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Synthesis, spectroscopic characterization and X-ray crystal structures of oxo-bridged oxo(haloaryl) imido hydrotris(3,5-dimethylpyrazolyl)borate molybdenum(V) complexes

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Reaction of the oxomolybdenum(V) precursor [MoTp*(O)Cl$_2$] (Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) with *m*-fluoroaniline, H$_2$NC$_6$H$_4$F, in toluene afforded the pair of geometric isomers of [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC$_6$H$_4$F)] (**1a**, *cis*; **1b**, *trans*). Similarly the reaction with *m*-iodoaniline yielded the compound [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC$_6$H$_4$I)] (**2**). This is a new synthetic method for preparing Mo–O–Mo bridged oxo(imido) molybdenum(V) species by double deprotonation of the anilines. The complexes were characterized by IR and ^{1}H-NMR. spectroscopy, FAB mass spectrometry, elemental analysis and X-ray crystallography which revealed that the two chloro ligands are *trans* to each other in **1b** and **2**, whereas they are *cis* to each other in **1a**. All compounds have Mo–O–Mo linkages and near linear arylimido moieties.

Keywords: Imido complexes; Mo(V) complexes; Oxo-imido complexes; Oxo-bridged molybdenum; Oxo complexes; Tris(pyrazol)borate complexes

1. Introduction

Poly(pyrazolyl)borate ligands were first synthesised by Trofimenko [1]. Hydrotris(3,5-dimethyl-1-pyrazolyl)borate, Tp*, is a facially co-ordinating ligand similar to the 6e⁻ donor Cp* (pentamethylcyclopentadienyl). It has been used to stabilize mononuclear Mo(V) complexes and allows a systematic investigation of their electronic and spectroscopic properties [2]. The sterically encumbering nature of the Tp* ligand compared with Cp* is very well known and has been investigated for catalyst systems [3,4]. Molybdenum is considered as a trace element, presents several oxidation states, and therefore may change easily its coordination number and form mono and binuclear

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oxo complexes, which are of great importance from basic as well as applied points of view. The propensity of oxomolybdenum species in higher oxidation states to form di-, tri- and polynuclear complexes is well known [5]. Molybdenum is a relevant element for the synthesis of many homogeneous and heteregenous catalysts. The element is also essential in several enzymatic systems. It is also known that tris(pyrazolyl)borate ligands have had a significant impact on the modelling of the active centre of Mo enzymes [6]. One of the characteristics of molybdenum chemistry is related to the facile conversion between its oxidation states and changes of coordination number, observed particularly between Mo(IV), Mo(V) and Mo(VI). The chemistry of oxo Mo(V) complexes is of importance especially in industrial and biochemical catalysis [7].

Oxo and imido ligands commonly form multiple bonds when attached to transition metal centers. The chemistry of the corresponding complexes has experienced a remarkable growth recently [8,9]. Both the oxo and the imido groups permit stabilization of high formal oxidation states. In the case of the latter functionality, varying the electronic and steric characteristics of the organic group bonded to nitrogen allows the modification of the properties of the resulting metal complex.

Organoimido complexes of Mo(V) and Mo(VI) can be prepared by a wide range of methods that often make use of organic compounds as the imido transfer reagent [8,9]. There are several molybdenum imido compounds [10–15] and a number of related mixed terminal oxo–imido compounds reported [16–21] but limited information is available for transition metal compounds containing both imido and hydrotris (pyrazolyl)borate type ligands [16,22–29]. Although a number of systems involving μ-ligation in the presence of terminal imido groups have previously been reported [30–37], the chemistry of compounds having both arylimido and μ-oxo groups in the presence of tris(pyrazolyl)borate co-ligand is not widely explored.

In the present article, we report the synthesis, spectroscopic characterization and X-ray structures of a pair of geometric isomers [MoTp*(O)Cl](μ-O)[MoTp*(Cl) (≡NC$_6$H$_4$F)] (**1a**, *cis*; **1b**, *trans*) and the compound [MoTp*(O)Cl](μ-O)[MoTp*(Cl) (≡NC$_6$H$_4$I)] (**2**).

2. Experimental

2.1. *Materials and instrumentation*

All preparations and manipulations were carried out using Schlenk techniques under an oxygen-free nitrogen atmosphere. All glassware was oven dried at 120°C. Solvents were dried by standard procedures, distilled and kept under nitrogen over 4 Å molecular sieves.

The starting material [MoTp*(O)Cl$_2$] was prepared according to a published method [38].

Infrared spectra were recorded on a Magna IR spectrophotometer using pressed KBr disks. ^{1}H-NMR spectra were recorded in CDCl$_3$ on a 400 MHz High Performance Digital NMR spectrometer at TUBITAK (Research Council of Turkey). Mass spectra were measured on a Joel AX505 FAB device using Xe at 3 kV and a positive ion matrix *m*-NBA (*meta*-nitrobenzylalcohol). Elemental analysis were carried out using a Leco

CHNS 932 instrument. The crystal structure data collection was carried out using a Bruker SMART CCD area-detector diffractometer.

All yields are based on starting materials.

2.2. *Preparation of the complexes*

2.2.1. [MoTp*(O)Cl][(μ-O)[MoTp*(Cl)(≡NC₆H₄F)] (1a, *cis*; 1b, *trans*). A mixture of [MoTp*(O)Cl₂] (0.4 g, 0.83 mmol), 3-fluoroaniline (0.18 g, 1.66 mmol) and dry Et₃N (0.6 cm³) in dry toluene (20 cm³) was heated to reflux with stirring under N₂ for 14 h, during which time the solution became dark red-brown in colour. The mixture was cooled, filtered and evaporated to dryness. The residue was dissolved in dichloromethane and chromatographed on silica gel using CH_2Cl_2/n-hexane (9 : 1, v/v) as eluant. Two red-brown fractions were collected, isolated solids crystallised from CH_2Cl_2/n-hexane and identified, respectively, as [MoTp*(O)Cl][(μ-O)[MoTp*(Cl) (≡NC₆H₄F)] (*cis*) (**1a**) (0.2 g, 24%), Anal. Calcd. for $C_{36}H_{48}B_2Cl_2Mo_2N_{13}O_2F$ (%): C, 43.31; H, 4.84; N, 18.24. Found: C, 43.72; H, 5.12; N, 18.62, and [MoTp*(O) Cl][(μ-O)[MoTp*(Cl)(≡NC₆H₄F)] (*trans*) (**1b**) (0.16 g, 19%), Anal. Calcd. for $C_{36}H_{48}B_2Cl_2Mo_2N_{13}O_2F$ (%): C, 43.31; H, 4.84; N, 18.24. Found: C, 43.62; H, 4.37; N, 17.93.

2.2.2. [MoTp*(O)Cl][(μ-O)[MoTp*(Cl)(≡NC₆H₄I)] (2). A mixture of [MoTp*(O)Cl₂] (0.4 g, 0.83 mmol), 3-iodoaniline (0.36 g, 1.64 mmol) and dry Et₃N (0.6 cm³) in dry toluene (20 cm³) was heated to reflux with stirring under N₂ for 18 h. The mixture was then cooled and the solvent was removed *in vacuo*. The first dark-red solid purified by column chromatography (silica, dichloromethane/n-hexane) (2 : 3, v/v) as eluant was recrystallised from dichloromethane/n-hexane (2 : 3) to give a dark-red band identified as [MoTp*(O)Cl][(μ-O)[MoTp*(Cl)(≡NC₆H₄I)] (**2**) (0.27 g, 30 %), Anal. Calcd. for $C_{36}H_{48}B_2Cl_2Mo_2N_{13}O_2I$ (%): C, 39.52; H, 4.34; N, 16.92. Found: C, 39.12; H, 4.03; N, 16.74.

2.3. *X-Ray crystallography*

Single crystals of **1a**, **1b** and **2** were coated in paraffin oil and mounted on glass fibers. X-Ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo Kα radiation (λ = 0.71073 Å) [39]. Intensities were integrated [40] from several series of exposures, each exposure covering 0.3° in ω, and the total data set being a complete sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements [41]. The structures of **1a**, **1b** and **2** were solved by direct methods/Patterson synthesis, Patterson synthesis and direct methods respectively and refined by least squares on weighted F^2 values for all reflections (see table 5) [42]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms H(1A), H(2A) were located in the electron density difference map, assigned isotropic displacement parameters and refined without positional constraints. All other hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Complex neutral-atom scattering factors were used [43]. Crystal data,

data collection, structure solution and refinement parameters for compounds **1a**, **1b** and **2** are listed in table 5.

3. Results and discussion

3.1. *Synthetic studies*

Reaction of [MoTp*(O)Cl$_2$] with 3-fluoroaniline in the presence of triethylamine in toluene under reflux yielded a pair of geometric isomers [MoTp*(O)Cl](μ-O) [MoTp*(Cl)(≡NC$_6$H$_4$F)] (**1a**, *cis*; **1b**, *trans*). Similarly, the reaction of [MoTp*(O)Cl$_2$] with 3-iodoaniline produced [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC$_6$H$_4$I)] (**2**). The compounds are stable in air and soluble in chlorinated solvents. They can readily be separated from the reaction mixture by crystallisation from CH$_2$Cl$_2$/hexane. Crystals of **1a**, **1b** and **2** for X-ray analysis were obtained by slow evaporation of its saturated hexane solution at room temperature.

Although a wide range of synthetic approaches [9] to transition metal imido complexes have been established, use of amines as the imido source is most appealing because they have almost unlimited potential for imido functionalisation. The formation of **1a**, **1b** and **2** from the oxomolybdenum(V) compound [MoTp*(O)Cl$_2$], was accomplished by double protonation of aniline amines, a well-known [8,9] synthetic methodology for the preparation of organoimido complexes of Mo(V) and Mo(VI). Here, organic compounds are used as the imido transfer reagent. The interesting feature of the compounds **1a**, **1b** and **2** is the formation of a Mo–O–Mo linkage despite the steric barrier provided by the 3-methyl groups of the Tp* ligand. Previously reported compounds having an Mo–O–Mo linkage and a tris(pyrazolylborate) co-ligand were prepared by completely different methods. For example, a number of dinuclear oxo-bridged Mo(V) compounds with tris(pyrazolborate) co-ligand were produced by various combinations of oxygen atom transfer, conproportionation, aquation and hydrolysis reactions at Mo(VI) or Mo(V). For example, McCleverty *et al.* [44] prepared the compound [MoTp*(O)Cl]$_2$(μ-O) by the reaction of [MoTp*O$_2$Cl] and PPh$_3$ in toluene containing approximately 0.03% water. Miller *et al.* [45] prepared the same compound by treatment of 1,3-dimethoxy-*para-tert*-butylcalix[4]arene and [MoTp*(O)Cl$_2$] in toluene under reflux. The synthesis was successful in the absence of calixarene as well and it was suggested that the complex was formed due to the presence of adventitious water, probably sourced from triethylamine. Syntheses of geometric isomers of [MoTp(O)Cl]$_2$(μ-O) (Tp = hydrotris (pyrazolborate)) were accomplished in aqueous media. The *cis* (C_2) isomer of [MoTp(O)Cl]$_2$(μ-O) was prepared by reaction of KHB(pz)$_3$ with MoOCl$_5^{2-}$ and the related *trans* (C_i) isomer was obtained by treatment of HB(pz)$_3$MoCl$_3$ with H$_2$O/CH$_2$Cl$_2$ [41].

It could be suggested that in the reactions of [MoTp*OCl$_2$] with *m*-substituted haloaryl anilines (H$_2$NC$_6$H$_4$X, X = F or I), double deprotonation of the halo anilines takes place and the mononuclear species [MoTp*OCl(H$_2$NC$_6$H$_4$X)], [MoTp*OCl (HNC$_6$H$_4$X)] and [MoTp*OCl(≡NC$_6$H$_4$X)] (X = F or I) formed as intermediates. The mononuclear imido species, [MoTp*OCl(≡NC$_6$H$_4$X)], may further react with unreacted starting material to form the oxo-bridged bimetallic oxo(haloaryl) imido molybdenum(V) compounds [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC$_6$H$_4$F)] (**1a**, *cis*; **1b**, *trans*) and [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC$_6$H$_4$I)] (**2**) according to the following

Table 1. Characterisation data for **1a**, **1b** and **2**.

Complex	Colour	Yield (%)	FAB-MS
1a	Red-brown	24	998.2
1b	Red-brown	19	998.2
2	Dark-red	30	1106.1

Table 2. IR data for the complexes **1a**, **1b** and **2**.

Complex	v_{BH}	$v_{Mo=O}$	$v_{Mo\equiv N}$	$v_{Mo-O-Mo}$
1a	2548	957	1204	787
1b	2548	957	1204	786
2	2545	960	1205	787

reactions (X = F, **1a**, *cis*; **1b**, *trans*; X = I, **2**).

$$[MoTp^*OCl_2] + H_2NC_6H_4X \xrightarrow[\text{toluene}]{\Delta,\,Et_3N} [Cl_2(O)Tp^*Mo(HNC_6H_4X)]$$

$$\longrightarrow [Cl(O)Tp^*Mo(\equiv NC_6H_4X)] \xrightarrow{[MoTp^*OCl_2]} [Cl(O)Tp^*Mo(\mu\text{-O})MoTp^*Cl(\equiv NC_6H_4X)].$$
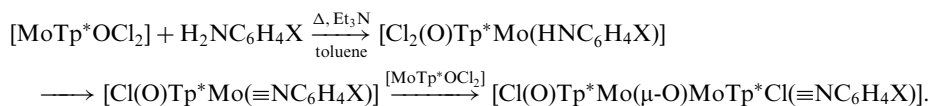
3.2. *Spectroscopic studies*

Molecular ion peaks determined from the mass spectrometric data are in accord with the suggested structures for **1a**, **1b** and **2** (see table 1). All complexes exhibit the expected absorptions due to the Tp* ligand (ca. 2500 cm^{-1} due to $v_{(BH)}$ and 1400 cm^{-1} associated with the pyrazolyl ring) in the IR spectra (refer to table 2). They possess bands at ca. 960 cm^{-1} characteristic of the terminal Mo=O unit for Mo(V) complexes. This value was reported as 964 cm^{-1} for the starting material [MoTp*(O)Cl$_2$] [38]. Both [MoTp(O)Cl$_2$](μ-O) (*cis*, C_2 isomer) and [MoTp(O)Cl$_2$] (μ-O), (*trans*, C_i isomer) exhibit peaks at 958 cm^{-1} for Mo=O of the terminal oxo groups [46]. The compound [MoTp(O)Cl]$_2$(μ-O) exhibits two $v_{(Mo=O)}$ stretches at 960 and 859 cm^{-1}. These have been reported as 961 and 971 cm^{-1} for [MoTp^{pr}(O)Cl] (μ-O)[MoTp^{pr}(O)(OH)] (Tp^{pr} = Hydrotris(3-isopropylpyrazolyl)borate) [45]. The IR spectrum of the mixed valence compound, [Mo(V)Tp*O$_2$](μ-O)[Mo(VI)Tp*(O)Cl] exhibits three $v_{(Mo=O)}$ bands in the region 850–1000 cm^{-1} assigned to Mo(V)=O (955 cm^{-1}) and *cis*-Mo(VI)O$_2$ (925, 895 cm^{-1}) [47]. A detailed infrared and Raman spectroscopic study was carried out for the geometric isomers (*cis*, C_2 and *trans*, C_i) of [MoTp(O)Cl$_2$](μ-O). According to this study, the peaks at 784 cm^{-1} and 456 cm^{-1} were assigned to the asymmetric stretch and the deformation mode of the linear oxo-bridged unit, respectively [48]. For the compound [MoTp*(O)Cl]$_2$(μ-O), a medium intensity band at 753 cm^{-1} was also assigned to a stretching mode of a bridging Mo–O–Mo unit [45]. Hence, the peaks observed for the new compounds **1a**, **1b** and **2** at ca. 755 cm^{-1} and 455 cm^{-1} could be assigned to asymmetric stretching and deformation modes of the Mo–O–Mo unit, respectively. The presence of the μ-oxo ligand was indicated by a strong, broad v_{as}(Mo–O–Mo) band at 750 cm^{-1} for the compound [Mo$^{(V)}$Tp*O$_2$](μ-O)[Mo$^{(VI)}$Tp*(O)Cl] [47] as well.

The two vibrations at ca. 3370 and 3450 cm^{-1} from the symmetric and asymmetric stretching modes of the NH$_2$ groups of the free ligands have completely disappeared in the IR spectra of **1a**, **1b** and **2**. This led us to think of the existence of either Mo=N or Mo≡N linkages. In general, identifying a $\nu_{(Mo=N)}$ or $\nu_{(M≡N)}$ vibration is a difficult task because of the variability in the Mo–N bond order and coupling of the Mo=N vibration to other vibrations in the molecule, in particular the adjacent N–C vibration of the imido group [9]. However, a value of 1100–1300 cm^{-1} for $\nu_{(Mo=N)}$ has been suggested [49] and McCleverty *et al.* [16] reported values in the range 1200–1250 cm^{-1} for the compounds [MoTp*(O)Cl(=NR)] (R = 4-tolyl or C$_6$H$_4$NMe$_2$-4). The IR spectra of the oxo-bridged oxo(arylimido) molybdenum(V) compounds **1a**, **1b** and **2** also exhibited peaks around 1200–1300 cm^{-1} and may be ascribed to $\nu_{(Mo≡N)}$.

The ^{1}H-NMR spectra of the complexes [MoTp*(O)Cl](μ-O)[MoTp*(Cl) (≡NC$_6$H$_4$X)] (R = F, I) exhibited all the expected peaks (see table 3) in accord with the structures determined by X-ray analysis. In general the signals attributable to the ligand Tp^{Me,Me} appeared as two groups of singlets in the region δ 5–6 due to the H(4) protons and δ 2–3 due to the methyl groups attached to the pyrazolyl ring. The low symmetry of the compounds **1a**, **1b** and **2** means that all three pyrazolyl H(4) protons and six methyl groups of the Tp* ligand, are non-equivalent in the NMR spectra. In the spectrum of **1a**, the H(4) protons appear as six singlets in the region δ 6.21–5.52 whereas three singlets were observed at δ 5.82, 5.74, 5.65 and δ 5.81, 5.72, 5.45 for **1b** and **2**, respectively, due to the H(4). This could be attributed to accidental degeneracy of the three H(4) resonances in two non-equivalent Tp* ligands. This effect has previously been observed by McCleverty *et al.* [50]. All compounds exhibited peaks (total integrated area equivalent to 36 protons) attributable to the methyl protons of

Table 3. ^{1}H NMR data for the complexes.

δ_H[a]	Multiplicity and assignment
1a	7.41 (d, 2H, *J* (HH) 8, C$_6$*H*$_4$F)
	7.18 (d, 2H, *J* (HH) 8, C$_6$*H*$_4$F)
	6.21 (s, 1H, Me$_2$C$_3$*H*N$_2$)
	6.13 (s, 1H, Me$_2$C$_3$*H*N$_2$)
	5.97 (s, 1H, Me$_2$C$_3$*H*N$_2$)
	5.93 (s, 1H, Me$_2$C$_3$*H*N$_2$)
	5.56 (s, 1H, Me$_2$C$_3$*H*N$_2$)
	5.52 (s, 1H, Me$_2$C$_3$*H*N$_2$)
	2.45–3.67 (m, 36H, *Me*$_2$C$_3$*H*N$_2$)
1b	7.19 (s, C$_6$*H*$_4$F)
	5.82 (s, 2H, Me$_2$C$_3$*H*N$_2$)
	5.74 (s, 2H, Me$_2$C$_3$*H*N$_2$)
	5.65 (s, 2H, Me$_2$C$_3$*H*N$_2$)
	2.28–3.56 (m, 36H, Me$_2$C$_3$*H*N$_2$)
2	7.69 (s, 1H, C$_6$*H*$_4$I)
	7.41 (d, 2H,C$_6$*H*$_4$I)
	6.95 (t, 1H, C$_6$*H*$_4$I)
	5.81 (s, 2H, Me$_2$C$_3$*H*N$_2$)
	5.72 (s, 2H, Me$_2$C$_3$*H*N$_2$)
	5.45 (s, 2H, Me$_2$C$_3$*H*N$_2$)
	1.96–2.68 (m, 36H, *Me*$_2$C$_3$HN$_2$)

[a]In CDCl$_3$.

the Tp* ligand in the region δ 2–3. For **1a**, the C_6H_4 protons are split into two sets of two whereas for **1b** they are equivalent. For **2**, C_6H_4 protons are split into a singlet, a doublet and a triplet. NH protons generally appear as a sharp singlet in the range δ 11–13 ppm [9]. The ^1H NMR spectra of **1a**, **1b** and **2** did not display any signals in this region, which further supports the formation of Mo=N or Mo≡N linkages.

3.3. *Description of crystal structures*

An ORTEP view of the molecular structure of **1a** is shown in figure 1. Selected bond distances and bond angles are listed in table 4. The structure of [MoTp*(O)Cl](μ-O) [MoTp*(Cl)(≡NC_6H_4F)] (**1a**) reveals two non-equivalent MoTp*Cl units connected by a single oxo bridge. There are two pseudo-octahedral metal centers with three nitrogen atoms of each Tp* ligand occupying one face of the octahedron. Mo(1) is coordinated by facial Tp*, terminal oxo, terminal chloro and bridging oxo ligands whereas Mo(2) is coordinated by facial Tp*, terminal chloro, arylimido and bridging oxo ligands. The two chlorine atoms are *cis* to each other. The complex contains a nearly linear Mo–O–Mo bridge (172.98(15)°) which is very close to the value reported for [MoTp*(O)Cl]$_2$(μ-O) [177.4(4)°] [45]. Lincoln and Koch have reported [46] the structures of two related geometric isomers (*cis*, C_2 and *trans*, C_i). The reported Mo–O–Mo bond angles for these compounds are comparable to those encountered here [177.3(2) for the C_2 dimer and 180.0° for the *trans* C_i dimer].

The interesting feature of the structure of **1a** is the presence of a Mo–N–R linkage which is considered to be essentially linear with a Mo(2)–N(61)–C(61) bond angle of
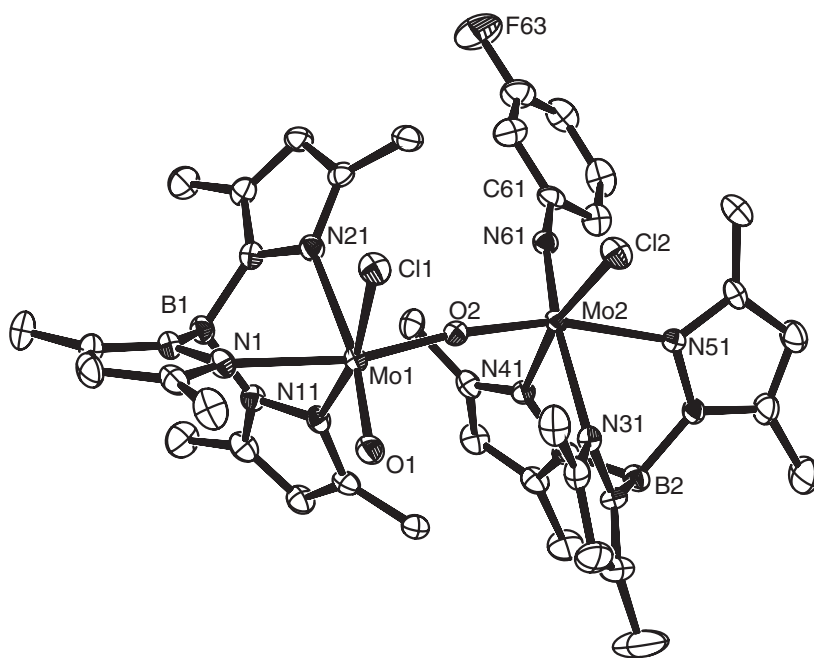

Figure 1. An ORTEP view of **1a**, showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

Table 4.   Selected bond lengths [Å] and angles [°] for **1a**, **1b** and **2**.

1a · 5/2CH$_2$Cl$_2$		**1b** · C$_4$H$_{10}$		**2** · C$_6$H$_{14}$ · C$_2$H$_5$OH	
Mo(2)–N(61)	1.743(3)	Mo(1)–N(1)	1.726(3)	Mo(2)–N(1)	1.711(6)
Mo(2)–O(2)	1.899(2)	Mo(1)–O(1)	1.899(3)	Mo(2)–O(1)	1.901(5)
Mo(1)–O(1)	1.677(3)	Mo(2)–O(2)	1.681(3)	Mo(1)–O(1)	1.874(5)
Mo(1)–O(2)	1.871(2)	Mo(2)–O(1)	1.877(3)	Mo(1)–O(2)	1.675(6)
Mo(2)–Cl(2)	2.3998(10)	Mo(1)–Cl(1)	2.4151(10)	Mo(2)–Cl(1)	2.4013(18)
Mo(1)–Cl(1)	2.4006(11)	Mo(2)–Cl(2)	2.3988(10)	Mo(1)–Cl(2)	2.3914(19)
Mo(1)–N(11)	2.174(3)	Mo(2)–N(41)	2.162(3)	Mo(1)–N(12)	2.156(6)
Mo(1)–N(1)	2.215(3)	Mo(2)–N(51)	2.209(3)	Mo(1)–N(8)	2.212(6)
Mo(1)–N(21)	2.324(3)	Mo(2)–N(61)	2.348(3)	Mo(1)–N(10)	2.355(6)
Mo(2)–N(31)	2.285(3)	Mo(1)–N(31)	2.177(3)	Mo(2)–N(4)	2.163(6)
Mo(2)–N(41)	2.171(3)	Mo(1)–N(11)	2.215(3)	Mo(2)–N(6)	2.206(6)
Mo(2)–N(51)	2.207(3)	Mo(1)–N(21)	2.292(3)	Mo(2)–N(2)	2.296(6)
Bond angles					
Mo(1)–O(2)–Mo(2)	172.98(15)	Mo(2)–O(1)–Mo(1)	169.57(15)	Mo(1)–O(1)–Mo(2)	168.8(3)
C(61)–N(61)–Mo(2)	161.5(3)	C(1)–N(1)–Mo(1)	178.3(3)	C(11)–N(1)–Mo(2)	176.3(6)
O(1)–Mo(1)–O(2)	104.86(12)	O(2)–Mo(2)–O(1)	102.61(13)	O(2)–Mo(1)–O(1)	102.8(3)
N(61)–Mo(2)–O(2)	105.16(13)	N(1)–Mo(1)–O(1)	99.49(14)	N(1)–Mo(2)–O(1)	100.2(3)
N(61)–Mo(2)–Cl(2)	98.87(11)	N(1)–Mo(1)–Cl(1)	95.63(11)	N(1)–Mo(2)–Cl(1)	98.4(2)
O(2)–Mo(2)–N(41)	92.54(11)	O(1)–Mo(1)–N(21)	86.91(12)	O(1)–Mo(2)–N(2)	86.9(2)
O(2)–Mo(2)–N(31)	85.69(11)	O(1)–Mo(1)–N(11)	165.26(12)	O(1)–Mo(2)–N(4)	90.8(2)
O(2)–Mo(2)–N(51)	163.83(11)	O(1)–Mo(1)–N(31)	90.80(12)	O(1)–Mo(2)–N(6)	165.4(2)
O(1)–Mo(1)–N(11)	91.20(12)	O(2)–Mo(2)–N(41)	92.91(13)	O(2)–Mo(1)–N(8)	91.6(3)
O(1)–Mo(1)–N(1)	91.16(12)	O(2)–Mo(2)–N(51)	91.24(13)	O(2)–Mo(1)–N(10)	169.4(3)
O(1)–Mo(1)–N(21)	169.15(12)	O(2)–Mo(2)–N(61)	169.36(13)	O(2)–Mo(1)–N(12)	93.6(3)
O(2)–Mo(2)–Cl(2)	93.49(8)	O(2)–Mo(2)–Cl(2)	97.43(10)	O(2)–Mo(1)–Cl(2)	98.7(2)
O(1)–Mo(1)–N(1)	91.16(12)	O(1)–Mo(2)–Cl(2)	96.13(8)	O(1)–Mo(1)–Cl(2)	96.10(16)
O(1)–Mo(1)–Cl(1)	97.20(10)	O(1)–Mo(1)–Cl(1)	97.12(8)	O(1)–Mo(2)–Cl(2)	98.7(2)
O(2)–Mo(1)–Cl(1)	92.64(8)	N(1)–Mo(1)–O(1)	99.49(14)	O(1)–Mo(2)–N(1)	100.2(3)

161.5(3)° within the range 160–180° suggested by Dehnicke [49]. For the compounds [Tp*Mo(NAr)$_2$Cl] and [Tp*Mo(NAr)(NBu^t)Cl] (Ar = 2,6-Pr$^i_2$C$_6$H$_3$) the Mo–N–C bond angles were reported as 173.06(16) and 168.25(16)° respectively [35]. The Tp* ligand is coordinated to each molybdenum atom with Mo–N bond lengths (table 4) typical for this type of compound [46]. For **1a**, the Mo(1)–O(1) distance is 1.677(3) (Å). The Mo(1)–O(2) and Mo(2)–O(2) bond distances are 1.871(2) and 1.899(2) Å which are close to the values of 1.908(4) and 1.880(4) Å reported for [MoTp^{Pr}OCl](μ-O)[MoTp^{Pr}O(OH)] (Tp^{Pr} = hydrotris(3-isopropylpyrazolyl)borate) [45]. Mo(1)–Cl(1) and Mo(2)–Cl(2) distances of 2.4006(11), 2.3998(10) Å, respectively, are all also within the usual ranges [46] and comparable to the values 2.346(2) and 2.364(2) Å for [MoTp(O)Cl]$_2$(μ-O) (*cis*, C_2 dimer).

An ORTEP view of the molecular structure of **1b** is shown in figure 2 and selected bond distances and bond angles are listed in table 4. The X-ray structure determination of **1b** reveals it to be a geometrical isomer of **1a**. The dimer possesses no crystallographically imposed symmetry. The chloride ligands are *trans* to each other. The Mo–O–Mo angle of 169.57(15)° deviates considerably from linearity in comparison to **1a**. For [MoTp*(O)Cl]$_2$(μ-O) (*trans*, C_i), a linear Mo–O–Mo bond (180.0°) was reported whereas for [MoTp^{Pr}OCl](μ-O)[MoTp^{Pr}O(OH)], this linkage was non-linear (158.5(2)°) [45]. For **1b**, the Mo(1)–N(1)–C(1) bond angle of 178.3(3)° is very close to linear and comparable to the value 173.06(16)° reported for [Tp*Mo(NAr)$_2$Cl] [35]. The Mo(1)–O(1), Mo(2)–O(1), Mo(2)–O(2), Mo(1)–Cl(1), Mo(2)–Cl(2) distances of 1.899(3), 1.877(3), 1.681(3), 2.4159(5), 2.3988(10) Å for **1b** are also comparable to **1a** and within suggested ranges [46]. Mo(2)–N(62) and Mo(1)–N(1) bond lengths of
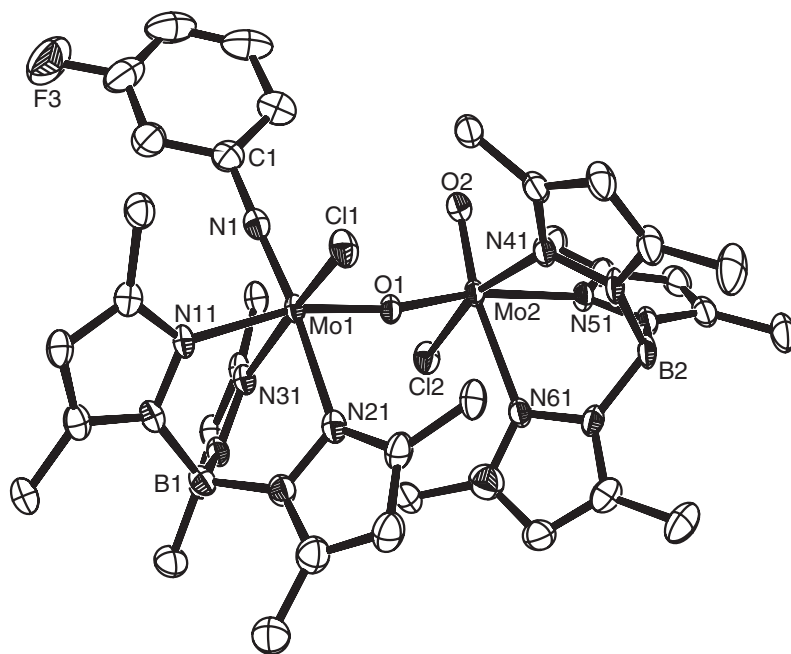

Figure 2. An ORTEP view of **1b**, showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

1.743(3) for **1a** and 1.726(3) Å for **1b** are also indicative of a Mo≡N bond and in agreement with reported values for compounds containing the Mo≡N bond. In the case of transition metals in high oxidation states, the free electron pair of the nitrogen atom participates in the M–N bond, resulting in a linear M–N–R arrangement with a M≡N triple bond [49]. In terms of electron counting the Mo≡N arrangement is also essential.

An ORTEP view of the molecular structure of **2** is shown in figure 3. As determined for **1a** and **1b**, there are two non-equivalent MoTp*Cl units connected by a single oxo bridge. Mo(1) is coordinated by facial Tp*, terminal oxo, terminal chloro and bridging oxo ligands whereas Mo(2) is coordinated by facial Tp*, terminal chloro, arylimido and a bridging oxo ligands The two chlorine atoms are *trans* to each other. There is a nearly linear Mo–O–Mo linkage with an angle of 168.8(3)°, which is close to 169.57(15)° and smaller than 172.98(15)° determined for **1b** and **1a**, respectively. The Mo(2)–N(1)–C(11) metal–imido moiety is almost linear with a bond angle of 176.3(6)°. This value is larger than the corresponding Mo(2)–N(61)–C(61) bond angle of 161.5(3)° found in **1a**, close to the Mo(1)–N(1)–C(1) bond angle of 178.3(3)° found in **1b**, and comparable to similar values reported previously [35,49]. The Mo(2)–N(1) bond distance of 1.711(6) Å is comparable to those in **1a** and **1b** is also indicative of a Mo≡N for compound **2**. Mo(1)–O(1), Mo(1)–O(2), Mo(2)–O(1), Mo(1)–Cl(2), Mo(2)–Cl(1) distances of 1.874(5), 1.675(6), 1.901(5), 2.3914(19), 2.4013(18) Å, respectively, are all in agreement with reported values [46].
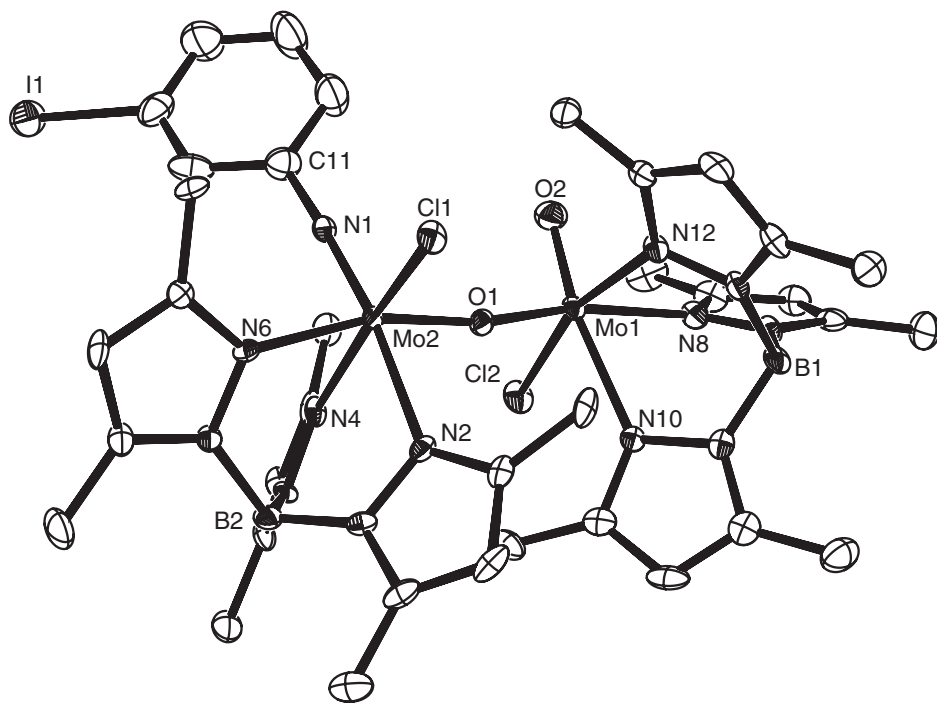

Figure 3. An ORTEP view of **2**, showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

Table 5. Crystal data and structure refinement details for **1a**, **1b** and **2**.

	1a $\cdot$ 5/2CH$_2$Cl$_2$	**1b** $\cdot$ C$_4$H$_{10}$	**2** $\cdot$ C$_6$H$_{14}$ $\cdot$ C$_2$H$_5$OH
Empirical formula	C$_{36}$H$_{48}$B$_2$Cl$_2$FMo$_2$N$_{13}$O$_2$ $\cdot$ 5/2CH$_2$Cl$_2$	C$_{36}$H$_{48}$B$_2$Cl$_2$FMo$_2$N$_{13}$O$_2$ $\cdot$ C$_4$H$_{10}$	C$_{36}$ H$_{48}$B$_2$Cl$_2$IMo$_2$N$_{13}$O$_2$ $\cdot$ C$_6$H$_{14}$ $\cdot$ C$_2$H$_5$OH
Formula weight	1210.51	1056.32	1238.37
Temperature/K	173(2)	293(2)	293(2)
Wavelength/Å	0.71073	1.54178	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2(1)/n$	$P\bar{1}$	$P2(1)/c$
Unit cell dimensions/Å,°	$a = 12.3726(15)$, $\alpha = 90$	$a = 10.35260(10)$, $\alpha = 96.8230(10)$	$a = 14.785(3)$, $\alpha = 90$
	$b = 25.148(3)$, $\beta = 92.556(2)$	$b = 10.85720(10)$, $\beta = 99.7700(10)$	$b = 10.269(2)$, $\beta = 99.89(3)$
	$c = 16.747(2)$, $\gamma = 90$	$c = 23.1456(2)$, $\gamma = 96.2990(10)$	$c = 36.795(7)$, $\gamma = 90$
Volume/Å^3	5205.7(11)	2523.16(4)	5503.6(19)
Z	4	2	4
Density (calculated) Mg m^{-3}	1.545	1.393	1.505
Absorption coefficient/ mm^{-1}	0.892	5.456	1.164
F(000)	2452	1086	2524
Crystal size/mm	$0.12 \times 0.12 \times 0.07$	$0.12 \times 0.12 \times 0.1$	$0.2 \times 0.08 \times 0.08$
θ range for data collection/°	1.46 to 27.52	1.96 to 70.06	1.64 to 27.49
Index ranges	$-16 \leq h \leq 16$, $-32 \leq k \leq 32$, $-21 \leq l \leq 21$	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-27 \leq l \leq 28$	$-19 \leq h \leq 19$, $-13 \leq k \leq 13$, $-47 \leq l \leq 47$
Reflections collected	54997	19529	62372
Independent reflections	11945 [$R_{int} = 0.0771$]	8505 [$R_{int} = 0.0364$]	12641 [$R_{int} = 0.0930$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	11945/0/624	8505/55/601	12641/98/635
Goodness-of-fit on F^2	$S = 1.053$	$S = 1.025$	$S = 1.137$
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0433$, $wR_2 = 0.1033$	$R_1 = 0.0429$, $wR_2 = 0.1190$	$R_1 = 0.0844$, $Wr_2 = 0.1953$
R indices (for all data)	$R_1 = 0.0924$, $wR_2 = 0.1270$	$R_1 = 0.0488$, $wR_2 = 0.1222$	$R_1 = 0.1078$, $wR_2 = 0.2059$
Largest diff. peak and hole/e Å^{-3}	1.726 and -1.469	1.263 and -0.728	2.791 and -2.690

The interesting feature related to compounds **1a**, **1b** and **2** is the Mo–N–C part of the metal–imido moiety. In general, two Lewis structures have been proposed for the metal nitrogen bond in imido complexes [51].

$$
\begin{array}{cc}
\text{R} & \text{R} \\
| & \diagup \\
\text{N} & \text{N} \\
\||| & \|| \\
\text{Mo} & \text{Mo}
\end{array}
$$

In structure (A), the nitrogen acts as a six electron donor and a Mo–N–R angle close to 180° is expected; in structure (B), the nitrogen acts as a four electron donor and the Mo–N–R linkage is bent. The majority of known Mo(V) and Mo(VI) imido compounds have linear linkages [51]. In **1a**, **1b** and **2**, the Mo–N–C moieties are almost linear and related bond lengths and bond angles are all in agreement with a molybdenum–nitrogen bond order of three.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 236291 for compound **1a** · 2.5CH$_2$Cl$_2$, CCDC No. 236252 for compound **1b** · C$_4$H$_{10}$, CCDC No. 236292 for compound **2** · C$_6$H$_{14}$ · C$_2$H$_5$OH. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, UK CB2 1EZ (Fax: +44 1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www://www.ccdc.cam.ac.uk).

Acknowledgments

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