Reactions of the solvent-stabilized compound $[MoOCl_2(THF)_2]$ with aromatic nitrogen donor ligands: spectroscopic characterization and semiempirical AM1* calculations

Gülşah KILIÇKAYA[1], **Başak DOĞAN**[1], **Nursel ACAR**[2],
Işıl TOPALOĞLU SÖZÜER[1,*]

[1]*Department of Chemistry, Faculty of Science, İzmir Institute of Technology, Gülbahçe,*
35430 Urla, İzmir-TURKEY
e-mail: isiltopaloglu@iyte.edu.tr
[2]*Deparment of Chemistry, Faculty of Science, Ege University,*
35100 Bornova, İzmir-TURKEY

Reaction of the solvent-stabilized dioxo-molybdenum(VI) compound $[MoO_2Cl_2(THF)_2]$ with PPh_3 yielded the oxomolybdenum(IV) species $[MoOCl_2(THF)_2]$ (**1**) by the removal of one oxygen atom as PPh_3O. The complexes $[MoOCl_2(=NC_6H_4CN)]$ **2**, $[MoOCl_2(CNC_6H_4OH)]$ **3**, $[MoOCl_2(=NC_6H_4NH_2)]$ **4**, and $[MoOCl_2(=NC_6H_4OCH_3)]$ **5**, were synthesized by the reactions of $[MoOCl_2(THF)_2]$ with XC_6H_4Y (X $= NH_2$, Y = CN; X= CN, Y = OH; X = Y = NH_2; X = NH_2, Y = OCH_3). All the new compounds were characterized by elemental analyses, and FTIR, UV-Vis, and ^1H- and ^{13}C-NMR spectra. Geometrical parameters and molecular orbital calculations showed that compounds **2-5** are stabilized by a charge transfer between the Mo center and the phenyl ring.

Key Words: Mo(VI) complexes; oxo-imido complexes; oxomolybdenum complexes; oxygen atom.

Introduction

Transition metal-oxo transfer systems are of great importance due to their potential relevance to oxygen atom transfer processes in a wide range of catalytic reactions.[1−3] Molybdenum compounds have an important place

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*Corresponding author

in this field since they are found in many catalytic systems involving oxidation reactions, both in industrial processes and in nature.[4−6] In recent years, several oxomolybdenum(VI) complexes, $[MoO_2X_2(L^1)_n]$,[7−12] $[MoO_2X(L^2)_m(L^1)_n]$ and $[MoO_2(L^2)_m(L^1)_n]$[13,14] (X = F, Cl, Br, CH$_3$; L = mono or bidantate neutral (L^1) or anionic (L^2) N-, O-, S- ligand) with the *cis*-MoO$_2$ fragment have been examined as homogeneous catalysts for the reaction of olefins with *tert*-butyl hydroperoxide.

Several dioxomolybdenum(VI) complexes have also been reported as new catalysts and to model active sites of molybdenum oxotransferase enzymes.[15−20] Oxygen atom transfer (OAT) reactions between *cis*-dioxomolybdenum(VI) complexes and tertiary phosphine have been of great interest as model reactions in molybdenum oxotransferases such as sulfite oxidase.[2,21−24] In these catalytic reactions the oxidation states of molybdenum changes between +6 and +4.[25−32] It has been reported that[33] PPh$_3$ abstracts an oxo group from dioxobis(N,N-dialkyldithiocarbamato)molybdenum(VI) $[MoO_2(S_2(S_2CNR_2)_2(THF)_2]$, yielding $[MoO(S_2(S_2CNR_2)_2(THF)_2]$ and OPPh$_3$. So far, many oxo-, dioxo-, or μ-oxo- molybdenum compounds bearing ligands with NN, NS, and NSO donor atoms[34,35] and non-sulfur donor atoms[28,36,37] have been reported and tested for their oxygen atom transfer capability.

The solvent-stabilized $[MoO_2X_2(Solv)_2]$ (X = Cl or Br; Solv: THF or RCN) complexes are known as useful synthetic precursors for preparing oxomolybdenum species with various nitrogen and oxygen donor ligands. $[MoO_2X_2(NCR)_2]$ and $[MoO_2X_2(THF)_2]$ were prepared by dissolving the dioxomolybdenumdichloride or bromide in NCR (R = CH$_3$ or C$_6$H$_5$) or THF. Organic ligands with donor functionalities such as nitrogen react readily with complexes of the type $[MoO_2X_2(Solv)_2]$.[7]

Recently, there has been significant interest in the chemistry of oxo and imido ligands and their complexes. Both the imido and oxo groups lead to stabilization of high formal oxidation states. Organo-imido 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.[38] Several molybdenum imido compounds[39−43] and a number of related mixed terminal oxo–imido compounds have previously been reported. We have previously described the synthesis and spectroscopic characterization of a family of oxo-bridged oxo(arylimido)molybdenum(V) complexes having the general formula $[Tp^*Mo(O)Cl](\mu$-O)$[Tp^*Mo(NAr)Cl]$ [Ar = C$_6$H$_4$X-4 (X = OMe, NO$_2^{44}$; Cl, Br[45]) or C$_6$H$_4$X-3 (X = F, I,[46] X = OEt, OPr[47]) by the reaction of $[MoTp^*(O)Cl_2]$ with the corresponding H$_2$NAr in refluxing toluene.

In the present paper, we report the reactions of $[MoOCl_2(THF)_2]$, with aromatic nitrogen donor ligands. The novel oxomolybdenum compounds obtained were characterized by elemental analyses, and FTIR and ^{1}H- and ^{13}C-NMR spectra. In addition, quantum chemical model calculations were carried out to discuss the nature and properties of the compounds using the semiempirical AM1* method.

Experimental

Materials

All preparations and manipulations were carried out under an oxygen-free nitrogen atmosphere using Schlenk techniques. All glassware was oven dried at 120 °C. Solvents were dried by standard procedures, distilled, and kept under nitrogen over 4 ? molecular sieves. $[MoO_2Cl_2]$ was purchased from Aldrich. $[MoO_2Cl_2(THF)_2]$ was prepared according to the literature method.[8,48]

Apparatus

FTIR spectra were recorded on a Magna IR spectrophotometer as pressed KBr disks.[1] H- and ^{13}C-NMR spectra were recorded in DMSO-d_6 on a 400 MHz High Performance Digital FT-NMR. Elemental analysis was carried out by using a LECO CHNS 932 instrument. All yields are based on the starting material containing compound. The UV spectra were recorded using a Perkin-Elmer Lambda 35 spectrophotometer.

Quantum chemical model calculations

Calculations were performed by using the program package VAMP 10.0[49] as implemented in Materials Studio 4.1[50]. Molecular properties in the electronic ground state were computed by using either the Restricted Hartree-Fock (RHF) or the Unrestricted Hartree-Fock formalisms with the AM1* Hamiltonian.[51] Full optimizations were carried out and the natures of the structures were characterized as minima with all positive frequencies. Spectroscopic properties of the closed shell structures were investigated using excited state calculations, which used a singles plus pair doubles (PECI) configuration interaction (CI) expansion with an active window of the 4 highest occupied and the 4 lowest unoccupied molecular orbitals. Unfortunately, these calculations cannot be extended to on open shell structures. The optimized structures are discussed in terms of geometries and energies (including heat of formation, ionization potentials, dipole moments etc.).

Preparation of complexes

[MoOCl$_2$(THF)$_2$] (1)

The solvent-stabilized compound, [MoO$_2$Cl$_2$(THF)$_2$], (0.40 g, 1.16 mmol) in THF (10 mL) was treated with PPh$_3$ (0.30 g, 1.16 mmol) under nitrogen and the reaction mixture was left to stir at room temperature for 8 h during which the solution became dark brown and a precipitation was formed. The mixture was cooled, filtered through celite, and evaporated to dryness. The residue was crystallized from CH$_2$Cl$_2$/n-hexane (1:4) and washed with n-hexane to afford the compound [MoOCl$_2$(THF)$_2$], as dark yellow microcrystals, (0.26 g, 68%).

[MoOCl$_2$(=NC$_6$H$_4$CN)] (2)

A solution of [MoOCl$_2$(THF)$_2$] (0.25 g, 0.77 mmol) in THF (10 mL) was treated with p-H$_2$NC$_6$H$_4$CN (0.09 g, 0.77 mmol) in THF (10 mL). The reaction mixture changed color immediately to brown and was stirred further for 2 h. The mixture was evaporated to dryness and the residue was crystallized from CH$_2$Cl$_2$/n-hexane (1:4) to afford the compound [MoOCl$_2$(=NC$_6$H$_4$)CN)], as light brown microcrystals (0.20 g, 65%).

[MoOCl$_2$(CNC$_6$H$_4$OH)] (3)

A solution of [MoOCl$_2$(THF)$_2$] (0.25 g, 0.77 mmol) in THF (10 mL) was treated with p-CNC$_6$H$_4$OH (0.09 g, 0.77 mmol). The mixture was stirred under nitrogen for 3 h. The resulting red solution was evaporated to dryness and crystallized from CH$_2$Cl$_2$/n-hexane (1:4) to yield the compound [MoOCl$_2$(CNC$_6$H$_4$OH)], as light brown microcrystals (0.13 g, 60%).

[MoOCl$_2$(=NC$_6$H$_4$NH$_2$)] (4)

A solution of [MoOCl$_2$(THF)$_2$] (0.25 g, 0.77 mmol) in THF (10 mL) was treated with p-H$_2$NC$_6$H$_4$NH$_2$ (0.08 g, 0.77 mmol). The solution turned beige within seconds and darkened to green over 10 min. After stirring for 3 h the color of the resulting solution turned black. The mixture was evaporated to dryness. The residue was crystallized from CH$_2$Cl$_2$/n-hexane (1:4) and washed with n-hexane. The compound [MoOCl$_2$(=NC$_6$H$_4$)NH$_2$)] was obtained as black microcrystals (0.13 g, 63%).

[MoOCl$_2$(=NC$_6$H$_4$OCH$_3$)] (5)

A solution of [MoOCl$_2$(THF)$_2$] (0.25 g, 0.77 mmol) in THF (10 mL) was treated with p-H$_2$NC$_6$H$_4$OCH$_3$ (0.09 g, 0.77 mmol). The mixture was stirred under nitrogen for 3 h. The resulting red solution was evaporated to dryness and crystallized from CH$_2$Cl$_2$/n-hexane (1:4) to yield the compound [MoOCl$_2$(=NC$_6$H$_4$OCH$_3$)], as dark brown microcrystals (0.14 g, 61%).
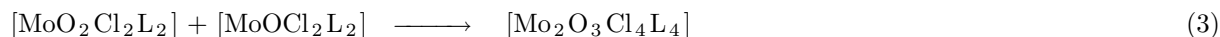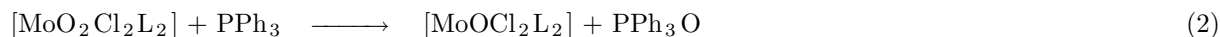
Results and discussion

Synthetic studies

The solvent-stabilized compound [MoO$_2$Cl$_2$(THF)$_2$] was obtained according to the literature method.[8,48] This compound was treated with PPh$_3$ in THF for the removal of one oxygen atom to obtain the related oxomolybdenum(IV) compound.

Oxidation of PPh$_3$

The oxidation of PPh$_3$ is thought to involve oxygen atom transfer from the solvent-stabilized dioxomolybdenum(VI) complex as in Eq. (1).

$$[\text{Mo}^{VI}\text{O}_2\text{Cl}_2(\text{THF})_2] + \text{PPh}_3 \xrightarrow[\text{18 h}]{\text{THF}} [\text{Mo}^{IV}\text{OCl}_2(\text{THF})_2] + \text{PPh}_3\text{O} \tag{1}$$

Several dioxomolybdenum(VI) compounds and several model systems were previously known to carry out 2-electron OAT processes that interconvert cis-[Mo^{VI}O$_2$]$^{2+}$ and [Mo^{IV}O]$^{2+}$ centers.[21,52] For example, oxo transfer reactions from [MoO$_2$Cl$_2$(DMF)$_2$] (DMF = dimethylformamide) and [MoO$_2$Cl$_2$(DMSO)$_2$] (DMSO = dimethylsulfoxide) to PPh$_3$ were investigated and the oxomolybdenum(IV) compounds [MoOCl$_2$(DMF)$_2$] and [MoOCl$_2$(DMSO)$_2$] were reported as the products.[53] In some reactions red-purple bimetallic molybdenum(V) species Mo$_2$O$_3$L$_4$ (L = acetylacetonato, S$_2$CNR$_2$, S$_2$PR$_2$) were reported as the major products of oxygen atom transfer reactions, which proceed as follows:

$$[\text{MoO}_2\text{Cl}_2\text{L}_2] + \text{PPh}_3 \longrightarrow [\text{MoOCl}_2\text{L}_2] + \text{PPh}_3\text{O} \tag{2}$$

$$[\text{MoO}_2\text{Cl}_2\text{L}_2] + [\text{MoOCl}_2\text{L}_2] \longrightarrow [\text{Mo}_2\text{O}_3\text{Cl}_4\text{L}_4] \tag{3}$$
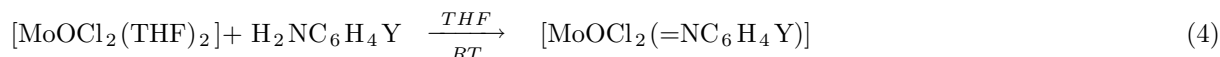
(L = monodentate ligand)

The extent of occurrence of the comproportionation reaction shown in Eq. (3) was reported to be strongly dependent on the electronic and steric nature of the ligands.[54] In our study, no evidence for a bimetallic

oxomolybdenum(V) compound was found; only a single new product was detected by thin layer chromatography (TLC) carried out during the reaction of $[MoO_2Cl_2(THF)_2]$ with PPh_3.

Reaction of $[MoOCl_2(THF)_2]$ with Aromatic Nitrogen Donor ligands

By the reaction of solvent-stabilized oxomolybdnum(IV) compound, $[MoOCl_2(THF)_2]$, with XC_6H_4Y (X=NH_2, Y = CN, **2**; X = OH, Y = CN, **3**; X = Y = NH_2, **4**; X = NH_2, Y = OCH_3 **5)** in THF, the novel mononuclear oxomolybdenum(IV) compounds of the type $[MoOCl_2(XC_6H_4Y)]$ were prepared.

$$[MoOCl_2(THF)_2] + H_2NC_6H_4Y \xrightarrow[RT]{THF} [MoOCl_2(=NC_6H_4Y)] \qquad (4)$$

(Y = CN, **2;** NH_2, **4;** OCH_3, **5**)

$$[MoOCl_2(THF)_2] + CNC_6H_4OH \xrightarrow[RT]{THF} [MoOCl_2(CNC_6H_4OH)] \qquad (5)$$

The air- and moisture-sensitive compounds **2-5** are red-brown in solution, nearly insoluble in non-polar solvents, but soluble in most polar solvents. All the new compounds were decomposed at ca. 139-153 °C. The analytical results, yields, and colors of complexes **1-5** are given in Table 1. The elemental analyses of the new compounds are in good agreement with the suggested formulation.

Table 1. The formula, formula weight, colors, melting points, yields, and elemental analyses results of compounds **1-5**.

Compound	Color (decomp. at)	mp (°C)	Yield (%)	Found (calcd)		
				C	H	N
$[MoOCl_2(THF)_2]$ $C_8H_{16}O_3Cl_2Mo$	Dark yellow	151-152	68	28.75(28.28)	5.55(4.92)	—
$[MoOCl_2(=NC_6H_4CN)]$ $C_7H_4N_2OCl_2Mo$	Light brown	145-146	65	27.79(28.11)	1.55(1.35)	9.60(9.39)
$[MoOCl_2(CNC_6H_4OH)]$ $C_7H_5NO_2Cl_2Mo$	Light brown	139-140	60	27.27(27.83)	1.97(1.66)	5.27(4.63)
$[MoOCl_2(=NC_6H_4NH_2)]$ $C_6H_6N_2OCl_2Mo$	Black	147-148	63	24.66(25.02)	2.27(2.09)	9.23 (9.72)
$[MoOCl_2(=NC_6H_4OCH_3)]$ $C_7H_7NO_2Cl_2Mo$	Dark brown	152-153	61	26.98(27.70)	2.72(2.31)	4.86(4.61)

Spectroscopic Studies

IR Spectra

IR spectra data for compounds **1-5** are given in Table 2. All the compounds show medium to strong bands in the region 937-972 cm^{-1} assignable to Mo=O moiety. It is well known that symmetric and antisymmetric stretching vibrations are observed in IR spectra near 900 cm^{-1} attributed to a *cis*-MoO_2^{2+} core.[55] $[MoO_2Cl_2]$ exhibited 2 bands at 940 and 905 cm^{-1} whereas $[MoOCl_2(THF)_2]$ exhibited only 1 Mo=O and at 937 cm^{-1}.[56]

This observation strongly supports the formation of the mononuclear oxomolybdenum(IV) by the removal of one oxygen atom as PPh_3O. In addition, the IR spectrum of PPh_3O revealed the presence of a band at

1190 cm^{-1}, which may be attributed to $\nu_{(P=O)}$. The possibility of the formation of a bimetallic product of the type $[Mo_2O_3Cl_4L_4]$ was disproved by the IR spectrum of **1** as no peaks were observed at ca. 740 or ca. 480 cm^{-1} for the symmetric and antisymmetric bridge vibrations of Mo-O-Mo, respectively.[56] Similarly, the oxomolybdenum(IV) compounds $[MoO(S_2PPh_2)_2]$ and $[MoO[(S_2P(i-Pr)_2]_2$ exhibited a single Mo=O stretching vibration at 970 and 975 cm^{-1} respectively.[54]

Table 2. Characteristic FTIR bands (cm^{-1}) for compounds **1-5**.

Complex	$\nu_{Mo=O}$	$\nu_{Mo=N}$	ν_{N-H}	ν_{NH2}	$\nu_{C\equiv N}$	ν_{C-OH}
1	937s	-	-	-	-	-
2	959s	1208s	absent	absent	2237s	-
3	969s	-	-	-	2253s	1122s
4	964s	1206s	absent	3329m	-	-
5	972s	1259s	1516m	absent	-	-

The characteristic Mo=O stretching vibrations of the other compounds, **2-5**, were observed in the range between 937 and 972 cm^{-1} as expected (see Table 2). All other characteristic ligand vibrations were interpreted by the comparison of the free ligand vibrations with those of the complexes.

In the IR spectrum of **2**, only one C≡N stretching mode is observed at 2237 cm^{-1}, which is shifted to higher wavenumber with respect to the free ligand (2216 cm^{-1}). There is no peak due to the NH stretching mode at ca. 3070 cm^{-1}. The 2 vibrations at ca. 3370 cm^{-1} and 3450 cm^{-1} from the symmetric and asymmetric stretching modes of the NH_2 groups of the free ligands completely disappeared, which seems to indicate the existence of either Mo=N or Mo≡N linkages. In general, identifying a $\nu_{(Mo=N)}$ or $\nu_{(M\equiv N)}$ vibration is difficult 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.[38] A value of 1100-1300 cm^{-1} for the $\nu_{(Mo=N)}$ has been suggested by Dehnicke.[57] McCleverty et al.[58] reported values in the range 1200-1250 cm^{-1} for the compounds $[MoTp^*(O)Cl(=NR)]$ (R= 4-tolyl, and $C_6H_4NMe_2$-4). The dinuclear compounds of the type $[MoTp^*(O)Cl](\mu$-O$)[MoTp^*(Cl)(\equiv NC_6H_4Y)]$ (Y = *p*-F, *p*-Br, *m*-I, *m*-Cl, *p*-OMe, *p*-OEt, *p*-OPr, *p*-OBu, *p*-NO$_2$) also exhibited peaks at ca. 1200-1300 cm^{-1}, which were ascribed to $\nu_{(Mo=N)}$.[44−47] Therefore, a Mo=N or Mo≡N linkage could be suggested for compound **2** as well. For compound **3**, the band observed at 1122 cm^{-1} was attributed to ν_{C-OH}, revealing that the ring-bound hydroxyl group did not undergo a deprotonation reaction and was coordinated to molybdenum. The band observed at 2253 cm^{-1} was interpreted as ν_{CN} for the coordinated CN group, implying a shift upon coordination in the positive range 20-40 cm^{-1}. For compound **4**, the vibrations observed at 3418 and 3333 cm^{-1} were assigned as the symmetric and asymmetric stretching modes of a NH_2 group. The lack of bands due to NH group at ca. 3200 cm^{-1} suggested a Mo=N linkage for the second NH_2 group and the band observed at 1261 cm^{-1} was attributed to the Mo=N linkage. The IR spectrum of compound **5** did not display any peak at ca. 1200 cm^{-1} due to Mo-OCH$_3$ linkage, revealing that there is no coordination through methanol. The lack of peaks due to the symmetric and antisymmetric modes of a NH_2 and a NH group suggest double deprotonation reaction results in the formation of a Mo=N linkage as was the case for compounds **2** and **4**. The values for Mo=N linkages in compounds **2**, **4**, and **5** are comparable to the values for the previously reported oxo-imido molybdenum(V) compounds.[44−47]

UV Spectra

The UV spectra of compounds **2-5** are shown in Figure 2. The bands observed at ca. 300 nm in DMSO are in agreement with the computed AM1* results found at ca. 336 nm. The shifts could be due to the change of solvent from THF to DMSO.
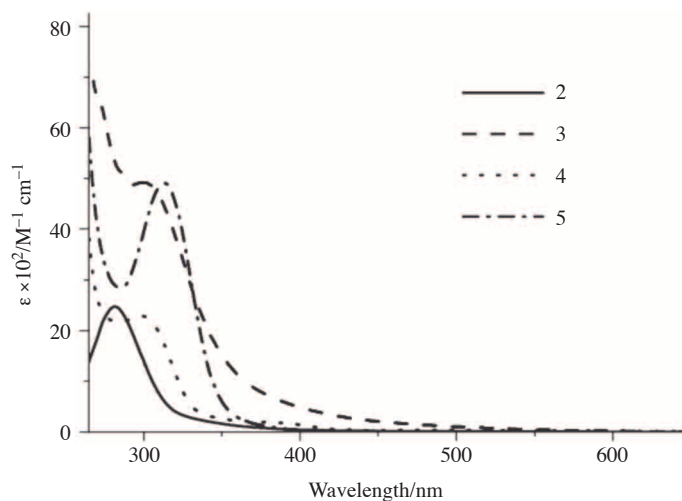

Figure 1. UV/Vis absorption spectra of compounds **2-5** in DMSO.

^{31}P-, ^{1}H-, and ^{13}C-NMR Spectra

The ^{31}P-NMR spectrum of **1** was run to check the possible coordination of PPh$_3$ to molybdenum and no peaks were observed. In the^{1}H-NMR spectrum of **2** (see Table 3) characterization was straightforward; no peak due to either NH$_2$ or NH protons was observed. The presence of the aromatic ring is confirmed by its respective signal. There are 2 doublets at δ 7.37 and 6.60 in the aromatic region of the ^{1}H-NMR spectrum that shifted to higher field, being associated with the aromatic protons adjacent to the imido functionality. The ^{13}C spectra of compounds **2-5** allow an assignment of the peaks based on ^{13}C shifts in the free ligand. For compound **2**, a slight downfield shield was observed for both the CN peak and the aromatic ring carbons due to the coordination with the molybdenum center (see Table 4).

The ^{1}H-NMR spectrum of **3** displayed a singlet at δ 10.5 attributed to a ring bound hydroxyl group, and 2 doublets at δ 7.5 and 6.9 for the aromatic group. ν(NH) and ν(NH$_2$) peaks are certainly absent in the spectrum and this strongly favors the existence of an imido moiety in complex **3**. The ^{13}C-NMR spectrum also supported the coordination through the CN side of the ligand. The CN carbon shifts downfield from 119.4 ppm (free ligand) to 132.2 ppm (in compound **3**).

The ^{1}H-NMR spectrum of **4** revealed 2 doublets at δ 7.30 and 6.64, which are attributed to C$_6$H$_4$ protons. The uncoordinated amine was clearly seen as a broad resonance at δ 3.33 and no high-field resonance was observed for a NH group. These observations reveal that only a single amine functionality reacted to produce an imido ligand, the second remaining unreacted. The ^{13}C-NMR spectrum of **4** displayed the expected signals for the aromatic ring carbons in the region between 132.7 and 119.4 ppm. Thus, it could be suggested that the

699

addition of $H_2NC_6H_4NH_2$ to a suspension of $[MoOCl_2(THF)_2]$ in THF at room temperature resulted in the formation of the mononuclear compound $[MoOCl_2(=NC_6H_4NH_2)]$.

Table 3. ^{1}H-NMR spectroscopic data for compounds **2**-**5**.

Compound	δ_H(A)	Multiplicity and Assignment[a]
2	7.37	(d, 2H, J (HH) 9, C$_6$$\underline{H}_4$)
	6.60	(d, 2H, J (HH) 9, C$_6$$\underline{H}_4$)
3	10.5	(s, 1H, OH)
	7.50	(d, 2H, C$_6$$\underline{H}_4$)
	6.90	(d, 2H, C$_6$$\underline{H}_4$)
4	7.30	(d, 2H, C$_6$$\underline{H}_4$)
	6.64	(d, 2H, C$_6$$\underline{H}_4$)
	3.33	(s, 2H, NH$_2$)
5	7.25	(d, 2H, J (HH) 11, C$_6$$\underline{H}_4$)
	7.01	(d, 2H, J (HH)11, C$_6$$\underline{H}_4$)
	3.79	(s, 3H, OCH$_3$)

A = relative intensity. [a]J values in Hz, in DMSO-d$_6$ (ppm)

Table 4. ^{13}C-NMR data for compounds **2**-**5**.

Ligand 2   Ligand 2   Ligand 2   Ligand 2
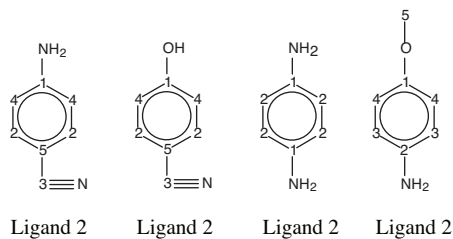
Compound	δ(ppm), assignment
2	153.6 (C1), 134.1 (C2), 129.4 (C3), 116.1 (C4), 96.2 (C5)
3	162.3 (C1), 134.8 (C2), 132.2 (C3), 129.4(C4), 117.1 (C3)
4	132.7 (C1), 132.2 (C2), 129.3 (C3), 119.4 (C4)
5	155.1 (C1), 144.6 (C2), 120.0 (C3), 115.3 (C4), 56.5 (C5)

(400 MHz, 293 K, DMSO)

The ^{1}H-NMR spectrum revealed 2 doublets at δ 7.25 and 7.01 for C$_6$H$_4$ protons and the peak at δ 3.79 was assigned to the OCH$_3$ group on the aromatic ring. A slight downfield shift occurs in the ^{13}C-NMR spectrum with the OCH$_3$ carbon and aromatic ring carbons. The OCH$_3$ carbon appearing at 56.5 ppm in **5** corresponds to 55.6 ppm in the free ligand due to coordination to the molybdenum center. All these spectroscopic data strongly support the formulation of **5** as $[MoOCl_2(=NC_6H_4OCH_3)]$.

Quantum chemical calculations

Some selected geometrical parameters calculated with AM1* are summarized in Table 5. The model calculations predict that the phenyl substituent in compounds **2-5** is essentially co-planar with the CNMo plane. The plane of the phenyl ring deviates from the plane with Mo by about $35°$ (torsional angle, α) except the CN substituent in compound **2** (about $50°$), thereby allowing a fair amount of conjugation between both parts of the molecule. In compound **3**, the fragment combining the Mo and the aromatic moiety is extended by a C atom, so that the geometry and the energetics differ significantly from those of the other structures in favor of stabilizing the suggested structure (see Figure 2, Table 6). At first glance, this may be attributed to the steric freedom that now allows the rotations of the large groups with negligible interference. In addition, the type of bonding may affect the stability. In structures **2, 4,** and **5** there is a double bond between Mo and N; but in **3** the Mo-N bond is a single bond. The double bond is between N and C in **3**.

Energy parameters for compounds **1-5** are given in Table 6. Compound **2** has the highest heat of formation value, which makes it thermodynamically the least stable compound, while compound **3**, with an enlarged N-C group, is the most stable of them. Therefore, it may be suggested that the large dihedral angle for compound **2**, which differs from the other substituents, distorts the interaction between the Mo center and the aromatic group causing the destabilization of compound **2** relative to the others. The size (or length) and the electronic nature of the fragment connecting the Mo center and the aromatic group may also be very important factors affecting stability.

The MOs of the closed shell structures are shown in Figure 3. The quantum chemical calculations yield similar molecular orbital schemes for the HOMO and LUMO. The open shell structure could only be obtained for compound **3**. In all compounds, HOMO and LUMO are strongly localized on the phenyl ring (donor) and the Mo center (acceptor), respectively.

According to the simplified one-electron concept, the HOMO $\rightarrow$ LUMO transition would represent a partially charge-transfer excitation with a very low extinction coefficient.[59] As is known in our previous studies the extinction coefficient is proportional to oscillator strength; thus a high oscillator strength may indicate a charge transfer.[60] The CI calculations predict the HOMO $\rightarrow$ LUMO transition to take a major contribution to the S_1 state only and to cause a large change in dipole moment (Table 6).

The calculated geometrical parameters of compounds **1-5** do not show significant differences except for the MoNCC dihedral angle and MoNC bond angle (Table 5). Thus it seems plausible to argue that the electronic properties mainly depend on the characteristics of the functional groups on the phenyl ring. Compounds **3-5** contain electron donating groups (EDGs) on the phenyl ring and compound **2** has an electron withdrawing group (EWG) on the phenyl ring. It may be claimed that the EDGs stabilize the structures whereas the EWG has a destabilizing effect as the former seems to increase the resonance. In addition, the contribution of electron delocalization from the bridging groups to either side of the molecule may also have a significant effect on stability as it may enhance charge and/or electron transfer in both directions as in the case of **3**, which has an additional CH in the bridging part. For a better understanding and comparison of the studied systems higher level calculations should be used.
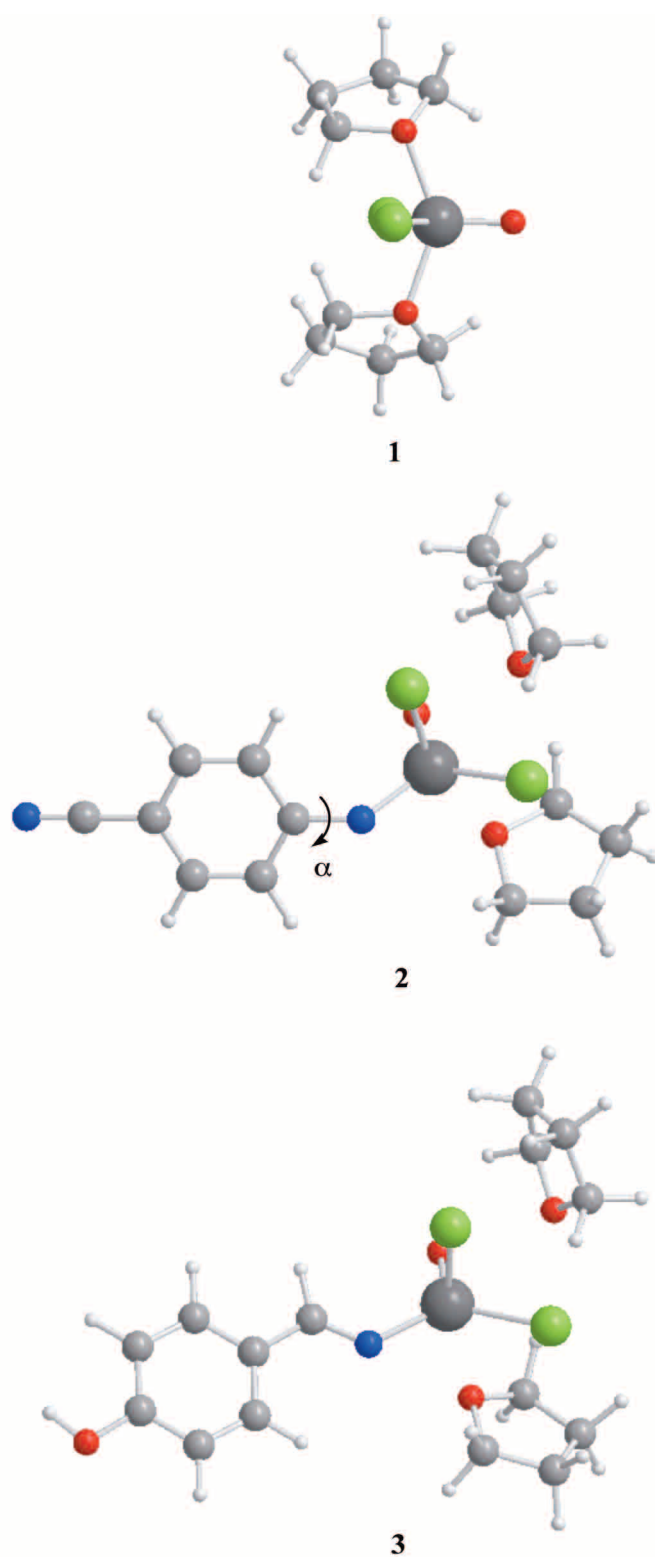
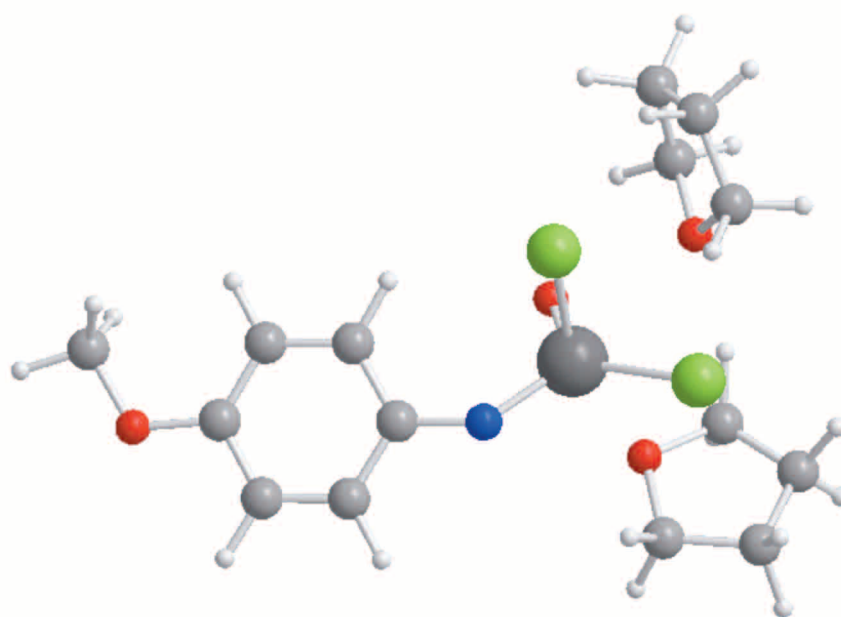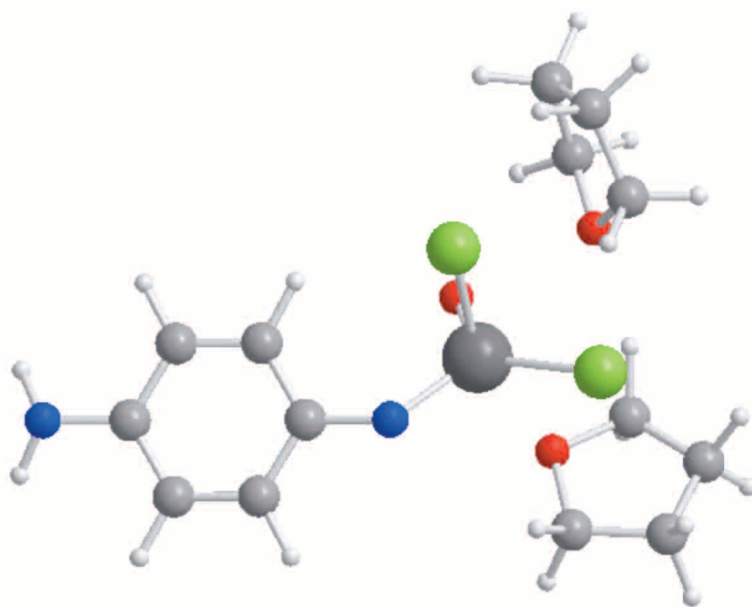**Figure 2.** Optimized structures of compounds **1-5**; α represents the MoNCC torsion.

4

5

Figure 2. Contunied.

Table 5. Some selected geometrical parameters compounds **1-5** calculated with AM1*.

Parameter	Compound				
	1	**2**	**3**	**4**	**5**
MoO	1.629	1.644	1.633	1.646	1.646
MoCl	2.285	2.225	2.224	2.227	2.227
	2.287	2.273	2.260	2.274	2.274
MoN	-	1.764	1.942	1.765	1.763
NC	-	1.381	1.283	1.385	1.384
CC	-	-	1.469	-	-
MoO_{THF}	2.082	2.759	2.942	2.758	2.754
MoO_{THF}	2.094	2.154	2.196	2.166	2.163
CO_{OH}	-	-	1.374	-	-
CO_{OCH3}	-	-	-	-	1.383
$O_{OCH3}C$	-	-	-	-	1.423
CC_{CN}	-	1.421	-	-	-
CN_{CN}	-	1.164	-	-	-
CN_{NH2}	-	-	-	1.399	-
MoNC	-	135.42	126.98	133.82	134.87
NCC	-	179.91	124.60	120.82	-
CCC	-	-	116.46	-	-
MoNCC	-	−53.01	179.09	−34.83	−34.39
NCCC	-	-	177.98	-	-
$HO_{OH}CC$	-	-	-	-	-
HNCC	-	-	-	25.53	-
	-	-	-	158.28	-
$C_{OCH3}O_{OCH3}CC$	-	-	-	-	−0.87

Table 6. Some selected parameters calculated with AM1* for compounds **1-5**.

Parameter	**1**	**2**	**3**	**4**	**5**
Heat Formation (ΔH_f, kcal/mol)	−231.02	−184.32	−265.66	−216.77	−253.08
Ionization Potential (IP, eV)[a]	7.88	8.83	8.57	7.92	8.23
Dipole Moment (μ Debye)	-	9.15	3.00	5.93	5.08
Transition Dipole Moment μ^2, Debye)	-	11.52	-	13.06	11.97
LUMO (eV)	-	−1.055	-	−0.689	−0.757
λ (nm, $S_0 \rightarrow S_1$)	-	337.0	-	344.3	335.8
Oscillator Strength (f)	-	0.722	-	1.320	1.270
MoC (Å)	-	4.877	6.656	4.790	4.811
MoC (Å)	-	5.248	6.277	5.290	5.301

[a]: IP energy is equal to the HOMO energy with the reverse sign according to Koopman's theorem
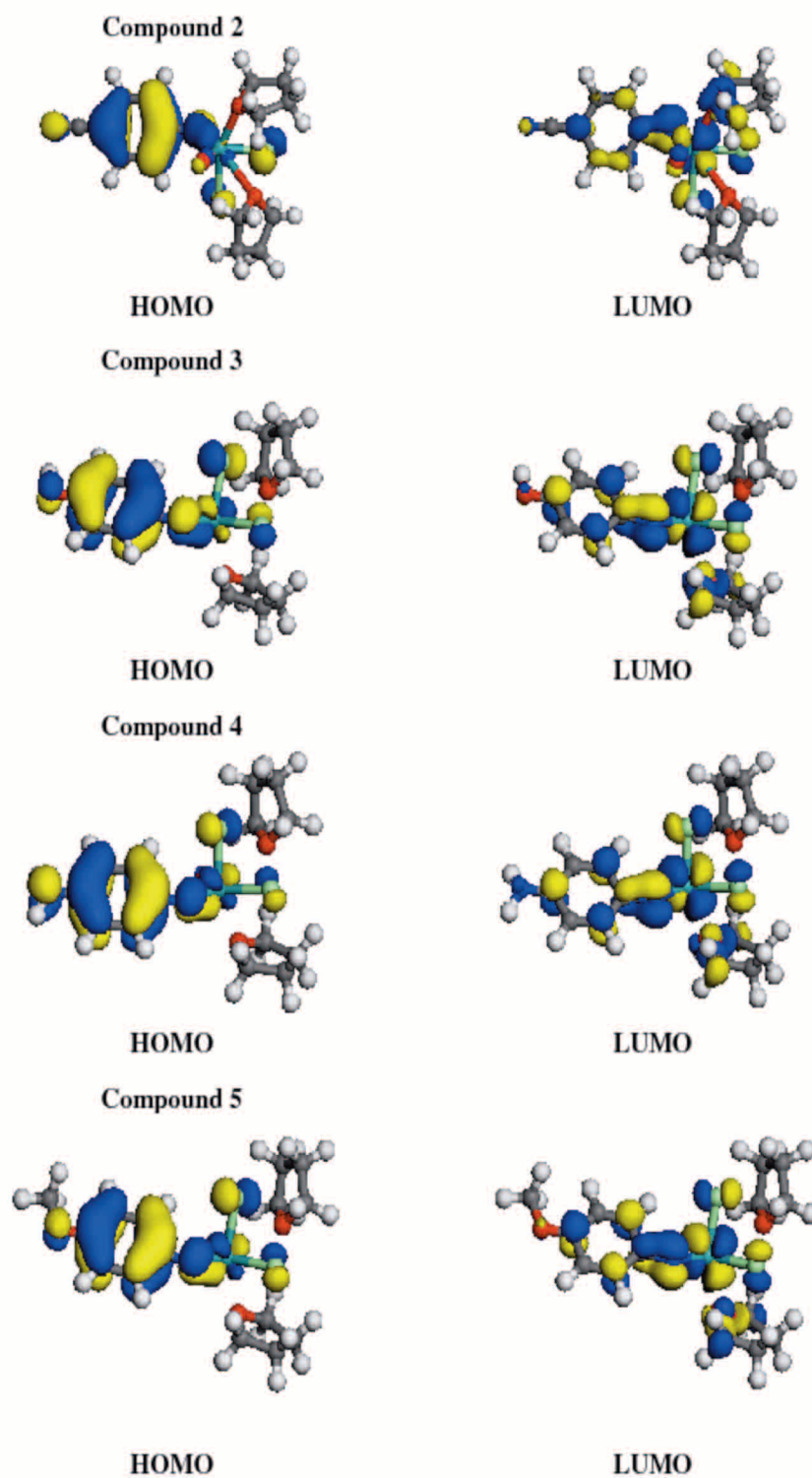
Figure 3. HOMO and LUMO orbitals of compounds **2-5** calculated with AM1*.

Conclusion

The chemistry described herein shows that the air-stable complexes of the type $[MoOCl_2(THF)_2(XC_6H_4Y)]$ ($X = NH_2$, $Y = CN$; $X= OH$, $Y = CN$; $X = NH_2$, $Y = NH_2$; $X = NH_2$, $Y = OCH_3$) could be prepared via an oxo group abstraction from the solvent-stabilized dioxomolybdenum(VI) compound. The spectroscopic data and molecular orbital calculations with the semiempirical AM1* method support their formulations as mononuclear compounds. These complexes might show important biological activities as molybdoenzymes, yet to be investigated.

Acknowledgements

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