Synthesis and characterization of two oxo-bridged oxo(arylimido) [tris(3,5-dimethylpyrazolyl)borato]molybdenum(V) complexes and crystal structure of [MoTp*(O)Cl](μ-O)[MoTp*(Cl)($\equiv$NC$_6$H$_4$OMe)]

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Abstract

Reaction of the oxo-molybdenum(V) compound, [MoTp*(O)Cl$_2$], [Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate] with *p*-methoxy and *p*-nitroaniline in the presence of Et$_3$N under N$_2$, afforded the oxo-bridged oxo(arylimido) molybdenum(V) complexes, [MoTp*(O)Cl](μ-O)[MoTp*(Cl)($\equiv$NC$_6$H$_4$R)] (1, R = OMe; 2, R = NO$_2$). The new compounds were characterized by elemental analysis, i.r., mass, and ^{1}H-n.m.r. spectra. The single crystal X-ray crystallographic determination of [MoTp*(O)Cl](μ-O)[MoTp*(Cl)($\equiv$NC$_6$H$_4$OMe)] was carried out to confirm that there is a Mo—O—Mo bridge and a near linear arylimido group in the structure.

Introduction

The tris(pyrazolyl)borate ligand was first synthesised by Trofimenko [1] and has assumed an important role in modern coordination chemistry [2]. It has been shown that there are strong analogies between the behaviour of metal complexes containing trispyrazolborato anions, and those containing the η^5-cyclopentadienyl ligand [1]. This ligand system has widely been used in inorganic and organometallic chemistry especially with d and f transition elements [3]. It was known that *tris*(pyrazolyl)borate ligands had a significant impact on the modeling of the active centre of Mo enzymes [4]. Also these ligands exhibit dynamic behaviour on the n.m.r. timescale [5]. The sterically encumbering nature of the Tp* (hydro-tris(3,5-dimethylpyrazol-1-yl)borate) ligand compared with Cp* (pentamethylcyclopentadienyl) is widely known and explored in high activity for catalyst systems [6, 7].

Molybdenum, considered as a trace element, presents several oxidation states, and therefore may change easily its coordination number to form mono and binuclear oxo complexes which is of great importance from basic as well as applied points of view. The propensity of oxo-molybdenum species in higher oxidation states to form di, tri and polynuclear complexes is well known [8]. Molybdenum is a relevant element for the synthesis of many homogeneous and heteregenous catalysts. The element is also essential in several enzymatic systems. One of the characteristics of the molybdenum chemistry is related to the easy conversion between its oxidation states and to the changes of coordination number, observed particularly between Mo(III), Mo(IV), Mo(V) and Mo(VI). The chemistry of oxoMo(V) complexes is of importance especially in industrial and biochemical catalysis [9].

Recently, interest in the chemistry of transition metal compounds that contain multiple bonded ligands has increased greatly due mainly to their involvement in many important reactions. Although quite a large number of bis(imido) [10–15] and dioxo [16] complexes of molybdenum are known, there is only a small amount of information on the related mixed terminal oxo-imido compounds [17–23]. Although a number of systems involving μ-ligation in the presence of terminal imido groups have previously been reported [23–30], only a few examples of molybdenum compounds containing both imido ligands and tris(pyrazolyl)borate co-ligand were known [17, 31, 32]. However, the area of μ-oxo complexes containing mixed oxo-arylimido ligands and Tp* co-ligand is still largely unexplored.

In the present paper, we report the synthesis and spectroscopic characterization of two novel binuclear oxo-bridged oxo(arylimido) molybdenum complexes [MoTp*(O)Cl](μ-O)[MoTp*(Cl)($\equiv$NC$_6$H$_4$R)] (R = OMe, NO$_2$) and the X-ray crystal structure of [MoTp*-(O)Cl](μ-O)[MoTp*(Cl)($\equiv$NC$_6$H$_4$OMe)].

Experimental

All preparations and manipulations were carried out using Schlenk techniques under an oxygen-free nitrogen

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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)Cl₂] was prepared according to Enamark's published method [33].

I.r. spectra were recorded on a Magna IR spectrophotometer as pressed KBr disks. ¹H-n.m.r. spectra were recorded in CDCl₃ on 400 MHz High Performance Digital f.t.-n.m.r. at TUBITAK (Research Council of Turkey). Mass spectra analyses were performed on Joel AX505 FAB device using Xe at 3 kV positive ion matrix *m*-NBA (*m*-nitrobenzyl alcohol). Elemental analysis were carried out by using a LECO CHNS 932 instrument. The crystal structure determination was done using a Bruker SMART CCD area-dedector diffractometer.

All yields are based on the starting material-containing compound.

[MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄OMe)] (1)

A mixture of [MoTp*(O)Cl₂] (0.3 g, 0.60 mmol), 4-methoxyaniline (0.14 g, 1.20 mmol) and dry Et₃N (0.6 cm³, 0.42 mmol) in dry toluene (20 cm³) was heated to reflux with stirring under N₂ for *ca.* 14 h, during which time the solution became dark red-brown. The mixture was then cooled, filtered and evaporated to dryness. The residue was dissolved in CH₂Cl₂ and chromatographed on silica gel using CH₂Cl₂/*n*-hexane (9:1, v/v) as eluant. The red-brown fraction was collected, crystallised from CH₂Cl₂/*n*-hexane to yield [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄OMe)], as dark red microcrystals, 0.15 g (51%).

[MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄NO₂)] (2)

A mixture of [MoTp*(O)Cl₂] (0.3 g, 0.60 mmol), 4-nitroaniline (0.16 g, 1.21 mmol) and dry Et₃N (0.6 cm³, 0.42 mmol) in dry toluene (20 cm³) was heated to reflux with stirring under N₂ for 16 h. The reaction was followed by tlc using the procedure described above for (1) to yield [MoTp*(O)Cl](μ-O) [MoTp*(Cl)(≡NC₆H₄NO₂)] as brown microcrystals, 0.12 g (40%).

Results and discussion

Synthetic studies

Reaction of [MoTp*(O)Cl₂] with H₂NC₆H₄R (R = OMe and NO₂) in the presence of triethylamine

in toluene produced oxo-bridged oxo(arylimido)-molybdenum complexes [MoTp*(O)Cl](μ-O)[MoTp*(Cl) (≡NC₆H₄R)] (R = OMe, NO₂). The reactions were performed at the reflux temperature over periods ranging from 14 to 16 h. Formation of the complexes was followed by thin layer chromatography, tlc, using CH₂Cl₂/*n*-hexane (v:v, different ratios) as eluant. The products were readily purified by column chromatography on silica gel 60 (70–230 mesh) using the same solvent mixture. The complexes are air-stable and soluble in chlorinated solvents.

The previously reported mononuclear oxo(arylimido) molybdenum(VI) trispyrazolborate complexes, [MoTp*-(O)Cl(=NR)] (R = 4-tolyl, C₆H₄NMe₂-4), containing mixed oxo-imido ligands and the Tp* co-ligand, were prepared by the reaction of [MoTp*(O)Cl₂] with two equivalents of RNH₂ in the presence of Et₃N [17]. Therefore, the formation of oxo-bridged molybdenum(V) compounds, [MoTp*(O)Cl](μ-O)[MoTp*(Cl) (≡NC₆H₄R)], [(1) R = OMe; (2) R = NO₂] containing both terminal oxo, imido group and Tp* co-ligand by double deprotonation of amines is of interest and are the first examples for mixed oxo-arylimido Mo(V) compounds containing the Tp* co-ligand. The synthetic route shown in Scheme 1 can be suggested for the formation of complexes (1) and (2).

Spectroscopic studies

Molecular ion peaks (Table 1) determined from the mass spectrometric data are in accord with the suggested structure for [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄-NO₂)] and the structure obtained by the X-ray structure of [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄OMe)] (Figure 1).

I.r. spectral data (Table 2) for the complexes [MoTp*-(O)Cl](μ-O)[MoTp*(Cl) (≡NC₆H₄R)] (R = OMe and NO₂) are given in Table 2. Both complexes exhibit the expected absorptions due to the Tp* ligand (*ca.* 2500 cm⁻¹ due to $\nu_{(BH)}$ and 1400 cm⁻¹ associated with the pyrazolyl ring). They possess bands characteristic of the terminal Mo=O unit (*ca.* 960 cm⁻¹). This value was reported as 964 cm⁻¹ for the starting material [MoTp*(O)Cl₂] [33]. For the compounds [MoTp(O)Cl₂] (μ-O)(*cis*-isomer) and [MoTp(O)Cl₂](μ-O)(*trans*-isomer), the peak at 958 cm⁻¹ was assigned as Mo=O of the terminal oxo groups [34].

The compound [MoTp*(O)Cl]₂(μ-O) exhibited $\nu_{(Mo=O)}$ at 960 and 859 cm⁻¹. This value has 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] [35]. The

Table 1. Characterization data for the new complexes

Complex	Colour	Yield (%)	Elemental analytical data (calcd) (%)			
			C	H	N	FAB-MS
(1)	dark red	51	44.0(44.1)	4.9(5.1)	17.0(18.0)	1012.1
(2)	brown	40	41.65(42.2)	4.5(4.7)	18.35(19.1)	1029.5
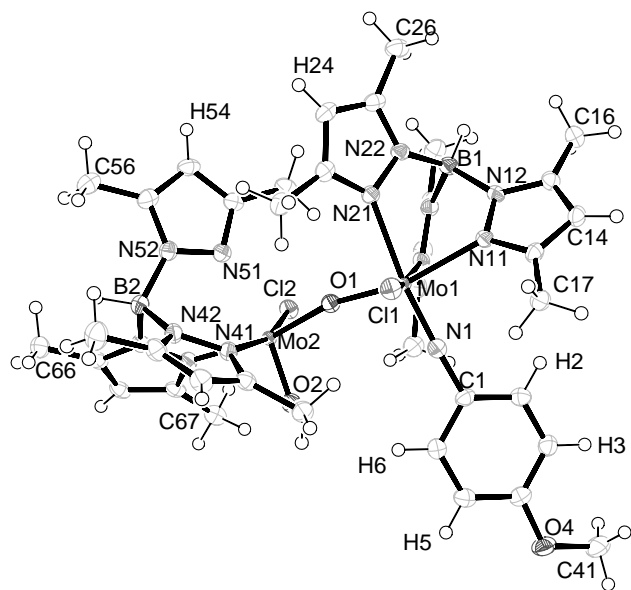
Figure 1. Molecular structure of the compound [MoTp*(O)Cl](μ-O)[MoTp*(Cl)($\equiv$NC$_6$H$_4$OMe)].

Table 2. I.r. data for the new complexes

Complex	υ_{BH}	$\upsilon_{Mo=O}$	$\upsilon_{Mo\equiv N}$	$\upsilon_{Mo-O-Mo}$
(1)	2548	957	1205	788
(2)	2546	961	1211	765

i.r. spectrum of the mixed valence compound, [Mo^{V}Tp*O$_2$](μ-O)[Mo^{VI}Tp*(O)Cl] exhibited three $v_{(Mo=O)}$ bands in the 850–1000 cm^{-1} region. The $v_{(Mo=O)}$ bands were assigned to Mo^V=O (955 cm^{-1}) and *cis*-Mo^{VI}O$_2$ (925, 895 cm^{-1}) [36]. A detailed i.r. and Raman spectroscopy study was carried out for the geometric isomers (*cis* and *trans*) of [MoTp(O)Cl$_2$](μ-O) [34]. According to this study, the peaks at 784 and 456 cm^{-1} were assigned to the asymmetric stretch and the deformation mode of the linear oxo-bridged unit, respectively [37]. For the compound [MoTp*(O)Cl]$_2$(μ-O), a symmetric stretch oxo-bridged unit was reported as 753 cm^{-1} [34]. Therefore, the peaks observed for the new compounds [MoTp*(O)Cl](μ-O)[MoTp*(Cl)($\equiv$NC$_6$H$_4$R)] (R = OMe, NO$_2$) at *ca.* 755 and 455 cm^{-1} could be assigned to an asymmetric stretch and deformation mode 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] [36] 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 i.r. spectra of all the new complexes. Indeed, the structure determined for the compound [MoTp*(O)Cl](μ-O)[MoTp*(Cl) ($\equiv$NC$_6$H$_4$OMe)] by X-ray diffraction analyses revealed a triple bond

between molybdenum and nitrogen. In general, identifying a $v_{(Mo=N)}$ or $v_{(Mo\equiv N)}$ vibration is a difficult task because of: (i) the variability in the Mo–N bond order, and (ii) coupling of the Mo=N vibration to other vibrations in the molecule, in particular the adjacent N–C vibration of the imido group [10]. However, a value of 1100–1300 cm^{-1} for the $v_{(Mo=N)}$ has been suggested [38] and McCleverty *et al.* [17] reported values in the 1200–1250 cm^{-1} range for the compounds [MoTp*(O)Cl(=NR)] (R = 4-tolyl, and C$_6$H$_4$NMe$_2$-4). The i.r. spectra of the oxo-bridged oxo(arylimido) molybdenum(V) compounds, [MoTp*(O)Cl](μ-O)[MoTp* (Cl)($\equiv$NC$_6$H$_4$R)], (R = OMe, NO$_2$) also exhibited peaks around 1200–1300 cm^{-1} range which may be ascribed to $v_{(Mo\equiv N)}$.

The ^{1}H-n.m.r. data (Table 3) of the new complexes [MoTp*(O)Cl](μ-O)[MoTp*(Cl)($\equiv$NC$_6$H$_4$R)] (R = OMe, NO$_2$) exhibited all the expected peaks. The four C$_6$H$_4$ protons are clearly split into two sets of two (implying the equivalance of H^2 with H^6, and H^3 with H^5, by free rotation of the phenyl ring with respect to the metal core). The signals attributable to the Tp* ligand appeared as two groups of singlets in the region 1.23–3.56 p.p.m. assigned to the pyrazolyl ring methyl protons and 5.28–6.21 p.p.m. due to the pyrazolyl ring C–H protons. The low symmetry of both compounds means that all three pyrazol H(4) protons and all six methyl groups of the Tp* ligand are non-equivalent. For [MoTp*(O)Cl](μ-O)[MoTp*(Cl)($\equiv$NC$_6$H$_4$OMe)] six pyr-

Table 3. ^{1}H-n.m.r. data for the new complexes (400 MHz, 293 K, CDCl$_3$)

Complex	$\delta_H(A)^a$	Multiplicity and assignments[b]
(1)	7.53	(d, 2H, J (HH) 8, C$_6$*H$_4$*OMe)
	6.77	(d, 2H, J (HH) 8, C$_6$*H$_4$*OMe)
	6.04	(s, 1H, Me$_2$C$_3$*H*N$_2$)
	5.94	(s, 1H, Me$_2$C$_3$*H*N$_2$)
	5.82	(s, 1H, Me$_2$C$_3$*H*N$_2$)
	5.79	(s, 1H, Me$_2$C$_3$*H*N$_2$)
	5.41	(s, 1H, Me$_2$C$_3$*H*N$_2$)
	5.36	(s, 1H, Me$_2$C$_3$*H*N$_2$)
	3.83	(s, 3H, OC*H$_3$*)
	3.20	(s, 6H, *Me$_2$*C$_3$HN$_2$)
	2.79	(s, 6H, *Me$_2$*C$_3$HN$_2$)
	2.71	(s, 6H, *Me$_2$*C$_3$HN$_2$)
	2.48	(s, 6H, *Me$_2$*C$_3$HN$_2$)
	2.37	(s, 6H, *Me$_2$*C$_3$HN$_2$)
	2.30	(s, 6H, *Me$_2$*C$_3$HN$_2$)
(2)	8.12	(d, 2H, J (HH) 9, C$_6$*H$_4$*NO$_2$)
	6.90	(d, 2H, J (HH) 9, C$_6$*H$_4$*NO$_2$)
	5.85	(s, 2H, Me$_2$C$_3$*H*N$_2$)
	5.68	(s, 2H, Me$_2$C$_3$*H*N$_2$)
	5.57	(s, 2H, Me$_2$C$_3$*H*N$_2$)
	2.71	(s, 6H, *Me$_2$*C$_3$HN$_2$)
	2.37	(s, 6H, *Me$_2$*C$_3$HN$_2$)
	2.34	(s, 6H, *Me$_2$*C$_3$HN$_2$)
	2.32	(s, 6H, *Me$_2$*C$_3$HN$_2$)
	2.29	(s, 6H, *Me$_2$*C$_3$HN$_2$)
	2.11	(s, 6H, *Me$_2$*C$_3$HN$_2$)

^{a} In CDCl$_3$; A = relative intensity; ^{b} J values in Hz.

Table 4. Crystal data and structure refinement for [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄OMe)]

Empirical formula	$C_{37} H_{51} B_2 Cl_2 Mo_2 N_{13} O_3$
Formula weight	1010.31
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a	11.0200(2) Å
b	11.5868(2)
c	18.7414(3) Å
α	77.3320(10)°
β	76.8440(10)°
γ	75.8450(10)°
Volume	2225.27(7) Å³
Z	2
Density (calculated)	1.508 mg m⁻³
Absorption coefficient	0.735 mm⁻¹
F(0 0 0)	1032
Crystal size	0.08 × 0.08 × 0.03 mm
θ range for data collection	1.13–25.70°
Index ranges	−13 ≤ h ≤ 12, −13 ≤ k ≤ 14, −22 ≤ l ≤ 20
Reflections collected	15997
Independent reflections	7504 [R_{int} = 0.0226]
Completeness to θ = 25.70°	88.7%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7504/0/553
Goodness-of-fit on F^2	S = 0.924
R indices [for 6435 reflections with I > 2(I)]	R_1 = 0.0227, wR_2 = 0.0533
R indices (for all 7504 data)	R_1 = 0.0267, wR_2 = 0.0540
Weighting scheme	$w^{-1} = \sigma^2(F_0^2) + (aP)^2 + (bP)$, where $P = [max(F_0^2, 0) + 2F_c^2]/3$ a = 0.0316, b = 0.0000
Largest diff. peak and hole	0.375 and −0.489 eÅ⁻³

Table 5. Selected bond lengths (Å) and angles (°) for [MoTp*(O)Cl](μ-O)[MoTp* (Cl)(≡NC₆H₄OMe)]

Bond lengths	
Mo(1)—N(1)	1.7391(19)
Mo(1)—O(1)	1.9004(14)
Mo(1)—Cl(1)	2.4159(5)
O(1)—Mo(2)	1.8731(14)
N(1)—C(1)	1.381(3)
Mo(2)—O(2)	1.6779(16)
Mo(2)—Cl(2)	2.3918(5)
B(1)—N(22)	1.522(3)
B(1)—N(12)	1.544(3)
B(1)—N(32)	1.546(3)
B(2)—N(52)	1.525(3)
B(2)—N(42)	1.547(3)
B(2)—N(62)	1.546(3)
Mo(1)—N(11)	2.2185(17)
Mo(1)—N(21)	2.2768(18)
Mo(1)—Cl(1)	2.4159(5)
Mo(2)—N(41)	2.1600(18)
Mo(2)—N(61)	2.2180(17)
Mo(2)—N(51)	2.3811(18)
Bond angles	
Mo(2)—O(1)—Mo(1)	164.99(9)
C(1)—N(1)—Mo(1)	176.67(7)
N(1)—Mo(1)—O(1)	100.16(7)
N(1)—Mo(1)—N(11)	93.09(7)
N(1)—Mo(1)—Cl(1)	97.03(6)
O(1)—Mo(1)—Cl(1)	98.45(5)
N(11)—Mo(1)—Cl(1)	88.19(5)
O(2)—Mo(2)—O(1)	101.60(7)
O(1)—Mo(2)—N(41)	92.23(7)
O(2)—Mo(2)—Cl(2)	98.93(5)
O(1)—Mo(2)—Cl(2)	95.32(5)
N(31)—Mo(1)—N(11)	81.70(7)
N(41)—Mo(2)—N(61)	82.96(7)
O(2)—Mo(2)—N(51)	169.67(7)
O(1)—Mo(2)—N(51)	88.30(6)
N(41)—Mo(2)—N(51)	82.27(7)
N(61)—Mo(2)—N(51)	78.69(6)
O(2)—Mo(2)—N(61)	91.26(7)
O(1)—Mo(2)—N(61)	166.60(7)
N(41)—Mo(2)—N(61)	82.96(7)

azol H(4) signals were observed in the range δ 6.04–5.36 due to the two non-equivalent Tp* ligand, whereas in the spectrum of [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄NO₂)] three signals were observed. The reason for observing three resonances instead of six in [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄NO₂)] 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. [39, 40]. The low symmetry of these compounds also means six methyl resonances for each Tp* ligand must be observed in the area of 1.5–3.5 p.p.m. Indeed, six resonances attributible to the metyl groups of Tp* ligand were observed for the compounds [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄OMe) and [MoTp*(O)-Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄NO₂)] in the region δ 3.20–2.30 and 2.71–2.11 respectively. The observation of only six resonances (total integrated area equivalent to 12 protons) instead of 12 could also be attributed to accidental degeneracy of six methyl resonances of two inequivalent Tp* ligands.

Generally NH₂ and NH protons appear in the δ 11.14–13.15 p.p.m. range [10]. No broad signals typical of amine or amide protons were observed in the

¹H-n.m.r. spectra of the new compounds which leads us to believe that they are either Mo=N or Mo≡N linkages.

Crystal structure determination and refinement

A single crystal of [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄OMe)] was recrystallized from a CH₂Cl₂/hexane mixture and coated in high-vacuum grease and mounted on a glass fibre. A view of the molecular structure of [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄OMe)] along with the atomic labelling scheme is shown in Figure 1. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with CuKα radiation (λ = 1.54184 Å) [41]. Intensities were integrated [42] from several series of exposures, each exposure covering 0.3° in ω, and the total data set being a sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measure-

ments [43]. The structure was solved by Patterson synthesis and refined by least squares on weighted F^2 values for all reflections (Table 4) [44]. 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. Refinement proceeded smoothly to give the residuals shown in Table 4. Complex neutral-atom scattering factors were used [45].

Crystal structure of [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄OMe)]

*Crystal structure of [MoTp*(O)Cl](μ-O)[MoTp*(Cl) (≡NC₆H₄OMe)]*

The compound [MoTp*(O)Cl](μ-O)[MoTp*(Cl) (≡NC₆H₄OMe)] is comprised of two unidentical MoTp*Cl unit connected by a single oxo-bridge. There are two pseudo-octahedral metal centers with three nitrogen atoms of the Tp* ligand occupying one face of the octahedron (Figure 1).

Mo(2) is coordinated by facial Tp*, terminal oxo, chloro and bridging oxo ligands whereas the Mo(1) is coordinated by facial Tp*, chloro, arylimido and a bridging oxo ligand. The two chloride atoms were *trans* to each other. Atomic co-ordinates and selected bond distances and bond angles are given in Table 5. The Mo(1)—O(1), Mo(2)—O(1), Mo(2)—O(2), Mo(1)—Cl(1), Mo(2)—Cl(2), distances of 1.9004(14), 1.8731(14),

1.6779(16), 2.4159(5), 2.3918(5), 1 Å, respectively, are all within respected ranges [37]. The Mo(1)—(μ-O) distance was reported [46] as 1.8886(9) Å in [{MoTp*(O)Cl}₂](μ-O). The X-ray crystal structures of two geometric isomers of the related complex [MoTp*-(O)-Cl]₂(μ-O) (Tp = hydrotrispyrazolborate) were reported by Lincoln and Koch. The reported bond distances are comparable to those encountered here. For instance, in the *trans* isomer, the Mo(1)—(μ-O) distances of 1.861(1) Å is reported [34] which is comparable to the above value for MoTp*(O)Cl](μ-O) [MoTp*(Cl) (≡NC₆H₄OMe)].

For [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄OMe)], deviations from octahedral geometry are manifest in the bond angles O(2)—Mo(2)—O(1) (101.60(7)°) and O(1)—Mo(1)—N(11) (164.28(7)°). These values are in accord with the data reported for [MoTp*OCl]₂(μ-O) and [MoTp^Pr OCl](μ-O)[MoTp^Pr O(OH)] [35]. The Mo(1)—O(1)—Mo(2) angle of 164.99(9)° deviates considerably from linearity (cf. 177.4(4)° for (*cis*) [MoTp*-(O)-Cl]₂(μ-O) and 177.3(2)° and 180° for (*trans*) [MoTp(O)Cl]₂(μ-O) [34]. This value is comparable to the one (158.5(2)°) reported (36) for the compound [MoTp^Pr-OCl](μ-O)[MoTp^Pr O(OH)] 176.67(17).

Molybdenum nitrogen multiple bond could either be a double bond with Mo—N—C angle of 120° or a triple bond with Mo—N—C angle of 180°. In the first case imido group acts as a four electron donor with no lone pair in the latter case it behaves as a six electron donor. The Mo(1)—N(1)—C(1) bond angle of 176.67(17)° for [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄OMe)] is indicative
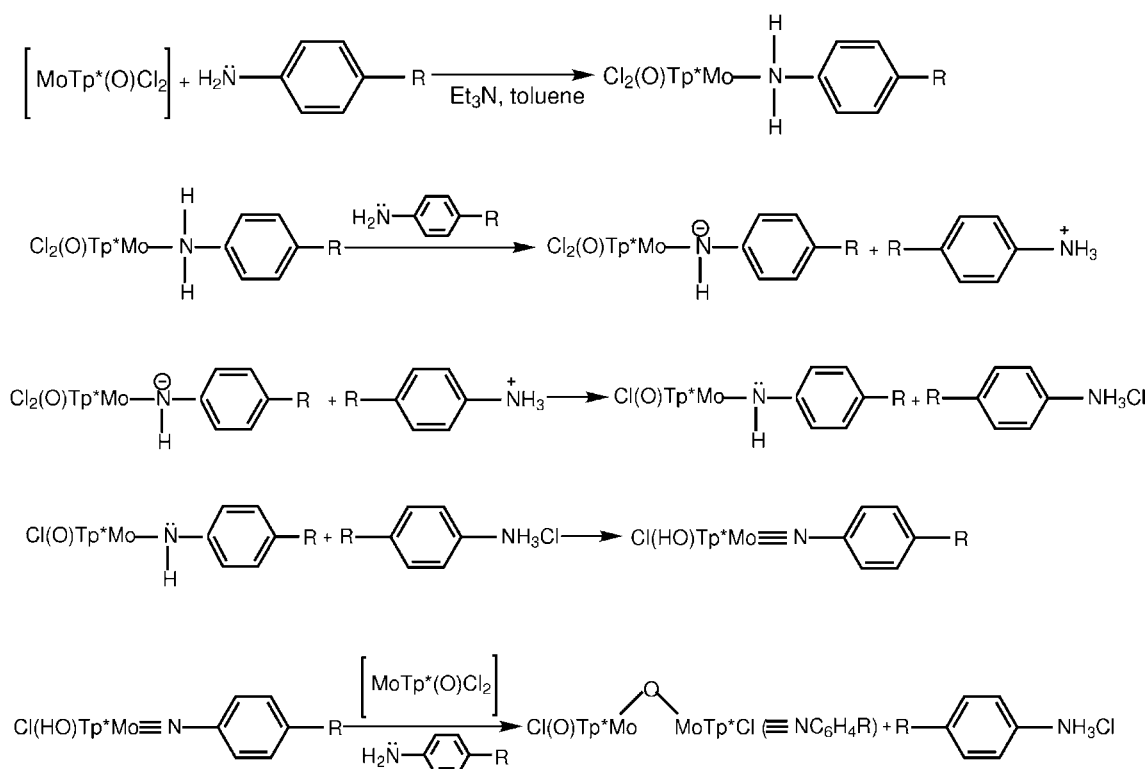
Scheme 1. Synthetic route for the formation of *(1)* and *(2)*.

of a linear Mo—N—C(aryl) unit. The typical range for this arrangement was reported as 160–180° [38]. Mo(1)—N(1) bond length of 1.7391(19) Å is also indicative of a Mo≡N bond. This value is in accord with the reported bond length values for compounds containing Mo≡N bond and shorter than the Mo=N ones [38].

In conclusion, complexes [MoTp*(O)Cl](μ-O) [MoTp*(Cl)(≡NC$_6$H$_4$R)] (R=OMe, NO$_2$) described herein are one of the rare examples of a family of oxo-bridged oxo(arylimido) Mo(V) complexes containing *tris*(pyrazol)borate co-ligand.

Acknowledgements

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 234654.

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