogen atoms were constrained with a riding model, other atoms were refined anisotropically. The absolute structure of **1** was indicated by refinement of an enantiopole parameter[12] to −0.03(4). Residuals are defined as $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ for all data, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections having $F_o^2 > 2\sigma(F_o^2)$ for comparison with conventional refinements on F.

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 186/250.

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