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Reactivity of molybdenum complexes containing mixed NHNPhR and NNPhR hydrazido ligands (R = Ph, Me) toward di-imines. X-ray crystal structures of $[MoO(NNPh_2)Cl_2(bpy)] \cdot CH_2Cl_2$, $[MoO(NNPh_2)Cl_2(phen)] \cdot CH_2Cl_2$ and $[Mo(NNPh_2)_2Cl_2(phen)]$

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Abstract

Complexes of the type $[Mo(NHNPhR)(NNPhR)(acac)Cl_2]$ (R = Ph (**I**); Me (**II**)) react in dichloromethane with the di-imines 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) to yield, after slow evaporation under air of the solvent, the species $[MoO(NNPhR)Cl_2(bpy)]$ (R = Ph (**III**); Me (**IV**)) and $[MoO(NNPhR)Cl_2(phen)]$ (R = Ph (**V**); Me (**VI**)). When these reactions are carried out in toluene under inert atmosphere, **I** and **II** give the bis-hydrazido(2−) complexes $[Mo(NNPhR)_2Cl_2(bpy)]$ (R = Ph (**VII**); Me (**VIII**)) and $[Mo(NNPhR)_2Cl_2(phen)]$ (R = Ph (**IX**); Me (**X**)). The crystal structures of **III**, **V** and **IX** are reported. Crystals of **III** are orthorhombic, space group *Pbca*, with cell parameters $a = 15.290(6)$, $b = 16.225(8)$, $c = 19.954(9)$ Å, $Z = 8$, $R = 0.036$ and $R_w = 0.044$. Crystals of **V** are triclinic, space group $P\bar{1}$, with $a = 8.935(1)$, $b = 12.960(2)$, $c = 13.443(2)$ Å, $\alpha = 61.84(1)$, $\beta = 74.75(1)$, $\gamma = 86.96(1)°$, $Z = 2$, $R = 0.036$ and $R_w = 0.044$. Crystals of **IX** are triclinic, space group $P\bar{1}$, with $a = 9.812(4)$, $b = 10.459(4)$, $c = 17.979(7)$ Å, $\alpha = 73.69(3)$, $\beta = 77.98(3)$, $\gamma = 66.30(3)°$, $Z = 2$, $R = 0.038$ and $R_w = 0.043$. All complexes display similar pseudooctahedral geometries with the hydrazido(2−) ligands adopting the nearly linear coordination mode.

Keywords: Molybdenum complexes; Hydrazido complexes; Bidentate nitrogen ligand complexes; Crystal structures

1. Introduction

There are few examples in the literature of metal complexes containing both organohydrazido(1−) and organohydrazido(2−) ligands adopting the ‘end-on’ configuration in the same inner coordination sphere [1–3]. Recently, we have reported the synthesis and characterization of complexes formulated as $[Mo(NHNPhR)(NNPhR)(acac)X_2]$ (R = Me, Ph; X = Cl, Br, I), where the organodinitrogen ligands possess such a similar conformation [4]. These compounds have proved to be versatile precursors for the synthesis of a wide variety of phosphine complexes containing the *cis*-$Mo(NNPhR)_2$ moiety [5]. Certainly, the interesting chemical properties observed for these compounds are due to the lability of the ancillary ligand acac and its ability to deprotonate the NHNPhR ligand, thus regenerating the acetylacetone (Hacac) molecule.

As a new contribution to the study of the chemical properties of hydrazido complexes [6] we report, in this article, the reactivity of the molybdenum complexes $[Mo(NHNPhR)(NNPhR)(acac)Cl_2]$ (R = Ph (**I**); Me (**II**)) toward di-imines in dichloromethane and toluene. The new coordination compounds obtained from these reactions were characterized by elemental analyses, spectroscopic methods and were formulated as $[MoO(NNPhR)Cl_2(bpy)]$ (R = Ph (**III**); Me (**IV**)), $[MoO(NNPhR)Cl_2(phen)]$ (R = Ph (**V**); Me (**VI**)), $[Mo(NNPhR)_2Cl_2(bpy)]$ (R = Ph (**VII**); Me (**VIII**)) and $[Mo(NNPhR)_2Cl_2(phen)]$ (R = Ph (**IX**); Me (**X**)). The X-ray crystal structures of complexes **III**, **V** and **IX** have been determined in order to correlate the *trans* influence of the oxo and hydrazido(2−) ligands on the nitro-

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gen atoms of the di-imines ligands. Finally, the electrochemical behavior of complexes **V** and **IX** was also explored.

2. Experimental

2.1. Chemicals

2,2′-Bipyridine and 1,10-phenanthroline were obtained from commercial sources and used without further purification. Complexes **I** and **II** were synthesized as previously described [4]. Dichloromethane and toluene were distilled from P_4O_{10} and sodium benzophenone ketyl, respectively. All synthetic manipulations were carried out utilizing standard Schlenk techniques unless specified. Dinitrogen was used as inert atmosphere.

2.2. Preparation of complexes

2.2.1. Oxo-hydrazido(2−) complexes. General procedure

To a solution of 0.50 mmol of complexes **I** or **II** (0.260 and 0.320 g, respectively) in dry dichloromethane (50 ml) was added 0.50 mmol of bpy or phen (0.078 and 0.090 g, respectively). The reaction mixture was refluxed for 0.5 h and allowed to evaporate slowly under air for one or two weeks yielding deep purple (**III–V**) and brick red (**VI**) crystalline solids. These materials were filtered off, washed with three portions of 10 ml of CH_2Cl_2 , and dried in vacuo. Complexes **III–VI** are sparingly soluble in CH_2Cl_2. Suitable crystals for an X-ray structure determination were directly obtained for complexes **III** and **V**.

2.2.1.1. [MoO(NNPh$_2$)Cl$_2$(bpy)]·CH$_2$Cl$_2$ (III)

Yield 50%. M.p. 235 °C, dec. *Anal.* Calc. for $C_{23}H_{20}Cl_4MoN_4O$: C, 45.6; H, 3.33. Found: C, 45.8; H, 3.42%. UV–Vis ((CH_2Cl_2), λ_{max} (nm) (log ϵ)): 268 (4.36), 304 (4.23), 348 (3.80), 382 (3.74), 504br (3.12). IR (cm^{-1}, KBr): 3049(w), ν(CH); 1600(m), ν(NN); 1490(m), ν(CC); 905(s), ν(Mo=O). ^{1}H NMR ($CDCl_3$, δ (ppm), TMS): 5.31 (s, 2H, CH_2Cl_2); 7.02–9.92 (m, 18H, phenyl and bpy).

2.2.1.2. [MoO(NNPhMe)Cl$_2$(bpy)] (IV)

Yield 69%. M.p. 233 °C, dec. *Anal.* Calc. for $C_{17}H_{16}Cl_2MoN_4O$: C, 44.5; H, 3.51. Found: C, 44.6; H, 3.64%. UV–Vis ((CH_2Cl_2), λ_{max} (nm) (log ϵ)): 268 (4.38), 304 (4.24), 350 (3.85), 390sh (3.73), 504br (3.10). IR (cm^{-1}, KBr): 3076(w), ν(CH); 2922(w), ν(CH); 1599(m), ν(NN); 1473(s), ν(CC); 905(s), ν(Mo=O). ^{1}H NMR (DMSO-d$_6$, δ (ppm), TMS): 3.65, 4.16, 4.34 (s, 3H, CH_3N); 7.23–9.61 (m, 13H, phenyl and bpy).

2.2.1.3. [MoO(NNPh$_2$)Cl$_2$(phen]·CH$_2$Cl$_2$ (V)

Yield 85%. M.p. 275 °C, dec. *Anal.* Calc. for $C_{25}H_{20}Cl_4MoN_4O$: C, 47.6; H, 3.20. Found: C, 47.7; H, 3.19%. UV–Vis ((CH_2Cl_2), λ_{max} (nm) (log ϵ)): 276 (4.73), 298sh (4.35), 338br (3.88), 382br (3.83), 506br (3.18). IR (cm^{-1}, KBr): 3048(w), ν(CH); 1587(m), ν(NN); 1488(m), ν(CC); 901(s), ν(Mo=O). ^{1}H NMR ($CDCl_3$, δ (ppm), TMS): 5.31 (s, 2H, CH_2Cl_2); 7.36–10.15 (m, 18H, phenyl and phen).

2.2.1.4. [MoO(NNPhMe)Cl$_2$(phen)] (VI)

Yield 55%. M.p. 295 °C. *Anal.* Calc. for $C_{19}H_{16}Cl_2MoN_4O$: C 47.2; H, 3.34. Found: C, 46.8; H, 3.52%. UV–Vis ((CH_2Cl_2), λ_{max} (nm) (log ϵ)): 276 (4.58), 298sh (4.18), 342 (3.76), 384br (3.66), 514br (2.94). IR (cm^{-1}, KBr): 3055(w), ν(CH); 2930(w), ν(CH); 1586(m), ν(NN); 1473(s), ν(CC); 903(s), ν(Mo=O). ^{1}H NMR (DMSO-d$_6$, δ (ppm), TMS): 3.64, 4.15, 4.50 (s, 3H, CH_3N); 6.85–10.00 (m, 13H, phenyl and phen).

2.2.2. Bis-hydrazido(2−) complexes. General procedure

To a suspension of 1.00 mmol of complexes **I** or **II** (0.520 or 0.640 g, respectively) in dry toluene (20 ml) was added 1.00 mmol of bpy or phen (0.160 and 0.180 g, respectively). The reaction mixture was refluxed for 15 min, under dinitrogen. Under these experimental conditions deep purple (**VII** and **IX**), deep orange (**VIII**) and brick red (**X**) microcrystalline solids began to form. The solids were filtered off, washed with toluene and hexane, and dried in vacuo.

2.2.2.1. [Mo(NNPh$_2$)$_2$Cl$_2$(bpy)] (VII)

Yield 93%. M.p. 257 °C, dec. *Anal.* Calc. for $C_{34}H_{28}Cl_2MoN_6$: C, 59.4; H, 4.11. Found: C, 59.0; H, 4.32%. UV–Vis ((CH_2Cl_2), λ_{max} (nm) (log ϵ)): 246sh (3.07), 302 (4.60), 315sh (3.34), 356sh (4.03), 470br (3.74). IR (cm^{-1}, KBr): 3056(w), ν(CH); 2922(w), ν(CH); 1591(s), ν(NN); 1486(s), ν(CC). ^{1}H NMR ($CDCl_3$, δ (ppm), TMS): 6.91–8.78 (m, phenyl and bpy).

2.2.2.2. [Mo(NNPhMe)$_2$Cl$_2$(bpy)] (VIII)

Yield 80%. M.p. 205 °C, dec. *Anal.* Calc. for $C_{24}H_{24}Cl_2MoN_6$: C, 51.2; H, 4.29; N, 14.9. Found: C, 51.0; H, 4.32; N, 15.0%. UV–Vis ((CH_2Cl_2), λ_{max} (nm) (log ϵ)): 248sh (4.39), 300 (4.58), 312sh (4.50), 348sh (4.11), 480br (3.45). IR (cm^{-1}, KBr): 3056(w), ν(CH); 2922(w), ν(CH); 1592(s), ν(NN); 1489(s), ν(CC). ^{1}H NMR ($CDCl_3$, δ (ppm), TMS): 3.64, 4.11, 4.25 (s, 6H, CH_3N); 6.86–9.94 (m, 18H, phenyl and bpy).

2.2.2.3. [Mo(NNPh$_2$)$_2$Cl$_2$(phen)] (IX)

Yield 83%. M.p. 260 °C, dec. *Anal.* Calc. for $C_{36}H_{28}Cl_2MoN_6$: C, 60.8; H, 3.97. Found: C, 59.6; H, 4.14%. UV–Vis ((CH_2Cl_2), λ_{max} (nm) (log ϵ)): 276 (4.72), 286sh (4.57), 360sh (4.02), 460br (3.73). IR (cm^{-1}, KBr): 3056(w), ν(CH); 1589(s), ν(NN); 1489(s), ν(CC). ^{1}H NMR ($CDCl_3$, δ (ppm), TMS): 6.94–9.02 (m, phenyl and phen).

2.2.2.4. *[Mo(NNPhMe)$_2$Cl$_2$(phen)] (**X**)*

Yield 75%. M.p. 220 °C, dec. *Anal.* Calc. for $C_{26}H_{24}Cl_2MoN_6$: C, 53.2; H, 4.12; N, 14.3. Found: C, 53.1; H, 4.11; N, 14.4%. UV–Vis ((CH$_2$Cl$_2$), λ_{max} (nm) (log ϵ)): 276 (4.50), 296sh (4.41), 346sh (4.06), 480br (3.39). IR (cm^{-1}, KBr): 3052(w), ν(CH); 2921(w), ν(CH); 1583(s), ν(NN); 1485(s), ν(CC). ^{1}H NMR (CDCl$_3$, δ (ppm), TMS): 3.55, 4.17, 4.31 (s, 6H, CH$_3$N); 6.80–10.18 (m, 18H, phenyl and phen).

2.3. *Physical measurements*

^{1}H NMR spectra were recorded in CDCl$_3$ and DMSO-d$_6$ on a Bruker FT AC/200 P spectrometer at 22 °C. IR spectra were obtained as KBr disks with a Perkin-Elmer model 1600 FT-IR spectrophotometer. Electronic spectra were recorded in CH$_2$Cl$_2$ solutions on a Hewlett Packard model 8452A spectrophotometer. Melting points were determined using a Kofler apparatus and were not corrected. Cyclic voltammetry (CV) measurements were made with a homemade potentiostat of conventional design using a three-electrode cell with platinum working and auxiliary electrodes and saturated calomel electrode (SCE) as the reference. All measurements were made at room temperature (20 °C) in CH$_2$Cl$_2$ with 0.1 M tetrabutylammonium hexafluorophosphate, Bu$_4$NPF$_6$, as the supporting electrolyte.

2.4. *X-ray data collection and crystal structure determination of complexes **III**, **V** and **IX***

X-ray diffraction data were collected on a Siemens R3m/V four-circle diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), in $\theta/2\theta$ scan mode at room temperature. Cell parameters were determined from least-squares fits of 25 reflections with $10 \leq 2\theta \leq 30°$. Two standard reflections, monitored every 98 reflections, showed no significant intensity variation during data collection from the samples. Intensities were corrected for Lorentz and polarization effects, and semi-empirical corrections were applied for absorption.

Crystal data, data collection and refinement parameters for compounds **III**, **V** and **IX** are summarized in Table 1. The three structures were solved by direct methods and refined on *F* by full-matrix least-squares calculations. The function

Table 1
Crystallographic data for compounds **III**, **V** and **IX**

	III	**V**	**IX**
Empirical formula	$C_{23}H_{20}Cl_4MoN_4O$	$C_{25}H_{20}Cl_4MoN_4O$	$C_{36}H_{28}Cl_2MoN_6$
Crystal size (mm)	0.40 × 0.36 × 0.20	0.32 × 0.22 × 0.20	0.40 × 0.40 × 0.l2
Crystal system	orthorhombic	triclinic	triclinic
Space group	*Pbca*	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	15.290(6)	8.935(1)	9.812(4)
b (Å)	16.225(8)	12.960(2)	10.459(4)
c (Å)	19.954(9)	13.443(2)	17.979(7)
α (°)	90.0	61.84(1)	73.69(3)
β (°)	90.0	74.75(1)	77.98(3)
γ (°)	90.0	86.96(1)	66.30(3)
Volume (Å^3)	4950(4)	1319.5(4)	1612(1)
Z	8	2	2
Molecular weight	606.2	630.2	711.5
Density (calc.) (Mg m^{-3})	1.627	1.586	1.466
F(000)	2432	632	724
Absorption coefficient (mm^{-1})	0.986	0.928	0.609
Max./min. transmission factors	0.202/0.111	0.990/0.823	0.825/0.650
Reflections collected	4561	7834	6225
2θ Range (°)	3–50	3–55	3–50
Index ranges			
h	0 to 18	0 to 11	−5 to 11
k	−7 to 19	−16 to 16	−11 to 12
l	−8 to 23	−16 to 17	−20 to 21
Independent reflections	4375	6084	5721
R_{int}	0.0134	0.0120	0.0119
Observed reflections	3026 ($F > 4\sigma(F)$)	5120 ($F > 6\sigma(F)$)	4794($F > 4\sigma(F)$)
Weighting scheme *g* ($w^{-1} = \sigma^2(F) + gF^2$)	0.0007	0.0020	0.0022
No. parameters refined	298	316	406
Final *R* indices			
R	0.036	0.036	0.038
R_w	0.044	0.044	0.043
Goodness-of-fit, *S*	1.11	1.18	1.02
Residual ρ_{max} (e Å^{-3})	0.60	1.36	0.73

minimized was $\sum w(F_o - F_c)^2$. The weighting scheme used was given by $w^{-1} = \sigma^2(F) + gF^2$. All non-H atoms were refined anisotropically. A riding model was applied to H atoms, placed at calculated positions with C–H = 0.96 Å, with the equivalent isotropic thermal parameters of their parent C atoms. All calculations were performed with the Siemens SHELXTL-PLUS system of programs [7].

3. Results and discussion

3.1. Reactivity and synthesis of complexes

We have previously reported [5] that in acetonitrile tertiary phosphines react with molybdenum complexes containing both hydrazido(1−) and hydrazido(2−) ligands, [Mo(NHNPhR)(NNPhR)(acac)Cl_2] (R = Ph (**I**); Me (**II**)), to give, after elimination of one acetylacetone molecule, five- and six-coordinated molybdenum complexes depending on the steric hindrance of the phosphines. These complexes exhibit, in all cases, the robust *cis*-Mo$(NNPhR)_2$ core and one or two ancillary phosphine ligands. The chloro ligands are retained in the inner coordination sphere of molybdenum.

This type of reaction was now repeated using bpy and phen, both in dichloromethane and toluene. In dichloromethane the di-imines react with complexes **I** and **II** to afford clean solutions which were allowed to stand in air. The slow evaporation of the solvent yields crystalline solids which were washed with abundant quantities of CH_2Cl_2. These new compounds were characterized by conventional spectroscopic techniques and formulated as [MoO(NNPhR)Cl_2(bpy)] (R = Ph (**III**); Me (**IV**)) and [MoO(NNPhR)Cl_2(phen)] (R = Ph (**V**); Me (**VI**)). The presence of the *cis*-MoO(NNPhR) moiety in complexes **III**–**VI** indicates unambiguously that the Mo$(NNPhR)_2$ group, initially present in the species formed in solution (Eq. (1)), undergoes a partial hydrolysis with loss of one PhRNN ligand (Eq. (2)) during the slow evaporation of the solvent under air. In fact, complex **V** was obtained contaminated with crystals of complex [Mo$(NNPh_2)_2Cl_2$(phen)] (**IX**) and it was possible to separate by hand suitable crystals of both complexes for X-ray structure determinations.

$$[\mathrm{Mo(NHNPhR)(NNPhR)(acac)Cl_2}] + \text{N-N} \rightarrow [\mathrm{Mo(NNPhR)_2Cl_2(N\text{-}N)}] + \mathrm{Hacac} \quad (1)$$

$$[\mathrm{Mo(NNPhR)_2Cl_2(N\text{-}N)}] + \mathrm{H_2O} \rightarrow [\mathrm{MoO(NNPhR)Cl_2(N\text{-}N)}] + \mathrm{PhRNNH_2} \quad (2)$$

N-N = bpy, phen

A comparable observation was recently reported for the ionic complex [Re$(NNPhMe)_2Cl_2(PPh_3)$][PF_6] which afforded, after recrystallization from a CH_2Cl_2/MeOH mixture, the unexpected oxo-hydrazido complex, [ReO(NNPhMe)Cl$(PPh_3)_2$][PF_6]$_2$ [8].

On the other hand, in dry toluene, the di-imines bpy and phen react with complexes **I** and **II** to produce cleanly bis-hydrazido(2−) complexes formulated as [Mo$(NNPhR)_2Cl_2$(bpy)] (R = Ph (**VII**); Me (**VIII**)) and [Mo$(NNPhR)_2Cl_2$(phen)] (R = Ph (**IX**); Me (**X**)). These complexes are sparingly soluble in toluene and rapidly precipitate as microcrystalline materials. Presumably, this property prevents or minimizes the hydrolysis of one PhRNN ligand of the Mo$(NNPhR)_2$ moiety present in complexes **VII**–**X**.

The formulations attributed to both types of complexes, **III**–**VI** and **VII**–**X**, are consistent with analytical and spectroscopic data and with the X-ray crystallographic studies of **III**, **V** and **IX** (vide infra).

3.2. X-ray structures of complexes *III*, *V* and *IX*

Atomic coordinates for the structures of [MoO$(NNPh_2)$-Cl_2(bpy)]·CH_2Cl_2 (**III**), [MoO$(NNPh_2)Cl_2$(phen)]·CH_2Cl_2 (**V**) and [Mo$(NNPh_2)_2Cl_2$(phen)] (**IX**) are given in Tables 2, 3 and 4, respectively, and relevant bond distances

Table 2
Fractional atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^3) for complex **III**

	x	*y*	*z*	U_{eq} [a]
Mo	331(1)	8694(1)	3784(1)	34(1)
Cl(l)	1458(1)	7651(1)	3861(1)	53(1)
Cl(2)	−421(1)	9951(1)	3460(1)	46(1)
O	−61(2)	8616(2)	4580(1)	44(1)
N(1)	1244(2)	9125(2)	2925(2)	35(1)
N(2)	1337(2)	9615(2)	4183(2)	34(1)
N(3)	−418(2)	8102(2)	3288(2)	37(1)
N(4)	−1039(2)	7745(2)	2954(2)	38(1)
C(l)	1173(3)	8835(3)	2296(2)	44(2)
C(2)	1671(3)	9137(3)	1772(2)	52(2)
C(3)	2275(3)	9734(3)	1902(3)	57(2)
C(4)	2370(3)	10031(3)	2544(3)	50(2)
C(5)	1849(3)	9710(3)	3054(2)	38(1)
C(6)	1904(3)	9987(3)	3757(2)	37(1)
C(7)	2480(3)	10587(3)	3977(3)	48(2)
C(8)	2461(3)	10831(3)	4640(3)	53(2)
C(9)	1881(3)	10460(3)	5072(3)	49(2)
C(10)	1332(3)	9863(3)	4824(2)	42(2)
C(31)	−1809(3)	7453(3)	3294(2)	38(1)
C(32)	−1847(3)	7486(3)	3993(2)	50(2)
C(33)	−2578(4)	7210(3)	4323(3)	60(2)
C(34)	−3284(4)	6907(3)	3966(3)	62(2)
C(35)	−3260(3)	6894(3)	3280(3)	57(2)
C(36)	−2520(3)	7158(3)	2932(3)	47(2)
C(41)	−978(3)	7732(3)	2235(2)	37(1)
C(42)	−802(3)	7004(3)	1899(2)	46(2)
C(43)	−713(3)	7010(3)	1213(3)	54(2)
C(44)	−787(4)	7730(4)	867(3)	63(2)
C(45)	−964(4)	8457(4)	1195(3)	71(2)
C(46)	−1059(4)	8454(3)	1884(3)	56(2)
Cl(3)	171(1)	9371(1)	−1730(1)	86(1)
Cl(4)	−910(1)	9497(1)	−509(1)	101(1)
C(Ol)	−33(5)	9044(5)	−876(4)	106(3)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for complex **V**

	x	y	z	U_{eq} [a]
Mo	−3108(1)	3141(1)	3829(1)	35(1)
Cl(l)	−4049(1)	1193(1)	5442(1)	50(1)
Cl(2)	−1380(1)	4850(1)	2341(1)	53(1)
O	−4688(3)	3851(2)	4082(2)	46(1)
N(1)	−732(3)	2336(2)	4046(2)	39(1)
N(2)	−2297(3)	3512(2)	5115(2)	36(1)
N(3)	−3349(3)	2785(2)	2742(2)	41(1)
N(4)	−3580(3)	2654(2)	1910(2)	43(1)
C(1)	5(4)	1719(3)	3532(3)	52(2)
C(2)	1411(4)	1223(3)	3732(4)	59(2)
C(3)	2089(4)	1416(3)	4429(3)	54(2)
C(4)	1355(3)	2081(3)	4976(3)	43(1)
C(5)	1983(4)	2336(3)	5710(3)	51(1)
C(6)	1204(4)	2965(3)	6235(3)	52(2)
C(7)	−271(4)	3373(3)	6065(3)	41(1)
C(8)	−1144(4)	4002(3)	6595(3)	51(2)
C(9)	−2543(5)	4367(3)	6374(3)	53(2)
C(10)	−3078(4)	4102(3)	5639(3)	45(1)
C(11)	−902(3)	3146(2)	5325(2)	35(1)
C(12)	−73(3)	2506(2)	4763(2)	36(1)
C(31)	−4910(4)	3081(3)	1483(3)	43(1)
C(32)	−5849(5)	3763(3)	1876(3)	55(2)
C(33)	−7147(5)	4172(4)	1466(4)	67(2)
C(34)	−7543(5)	3896(4)	715(4)	77(3)
C(35)	−6599(6)	3228(5)	308(5)	88(3)
C(36)	−5264(5)	2810(4)	689(4)	71(3)
C(41)	−2409(4)	2093(3)	1398(3)	40(1)
C(42)	−2315(6)	909(3)	2011(3)	66(2)
C(43)	−1104(6)	395(3)	1547(4)	76(2)
C(44)	−54(5)	1068(3)	499(4)	61(2)
C(45)	−169(5)	2244(3)	−104(3)	60(2)
C(46)	−1342(4)	2776(3)	342(3)	55(2)
Cl(3)	−4091(2)	−1978(2)	1807(2)	141(1)
Cl(4)	−6912(3)	−1094(2)	1267(3)	196(2)
C(Ol)	−5423(12)	−936(7)	1766(6)	144(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for complex **IX**

	x	y	z	U_{eq} [a]
Mo	75(1)	396(1)	2701(1)	34(1)
Cl(1)	1011(1)	2267(1)	1901(1)	48(1)
Cl(2)	−144(1)	−1791(1)	3592(1)	52(1)
N(1)	1721(3)	−20(3)	3568(2)	40(1)
N(2)	2450(3)	−992(3)	2257(2)	41(1)
N(3)	−1383(3)	1680(3)	3174(2)	39(1)
N(4)	−2524(3)	2722(3)	3417(2)	41(1)
N(5)	−708(3)	176(3)	1963(2)	41(1)
N(6)	−1513(3)	153(3)	1466(2)	44(1)
C(1)	1337(5)	437(4)	4235(2)	51(2)
C(2)	2377(6)	131(5)	4755(3)	63(2)
C(3)	3845(6)	−636(5)	4567(3)	63(2)
C(4)	4310(4)	−1121(4)	3868(3)	51(2)
C(5)	5833(5)	−1866(5)	3601(3)	68(2)
C(6)	6202(5)	−2264(5)	2928(4)	71(2)
C(7)	5092(4)	−2001(4)	2436(3)	54(2)
C(8)	5411(5)	−2413(5)	1712(3)	66(2)
C(9)	4277(6)	−2113(5)	1301(3)	67(2)
C(10)	2801(5)	−1409(4)	1588(2)	53(2)
C(11)	3591(4)	−1283(3)	2677(2)	41(1)
C(12)	3188(4)	−800(4)	3397(2)	41(1)
C(31)	−3999(4)	3053(4)	3239(2)	38(1)
C(32)	−4353(4)	1992(4)	3101(2)	45(2)
C(33)	−5790(5)	2334(4)	2915(2)	53(2)
C(34)	−6838(5)	3695(5)	2879(2)	58(2)
C(35)	−6478(5)	4742(5)	3023(2)	54(2)
C(36)	−5055(4)	4427(4)	3195(2)	44(2)
C(41)	−2230(4)	3553(3)	3842(2)	39(1)
C(42)	−3071(4)	3816(4)	4539(2)	50(2)
C(43)	−2749(5)	4590(5)	4936(3)	62(2)
C(44)	−1611(5)	5086(5)	4648(3)	64(2)
C(45)	−757(5)	4814(4)	3965(3)	58(2)
C(46)	−1062(4)	4036(4)	3551(2)	48(2)
C(51)	−2827(4)	1374(4)	1250(2)	45(2)
C(52)	−4076(5)	1208(5)	1110(2)	61(2)
C(53)	−5331(5)	2419(8)	922(3)	84(3)
C(54)	−5356(6)	3756(7)	876(3)	91(3)
C(55)	−4136(7)	3903(5)	1029(3)	83(3)
C(56)	−2841(5)	2713(4)	1213(3)	58(2)
C(61)	−1010(4)	−1119(4)	1162(2)	42(2)
C(62)	−294(5)	−2432(4)	1632(2)	51(2)
C(63)	185(6)	−3659(5)	1333(3)	71(2)
C(64)	27(7)	−3581(7)	606(4)	90(3)
C(65)	−736(7)	−2275(7)	134(3)	85(3)
C(66)	−1218(6)	−1043(5)	410(2)	62(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

and angles are given in Table 5. ORTEP views of each molecule, in similar perspectives for sake of comparison, are presented in Fig. 1. The geometry about the molybdenum center in **III**, **V** and **IX** is best described as distorted octahedral with the chloro ligands occupying mutually *trans* positions.

The geometric parameters observed in **III** and **V** are quite similar to those described in the literature for other oxo-hydrazido(2−)molybdenum complexes [9–18]. The short Mo–N and N–N bond distances of 1.792(4) and 1.296(5) Å for **III**, and 1.791(4) and 1.276(5) Å for **V**, respectively, the nearly linear Mo–N–N bond angle of 172.4(3) and 173.1(2)° for **III** and **V**, respectively, and the nearly planar $MoNNC_2$ unit is indicative of an extensive delocalization of π-electron density throughout the hydrazidomolybdenum unit. The well known strong *trans* influence exerted by the oxo and hydrazido(2−) ligands [9–18] is also observed on the nitrogen atoms of bpy and phen in complexes **III** and **V**. Thus, the Mo–N(1) bond distances *trans* to the oxo ligands, 2.318(4) and 2.342(3) Å, respectively, are longer by ~0.12 and ~0.14 Å, compared with a normal Mo–N(bpy) distance [19]. Likewise, the Mo–N(2) bond distances *trans* to the $NNPh_2$ ligands, 2.289(4) and 2.286(3) Å, respectively, are also longer by ~0.08 Å compared to the same parameter [19]. Clearly, the *trans* influence of the oxo ligands is far more important than that of the hydrazido(2−) ligands. On

Table 5
Selected bond distances (Å) and bond angles (°) for complexes **III**, **V** and **IX**

	III	V	IX
Mo–Cl(1)	2.421(2)	2.425(1)	2.461(1)
Mo–Cl(2)	2.429(2)	2.419(1)	2.457(1)
Mo–O	1.703(3)	1.691(2)	
Mo–N(1)	2.318(4)	2.342(3)	2.310(4)
Mo–N(2)	2.289(4)	2.286(3)	2.309(3)
Mo–N(3)	1.792(4)	1.791(4)	1.779(3)
Mo–N(5)			1.773(4)
N(3)–N(4)	1.296(5)	1.276(5)	1.309(4)
N(4)–C(31)	1.439(6)	1.427(5)	1.429(5)
N(4)–C(41)	1.438(5)	1.454(5)	1.446(6)
N(5)–N(6)			1.319(5)
N(6)–C(51)			1.432(4)
N(6)–C(61)			1.443(5)
Cl(1)–Mo–Cl(2)	160.2(1)	161.5(1)	164.1(1)
Cl(1)–Mo–O	98.0(1)	98.3(1)	
Cl(2)–Mo–O	98.3(1)	97.6(1)	
Cl(1)–Mo–N(1)	80.1(1)	80.1(1)	86.5(1)
Cl(2)–Mo–N(1)	80.5(1)	81.5(1)	80.1(1)
Cl(1)–Mo–N(2)	87.4(1)	87.2(1)	79.4(1)
Cl(2)–Mo–N(2)	82.1(1)	84.5(1)	88.0(1)
Cl(1)–Mo–N(3)	96.7(1)	94.0(1)	90.3(1)
Cl(2)–Mo–N(3)	90.0(1)	90.9(1)	98.7(1)
Cl(1)–Mo–N(5)			97.8(1)
Cl(2)–Mo–N(5)			92.1(1)
O–Mo–N(1)	157.5(1)	156.6(1)	
O–Mo–N(2)	87.7(1)	86.2(1)	
O–Mo–N(3)	104.5(2)	104.9(1)	
N(1)–Mo–N(2)	69.8(1)	70.5(1)	70.8(1)
N(1)–Mo–N(3)	98.0(1)	98.5(1)	91.9(1)
N(2)–Mo–N(3)	166.4(1)	168.5(1)	160.3(2)
N(1)–Mo–N(5)			160.5(1)
N(2)–Mo–N(5)			91.3(1)
N(3)–Mo–N(5)			106.9(1)
Mo–N(3)–N(4)	172.4(3)	173.1(2)	171.3(3)
Mo–N(5)–N(6)			170.1(2)
N(3)–N(4)–C(31)	120.2(3)	120.9(3)	120.8(4)
N(3)–N(4)–C(41)	118.2(3)	117.1(3)	117.7(3)
C(31)–N(4)–C(41)	121.2(3)	122.0(3)	121.5(3)
N(5)–N(6)–C(51)			119.4(3)
N(5)–N(6)–C(61)			117.7(3)
C(51)–N(6)–C(61)			122.9(4)

the other hand, the Mo–O bond distances of 1.703(3) and 1.691(2) Å for **III** and **V**, respectively, lie within the normal range [9–15,20].

In complex **IX** the diphenylhydrazido(2−) ligands are *cis* to one another but *trans* to the nitrogen atoms of the phen ligand. The *trans* influence exerted by these ligands on the Mo–N(1) and Mo–N(2) bond distances is stronger than that exerted in complexes **III** and **V**, e.g. Mo–N(1) = 2.310(4) and Mo–N(2) = 2.309(3) Å for **IX** versus Mo–N(1) = 2.289(4) and 2.286(3) Å for **III** and **V**, respectively. The metrical parameters for the Mo$(NNPh_2)_2$ core (Table 5) are similar to those reported in the literature [5,19,21] and reveal extensive electronic delocalization throughout the $MoNNC_2$ units as well.

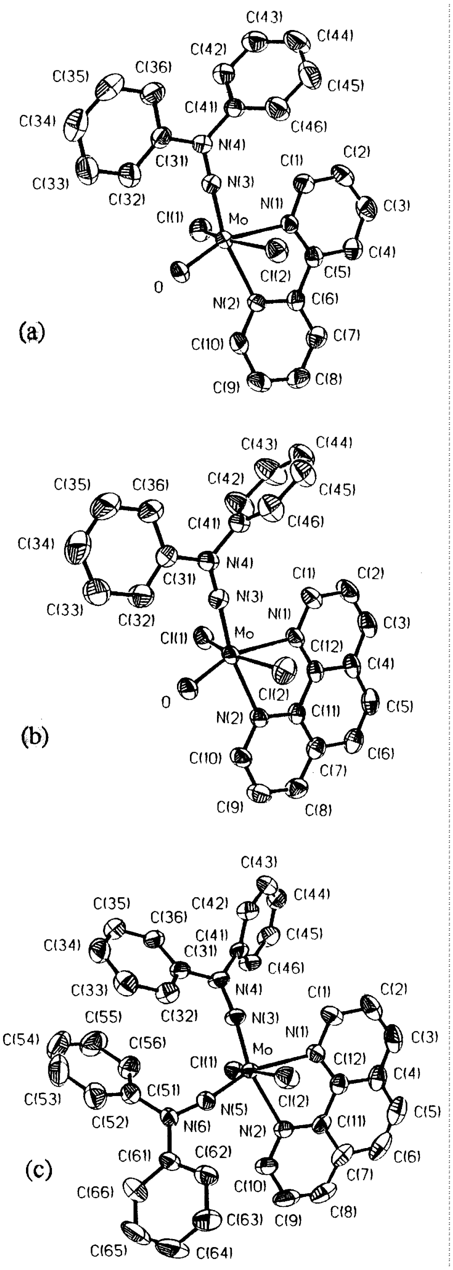

Fig. 1. Views of the molecular structures of (a) [$MoO(NNPh_2)Cl_2(bpy)$] (**III**), (b) [$MoO(NNPh_2)Cl_2(phen)$] (**V**) and (c) [$Mo(NNPh_2)Cl_2(phen)$] (**IX**), with 50% probability ellipsoids (hydrogen atoms omitted for clarity).

3.3. Spectroscopic studies

The characterization of complexes **III**–**X** was carried out by chemical analysis and by IR, UV–Vis and ^1H NMR spectroscopic techniques.

The IR spectra of oxo-hydrazido(2−) complexes, **III**–**VI**, display characteristic strong and sharp bands in the 1586–1600 and 901–905 cm^{-1} regions, assigned to $\nu(N{=}N)$ [1,11,19,22] and $\nu(Mo{=}O)$ [23], respectively. These spectra show also weak absorption bands in the 3048–3076 cm^{-1} region associated with $\nu(C–H)$ of the aromatic groups and, additionally, for complexes **IV** and **VI**, weak bands in the

2922–2930 cm^{-1} region associated with ν(C–H) of the methyl groups. On the other hand, excepting the absorption band corresponding to ν(Mo=O), the IR spectra of bis-hydrazido(2−) complexes, **VII**–**X**, are very similar to those exhibited by complexes **III**–**VI**.

The electronic spectra of compounds **III**–**X** were recorded in CH_2Cl_2. Complexes **III**–**VI** display comparable spectra indicating unambiguously the presence of similar compounds. An analogous conclusion can be attained in the case of complexes **VII**–**X**. The bands observed in the 266–300 and 340–360 nm regions, in all complexes studied, have been attributed to the Mo(NNPhR) chromophore [12,17,18], while the visible band observed in the range 376–400 nm for the oxo-hydrazido(2−) complexes could be assigned to an O(oxo) → Mo charge transfer transition [24]; this band is absent in the bis-hydrazido(2−) complexes.

The ^{1}H NMR spectra of complexes **III**, **V**, **VII** and **IX** in $CDCl_3$ are unexceptional except the presence, in the case of **III** and **V**, of a resonance at 5.31 ppm which confirms unambiguously that these complexes crystallize with one CH_2Cl_2 solvent molecule (vide supra). On the other hand, the spectra of complexes **IV** and **VI**, that contain the MoO(NNMePh) fragment, recorded in DMSO-d_6 due to their very low solubilities in $CDCl_3$, exhibit three methyl proton resonances in the 3.65–4.34 (**IV**) and 3.64–4.50 (**VI**) ppm regions. Probably, these resonances could arise (i) from the presence of two hydrazido rotamers (two resonances) and (ii) from a partial substitution of a chloride ligand by a DMSO solvent molecule (one resonance); the very low intensity resonance at 2.88 (**IV**) and 2.92 (**VI**) ppm, near to that of the free solvent chemical shift (2.50 ppm) is probably due to that coordinated DMSO. Likewise, the more salient feature of the spectra of **VIII** and **X**, that contain the $Mo(NNMePh)_2$ moiety, recorded at room temperature in $CDCl_3$, is the presence of three methyl proton resonances in the 3.55–4.31 ppm range, which could be explained by a mixture of two hydrazido rotamers in solution. The first rotamer, that contains alternate methyl groups (inequivalent hydrazido-methyl groups), exhibits two resonances with the same integrated intensity at 3.64 and 4.25 (**VIII**), and 3.55 and 4.31 (**X**) ppm, while the second, that contains inner methyl groups (equivalent hydrazido-methyl groups), exhibits only one resonance at 4.11 (**VIII**) and 4.17 (**X**) ppm [5]. Considering the integrated intensities for both complexes, the ratio inner/alternate rotamers is 1.85 for **VIII** and 2.00 for **X**.

3.4. Electrochemistry

Complexes **V** and **IX** were studied by cyclic voltammetry (CV) at a platinum electrode in dichloromethane. The number of electrons transferred in the various reduction and oxidation steps was estimated to be one by comparison to the CV of ferrocene under the same experimental conditions. In reduction, both complexes exhibit one irreversible process at −1.31 and −1.65 V, respectively. However, in oxidation, complex **V** exhibits only one nearly-reversible process at +1.24 V ($E_p^{ox} - E_p^{red} = 116$ mV at 100 mV s^{-1}), while complex **IX** exhibits two quasi-reversible successive processes at +0.65 and +0.83 V ($E_p^{ox} - E_p^{red} = 102$ and 130 mV at 100 mV s^{-1}, respectively). CV data for these primary processes were consistent with a diffusion-controlled charge transfer reaction; the various scans gave constant values of $i_{pa}/v^{1/2}$ and $i_{pc}/v^{1/2}$ over the range 20–300 mV s^{-1}. Likewise, i_{pa}/i_{pc}, for the anodic processes, were close to unity.

The electrochemical behavior of complex **V** is comparable to that of $[MoO(NNPh_2)(acac)_2]$ although, in this case, the acetylacetonate ligands shift the reduction and oxidation potentials to more negative values: $E_p^{red} = -1.70$ V; $E_p^{ox} = +1.20$ V, in DMF [17]. On the other hand, the electrochemical results depicted by complex **IX** can be compared, in general, to those observed in the phosphine complexes formulated as $[Mo(NNPhR)_2Cl_2(PPh_{3-x}Me_x)_2]$ (R = Ph, Me; $x = 1, 2$). However, these complexes display only one nearly-reversible oxidation process in the same region: $E_p^{red} = -1.42$ to -1.72 V; $E_p^{ox} = +0.83$ to $+0.93$ V, in CH_2Cl_2 [5].

4. Conclusions

The precedent study shows the potential of mixed [hydrazido(1−)][hydrazido(2−)] molybdenum complexes, [Mo(NHNPhR)(NNPhR)(acac)Cl_2] (R = Me, Ph), as precursors of new oxo[hydrazido(2−)] and bis-[hydrazido(2−)] molybdenum complexes containing di-imines as ancillary ligands. This property is a consequence of the susceptibility of the acetylacetonate ligand that can be substituted by nucleophilic reagents [5,17,18]. The substitution is accompanied by the deprotonation of the NHNPhR ligand, generating the second NNPhR ligand and one Hacac molecule [5]. Further studies on organometallic compounds derived from these complexes will be discussed in forthcoming publications.

5. Supplementary material

Lists of observed and calculated structure factors, anisotropic thermal parameters, H atom parameters, and full lists of bond distances and angles for complexes **III**, **V** and **IX**, are available from D. Boys on request.

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