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Synthesis and Characterization of Molybdenum Complexes Containing both End-on Organohydrazido(1–) and Organohydrazido(2–) Ligands. X-ray Crystal Structures of $[Mo(NHNPh_2)(NNPh_2)(acac)Cl_2]$ and $[Mo(NHNMePh)(NNMePh)(acac)Cl_2]$

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In acetonitrile, bis(acetylacetonato)dioxomolybdenum(VI), $[MoO_2(acac)_2]$, reacts with disubstituted hydrazine hydrohalides ($RR'NNH_3{}^+X^-$: R = R′ = Ph; R = Ph, R′ = Me; X = Cl, Br, I) to yield a new series of complexes, which have been characterized by elemental analysis, electrochemistry and spectroscopy (IR, UV–visible, and ^1H NMR) and formulated as $[Mo(NHNPh_2)(NNPh_2)(acac)X_2]$ (X = Cl (**1**), Br (**2**), I (**3**)) and $[Mo(NHNMePh)(NNMePh)(acac)X_2]$ (X = Cl (**4**), Br (**5**), I (**6**)). The X-ray crystal structures of **1** and **4** are reported. Crystals of **1** are monoclinic, space group $P2_1/a$, with $a = 9.352(1)$ Å, $b = 31.320(2)$ Å, $c = 9.612(1)$ Å, $\beta = 95.35(1)°$, and $Z = 4$. The structure was solved using 3833 unique reflections, and refinement gave final R and R_w values of 0.037 and 0.052, respectively. Crystals of **4** are triclinic, space group $P\bar{1}$, with $a = 7.765(1)$ Å, $b = 7.715(2)$ Å, $c = 17.910(2)$ Å, $\alpha = 89.18(1)°$, $\beta = 91.35(1)°$, $\gamma = 92.64(1)°$, and $Z = 2$. The structure was solved using 4515 unique reflections, and refinement gave final R and R_w values of 0.032 and 0.033, respectively. Both complexes display similar distorted octahedral geometries. The coordination sphere consists of two mutually *cis* organohydrazido ligands, two mutually *trans* chloro ligands and one chelated acetylacetonato ligand. The organohydrazido(2–) and organohydrazido(1–) ligands adopt the linear and bent "end-on" conformations, respectively.

Introduction

$[MoO_2(acac)_2]$ has proved to be a versatile precursor in the synthesis of a variety of molybdenum complexes containing organodinitrogen ligands as potential models[2,3] of intermediates in the conversion of coordinated dinitrogen into ammonia. This ability is due to the reactivity of the Mo═O functionality and the lability of the ancillary ligands. Indeed, condensation-type reactions between $[MoO_2(acac)_2]$ and substituted hydrazines of the type $RNHNH_2$ and $RR'NNH_2$ yield molybdenum complexes containing organodiazenido, NNR, and organohydrazido(2–), NNRR′, ligands, respectively. In this way, we have obtained (i) mono-, di-, and tetranuclear complexes containing the *cis*-$[Mo(NNR)_2]^{2+}$ moiety, *e.g.* $[Mo(NNR)_2(acac)_2]$,[4] $[\{Mo(NNR)_2(acac)(\mu\text{-}OR')\}_2]$,[5,6] and $[\{Mo(NNR)_2(\mu\text{-}MoO_4)(\mu\text{-}OR')\}_2]$,[6] and (ii) mono- and dinuclear complexes containing the *cis*-$[MoO(NNRR')]^{2+}$ moiety, *e.g.* $[MoO(NNRR')(acac)_2]$ and $[\{MoO(NNRR')(acac)(\mu\text{-}OR'')\}_2]$.[7,8] The displacement of one ancillary ligand results in the formation of alkoxo-bridged dinuclear complexes, while the formation of tetranuclear species containing bidentate bridging $[MoO_4]^{2-}$ units requires the displacement of both ancillary ligands from the starting compound. Although bis[hydrazido(2–)]molybdenum complexes have been obtained by condensation between $[MoO_2(SCNR''_2)_2]$ and $RR'NNH_2$ [R = R′ = Me, Ph; R = Me, R′ = Ph; R''_2 = Me_2, Et_2, Ph_2, $(CH_2)_5$],[9] all our attempts to synthesize similar complexes from $[MoO_2(acac)_2]$ and neutral $RR'NNH_2$ in alcohols or acetonitrile have been unsuccessful. However, the reaction of $[MoO_2(acac)_2]$ with $MePhNNH_3{}^+X^-$ and $Ph_2NNH_3{}^+X^-$ (X = Cl, Br, I) in acetonitrile yield a new series of complexes of the type $[Mo(NHNRR')(NNRR')(acac)X_2]$ containing both organohydrazido(1–) and organo-hydrazido(2–) ligands. This report deals with the syntheses, characterization, and electrochemical behavior of $[Mo(NHNRR')(NNRR')(acac)X_2]$ (R = R′ = Ph, X = Cl (**1**), Br (**2**), I (**3**); R = Me, R′ = Ph, X = Cl (**4**), Br (**5**), I (**6**)). Although a fairly large number of organohydrazido(2–) complexes are known,[2,3] organohydrazido(1–) complexes are less common,[10–35] and only a very few complexes containing both organohydrazido-

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Chart 1. "End-on" (**Ia** and **Ib**) and "Side-on" (II) Coordination Modes for the Organohydrazido(1−) Ligand

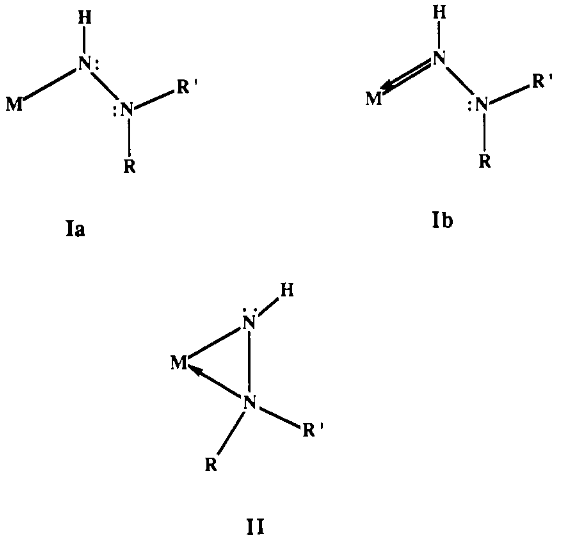

Table 1. Summary of X-ray Diffraction Data for Compounds 1 and 4

	[Mo(NHNPh$_2$)(NNPh$_2$)(acac)Cl$_2$]	[Mo(NHNMePh)(NNMePh)(acac)Cl$_2$]
fw	631.41	507.27
space group	$P2_1/a$	$P\bar{1}$
a, Å	9.352(1)	7.765(1)
b, Å	31.320(2)	7.715(2)
c, Å	9.612(1)	17.910(2)
α, deg	90.0	89.18(1)
β, deg	95.35(1)	91.35(1)
γ, deg	90.0	92.64(1)
V, Å^3	2803(1)	1071.3(7)
Z	4	2
T, °C	20	20
λ, Å	0.710 69	0.710 69
μ(Mo Kα), cm^{-1}	6.81	8.70
ρ_{calc}, g cm^{-3}	1.50	1.57
R^a	0.037	0.032
$R_w{}^b$	0.052	0.033

[a] $R = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o{}^2]^{1/2}$ ($w = 1.0$).

(2−) and organohydrazido(1−) ligands have been reported.[10–12,20,26] The X-ray crystal structures of **1** and **4** have been determined in order to ascertain the bonding modes of the hydrazido ligands in these complexes. Organohydrazido(1−) ligands can bind to a metal center either in the "end-on" conformation[10–21] or in the "side-on" η^2 conformation[22–35] (Chart 1), and, thus, can be formally considered as neutral one- or three-electron donors. An interesting example of isomerism between the "end-on" and "side-on" conformations has been recently reported for [WF$_4$(NHNMe$_2$)(NNMe$_2$)]$^-$.[36]

Table 2. Atomic Positional Parameters[a] and Temperature Factors[b] for [Mo(NHNPh$_2$)(NNPh$_2$)(acac)Cl$_2$]

atom	x/a	y/b	z/c	U(eq), Å^2
Mo(1)	0.25638(5)	0.10266(2)	0.31580(5)	0.0353
Cl(1)	0.0245(2)	0.10620(6)	0.4136(2)	0.0512
Cl(2)	0.4993(2)	0.08947(5)	0.2639(2)	0.0509
O(3)	0.2432(4)	0.0379(1)	0.3553(4)	0.0450
O(4)	0.3471(4)	0.1060(1)	0.5248(4)	0.0471
N(1)	0.2732(5)	0.1643(1)	0.3389(5)	0.0406
N(2)	0.2391(6)	0.2011(2)	0.2687(5)	0.0456
N(3)	0.1806(4)	0.0986(1)	0.1426(4)	0.0358
N(4)	0.1254(5)	0.0897(1)	0.0153(4)	0.0374
C(1)	0.2532(6)	0.2028(2)	0.1218(6)	0.0431
C(2)	0.3748(7)	0.1855(2)	0.0709(7)	0.0507
C(3)	0.3867(8)	0.1895(3)	−0.0720(8)	0.0618
C(4)	0.2823(9)	0.2083(2)	−0.1594(7)	0.0621
C(5)	0.1642(8)	0.2250(2)	−0.1057(7)	0.0605
C(6)	0.1484(7)	0.2233(2)	0.0339(6)	0.0499
C(7)	0.1894(6)	0.2364(2)	0.3420(6)	0.0433
C(8)	0.2339(8)	0.2775(2)	0.3130(7)	0.0573
C(9)	0.189(1)	0.3116(2)	0.3851(9)	0.0673
C(10)	0.098(1)	0.3057(3)	0.486(1)	0.0660
C(11)	0.0544(9)	0.2656(4)	0.5192(8)	0.0698
C(12)	0.0990(7)	0.2284(2)	0.4456(7)	0.0559
C(13)	0.2477(8)	−0.0299(2)	0.4533(8)	0.0627
C(14)	0.2830(6)	0.0161(2)	0.4646(6)	0.0418
C(15)	0.3515(7)	0.0325(2)	0.5855(7)	0.0516
C(16)	0.3803(7)	0.0757(2)	0.6116(6)	0.0488
C(17)	0.4567(8)	0.0905(3)	0.7476(7)	0.0636
C(21)	0.0182(6)	0.1173(2)	−0.0492(6)	0.0385
C(22)	0.0115(6)	0.1249(2)	−0.1917(6)	0.0465
C(23)	−0.0948(7)	0.1509(2)	−0.2546(6)	0.0551
C(24)	−0.1935(7)	0.1698(2)	−0.1762(7)	0.0584
C(25)	−0.1859(7)	0.1623(2)	−0.0318(7)	0.0560
C(26)	−0.0807(6)	0.1358(2)	0.0320(6)	0.0463
C(27)	0.1532(6)	0.0484(2)	−0.0404(5)	0.0357
C(28)	0.0515(6)	0.0291(2)	−0.1360(6)	0.0435
C(29)	0.0779(6)	−0.0112(2)	−0.1893(6)	0.0485
C(30)	0.2027(7)	−0.0331(2)	−0.1451(7)	0.0471
C(31)	0.3023(7)	−0.0139(2)	−0.0472(7)	0.0495

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] U(eq) = $[U(11)U(22)U(33)]^{1/3}$.

Experimental Section

Chemicals. 1-Methyl-1-phenylhydrazine, 1,1-diphenylhydrazine hydrochloride, hydrochloric acid, hydrobromic acid, hydroiodic acid, triethylamine, acetylacetone, tetrabutylammonium hexafluorophosphate, n-Bu$_4$NPF$_6$, and ammonium molybdate, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, were used as received. Reagent grade solvents were dried and distilled by standard methods prior to use. [MoO$_2$(acac)$_2$] was prepared as described in the literature.[37]

1,1-Diphenylhydrazine Hydrohalides, Ph$_2$NNH$_3$$^+X^-$ (X = Br, I). These compounds were prepared according to a modification of the procedure described in the literature.[38] KOH (1.23 g, 22 mmol) was added to a solution of Ph$_2$NNH$_3$$^+Cl^-$ (4.86 g, 22 mmol) in MeOH (15 mL). The resulting suspension was stirred until complete dissolution. Then, the solution was evaporated to dryness under *vacuo*. The residue was extracted with dry acetonitrile (15 mL), and KCl was removed by filtration. Then, the filtrate was treated with a slight excess of 40% aqueous HBr (3.7 mL, 25 mmol) or 57% aqueous HI (3.3 mL, 25 mmol) and the acidified solution was allowed to stand for 1 h; the crystalline solid was separated by filtration, washed with dry Et$_2$O, and dried in *vacuo*. Yield: 87% (X = Br); 49% (X = I).

1-Methyl-1-phenylhydrazine Hydrohalides, MePhNNH$_3$$^+X^-$ (X = Cl, Br, I). HX(g) was bubbled into a solution of MePhNNH$_2$ (9.6 mL, 82.4 mmol) in dry Et$_2$O (50 mL). The resulting crystalline solid was filtered off, washed with dry Et$_2$O, and stored in *vacuo* at −12 °C. These compounds are hygroscopic and decompose slowly. Yield: 94% (X = Cl); 93% (X = Br); 69% (X = I). HCl(g) was obtained from a concentrated aqueous solution as described in the literature.[39] HBr(g)

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Table 3. Atomic Positional Parameters[a] and Temperature Factors[b] for [Mo(NHNMePh)(NNMePH)(acac)Cl_2]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2
Mo(1)	0.21398(3)	0.39226(3)	0.25403(1)	0.0295
Cl(1)	0.4244(1)	0.1777(1)	0.27941(5)	0.0439
Cl(2)	−0.0503(1)	0.5416(1)	0.22734(5)	0.0462
O(3)	0.0544(3)	0.2498(3)	0.3283(1)	0.0366
O(4)	0.1187(3)	0.2149(3)	0.1729(1)	0.0375
N(1)	0.3159(3)	0.4945(3)	0.1644(1)	0.0350
N(2)	0.3987(3)	0.6377(3)	0.1378(1)	0.0375
N(3)	0.2929(3)	0.5445(3)	0.3194(1)	0.0314
N(4)	0.3341(3)	0.6616(3)	0.3690(1)	0.0334
C(1)	0.3891(4)	0.6736(4)	0.0601(2)	0.0357
C(2)	0.5251(5)	0.7521(5)	0.0247(2)	0.0495
C(3)	0.5130(6)	0.7916(5)	−0.0519(2)	0.0530
C(4)	0.3734(6)	0.7335(5)	−0.0931(2)	0.0565
C(5)	0.2398(6)	0.6492(6)	−0.0578(2)	0.0611
C(6)	0.2453(5)	0.6189(5)	0.0185(2)	0.0479
C(7)	0.4828(6)	0.7544(5)	0.1910(2)	0.0593
C(13)	−0.1585(5)	0.0606(5)	0.3781(2)	0.0497
C(14)	−0.0485(4)	0.1215(4)	0.3145(2)	0.0350
C(15)	−0.0650(4)	0.0347(4)	0.2468(2)	0.0415
C(16)	0.0195(4)	0.0797(4)	0.1816(2)	0.0359
C(17)	−0.0034(5)	−0.0330(5)	0.1142(2)	0.0523
C(21)	0.4937(4)	0.6573(4)	0.4901(2)	0.0308
C(22)	0.5181(4)	0.7494(4)	0.4747(2)	0.0383
C(23)	0.6719(5)	0.7391(5)	0.5149(2)	0.0429
C(24)	0.8019(4)	0.6426(5)	0.4892(2)	0.0436
C(25)	0.7791(4)	0.5545(5)	0.4230(2)	0.0440
C(26)	0.6249(4)	0.5601(4)	0.3824(2)	0.0377
C(27)	0.2052(4)	0.7878(5)	0.3839(2)	0.0456

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] $U(\mathrm{eq}) = [U(11)\mathrm{U}(22)\mathrm{U}(33)]^{1/3}$.

Table 4. Selected Bonds Lengths (Å) and Angles (deg) for [Mo($NHNPh_2$)($NNPh_2$)(acac)Cl_2]

Mo(1)–Cl(1)	2.445(1)	Mo(1)–Cl(2)	2.407(2)
Mo(1)–O(3)	2.070(4)	Mo(1)–O(4)	2.109(4)
Mo(1)–N(1)	1.948(5)	Mo(1)–N(3)	1.752(4)
O(3)–C(14)	1.278(7)	O(4)–C(16)	1.283(7)
N(1)–N(2)	1.359(6)	N(2)–C(1)	1.432(7)
N(2)–C(7)	1.412(7)	N(3)–N(4)	1.313(6)
N(4)–C(21)	1.423(7)	N(4)–C(27)	1.433(7)
C(1)–C(2)	1.389(8)	C(1)–C(6)	1.390(8)
C(2)–C(3)	1.394(9)	C(3)–C(4)	1.36(1)
C(4)–C(5)	1.37(1)	C(5)–C(6)	1.364(9)
C(7)–C(8)	1.387(9)	C(9)–C(10)	1.36(1)
C(10)–C(11)	1.37(1)	C(7)–C(12)	1.389(9)
C(8)–C(9)	1.36(1)	C(11)–C(12)	1.44(1)
C(13)–C(14)	1.480(9)	C(14)–C(15)	1.373(8)
C(15)–C(16)	1.398(9)	C(16)–C(17)	1.504(9)
C(21)–C(22)	1.386(8)	C(21)–C(26)	1.390(8)
C(22)–C(23)	1.380(8)	C(23)–C(24)	1.378(9)
C(24)–C(25)	1.403(9)	C(25)–C(26)	1.386(8)
C(27)–C(28)	1.396(8)	C(27)–C(32)	1.387(8)
C(28)–C(29)	1.393(8)	C(29)–C(30)	1.386(9)
C(30)–C(31)	1.396(9)	C(31)–C(32)	1.406(8)

Cl(2)–Mo(1)–Cl(1)	167.34(6)	O(3)–Mo(1)–Cl(1)	84.5(1)
O(3)–Mo(1)–Cl(2)	86.7(1)	O(4)–Mo(1)–Cl(1)	85.6(1)
O(4)–Mo(1)–Cl(2)	84.4(1)	O(4)–Mo(1)–O(3)	84.2(2)
N(1)–Mo(1)–Cl(1)	88.6(1)	N(1)–Mo(1)–Cl(2)	97.2(1)
N(1)–Mo(1)–O(3)	163.0(2)	N(1)–Mo(1)–O(4)	79.7(2)
N(3)–Mo(1)–Cl(1)	94.2(1)	N(3)–Mo(1)–Cl(2)	95.5(1)
N(3)–Mo(1)–O(3)	94.4(2)	N(3)–Mo(1)–O(4)	178.7(2)
N(3)–Mo(1)–N(1)	101.6(2)		
N(2)–N(1)–Mo(1)	140.5(4)	C(1)–N(2)–N(1)	118.7(5)
C(7)–N(2)–N(1)	119.4(5)	C(7)–N(2)–C(1)	121.9(5)
N(4)–N(3)–Mo(1)	171.9(4)	C(21)–N(4)–N(3)	118.4(4)
C(27)–N(4)–N(3)	118.1(4)	C(27)–N(4)–C(21)	122.1(4)

and HI(g) were obtained by dropwise addition of their aqueous solutions on P_4O_{10};[39] a nitrogen stream was used to sweep the hydrohalide into the hydrazine solution.

Table 5. Selected Bonds Lengths (Å) and Angles (deg) for [Mo(NHMePh)(NNMePh)(acac)Cl_2]

Mo(1)–Cl(1)	2.4102(8)	Mo(1)–Cl(2)	2.4336(8)
Mo(1)–O(3)	2.103(2)	Mo(1)–O(4)	2.108(2)
Mo(1)–N(1)	1.948(2)	Mo(1)–N(3)	1.750(2)
O(3)–C(14)	1.266(4)	O(4)–C(16)	1.277(4)
N(1)–N(2)	1.339(3)	N(2)–C(1)	1.416(4)
N(2)–C(7)	1.443(4)	N(3)–N(4)	1.301(3)
N(4)–C(21)	1.419(4)	N(4)–C(27)	1.460(4)
C(1)–C(2)	1.391(4)	C(1)–C(6)	1.381(5)
C(2)–C(3)	1.389(5)	C(3)–C(4)	1.359(6)
C(4)–C(5)	1.362(6)	C(5)–C(6)	1.383(5)
C(13)–C(14)	1.497(4)	C(14)–C(15)	1.394(5)
C(15)–C(16)	1.385(5)	C(16)–C(17)	1.500(4)
C(21)–C(22)	1.386(4)	C(21)–C(26)	1.391(4)
C(22)–C(23)	1.385(5)	C(23)–C(24)	1.374(5)
C(24)–C(25)	1.378(5)	C(25)–C(26)	1.388(4)

Cl(2)–Mo(1)–Cl(1)	164.83(3)	O(3)–Mo(1)–Cl(1)	86.50(6)
O(3)–Mo(1)–Cl(2)	82.32(6)	O(4)–Mo(1)–Cl(1)	84.00(6)
O(4)–Mo(1)–Cl(2)	84.93(6)	O(4)–Mo(1)–O(3)	85.47(8)
N(1)–Mo(1)–Cl(1)	97.88(8)	N(1)–Mo(1)–Cl(2)	90.20(8)
N(1)–Mo(1)–O(3)	163.61(9)	N(1)–Mo(1)–O(4)	79.33(9)
N(3)–Mo(1)–Cl(1)	97.13(8)	N(3)–Mo(1)–Cl(2)	94.19(8)
N(3)–Mo(1)–O(3)	95.9(1)	N(3)–Mo(1)–O(4)	178.3(1)
N(3)–Mo(1)–N(1)	99.2(1)		
N(3)–N(1)–Mo(1)	142.9(2)	C(1)–N(2)–N(1)	118.7(3)
C(7)–N(2)–N(1)	117.9(3)	C(7)–N(2)–C(1)	123.2(3)
N(4)–N(3)–Mo(1)	173.8(2)	C(21)–N(4)–N(3)	120.3(2)
C(27)–N(4)–N(3)	116.9(2)	C(27)–N(4)–C(21)	122.7(2)

Preparation of Hydrazido Complexes. General Procedure. [$MoO_2(acac)_2$] (4.0 g, 12.5 mmol) was dissolved in 50 mL of acetonitrile. $RR'NNH_3{}^+X^-$ (25 mmol) was added to this solution, and the mixture was stirred at room temperature for 1.5 h. The microcrystalline solid was filtered off, washed with dry Et_2O, and dried in *vacuo*. Recrystallization was carried out by dissolving the crude product in $CHCl_3$ and layering the solution with Et_2O.

(Acetylacetonato)dichloro{diphenylhydrazido(1−)}{diphenylhydrazido(2−)}molybdenum(VI), [Mo($NHNPh_2$)($NNPh_2$)(acac)Cl_2] (1). Yield: 65%. Mp: 177–178 °C dec. Anal. Calcd for $C_{29}H_{28}Cl_2MoN_4O_2$: C, 55.2; H, 4.47; N, 8.87. Found: C, 54.8; H, 4.58; N, 8.97. UV–vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 478 (4.09), 341 (4.19), 273 (4.50), 229 (4.40). IR (cm^{-1}, KBr): 3258 (w) ν(NH), 1595 (s) ν(NN), 1568 (s) 1545 (s), $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$. ^{1}H NMR ($CDCl_3$): δ 2.15 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 5.84 (s, 1H, C*H*), 7.03–7.39 (m, 20 H, 4C_6H_5), 12.64 (s, 1H, N*H*).

(Acetylacetonato)dibromo{diphenylhydrazido(1−)}{diphenylhydrazido(2−)}molybdenum(VI), [Mo($NHNPh_2$)($NNPh_2$)(acac)Br_2] (2). Yield: 62%. Mp: 189–190 °C dec. Anal. Calcd for $C_{29}H_{28}Br_2MoN_4O_2$: C, 48.4; H, 3.92; N, 7.78. Found: C, 48.5; H, 3.99; N, 8.06. UV–vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 476 nm (4.10), 343 (4.15), 276 (4.47), 229 (4.41). IR (cm^{-1}, KBr): 3252 (w) ν(NH), 1595 (s) ν(NN), 1565 (s) 1545 (s), $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$. ^{1}H NMR ($CDCl_3$): δ 2.13 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 5.87 (s, 1H, C*H*), 7.07–7.43 (m, 20 H, 4C_6H_5), 12.85 (s, 1H, N*H*).

(Acetylacetonato)diiodo{diphenylhydrazido(1−)}{diphenylhydrazido(2−)}molybdenum(VI), [Mo($NHNPh_2$)($NNPh_2$)(acac)I_2] (3). Yield: 59%. Mp: 160 °C. Anal. Calcd for $C_{29}H_{28}I_2MoN_4O_2$: C, 42.8; H, 3.47. Found: C, 42.3; H, 3.90. UV–vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 484 (4.05), 330 (sh, 4.25), 282 (4.59), 234 (4.59). IR (cm^{-1}, KBr): 3243(w), ν(NH), 1590 (s) ν(NN), 1560 (s) 1535 $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$. ^{1}H NMR ($CDCl_3$): δ 2.06 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 5.89 (s, 1H, C*H*), 7.07–7.52 (m, 20 H, 4C_6H_5), 13.0 (s, 1H, N*H*).

(Acetylacetonato)dichloro{methylphenylhydrazido(1−)}{methylphenylhydrazido(2−)}molybdenum(VI), [Mo(NHNMePh)(NNMePh)(acac)Cl_2] (4). Yield: 65%. Mp: 186 °C dec. Anal. Calcd for $C_{19}H_{24}Cl_2MoN_4O_2$: C, 45.0; H, 4.76; N, 11.0. Found: C, 44.5; H, 4.80; N, 11.0. UV–vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 427 (4.19), 340 (4.27), 266 (4.38), 232 (4.32). IR (cm^{-1}, KBr): 3254 (w) ν(NH), 1590 (s) ν(NN), 1570 (s) 1540 (s) $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$. ^{1}H NMR ($CDCl_3$): δ 2.21 (s, 3H, CH_3), 2.25 (s, 3H, CH_3); 4.11 (s, 3H, NCH_3), 4.36 (s, 3H, NCH_3), 5.86 (s, 1H, C*H*), 7.07–7.48 (m, 10 H, 2C_6H_5), 12.8 (s, 1H, N*H*).

(Acetylacetonato)dibromo{methylphenylhydrazido(1−)}{methylphenylhydrazido(2−)}molybdenum(VI), [Mo(NHNMePh)(NNMePh)(acac)Br_2] (5). Yield: 74%. Mp: 187 °C. Anal. Calcd for $C_{19}H_{24}Br_2MoN_4O_2$: C, 38.3; H, 4.05; N, 9.40. Found: C, 38.1; H, 4.10; N, 9.50. UV–vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 432 (4.20), 327 (4.24), 273 (4.37), 233 (4.40). IR (cm^{-1}, KBr): 3248 (w) ν(NH), 1585 (s) ν(NN), 1568 (s) 1535 (s) $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$. ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 4.12 (s, 3H, NCH_3), 4.16 (s, 3H, NCH_3), 5.88 (s, 1H, C*H*), 7.07–7.60 (m, 10 H, 2C_6H_5), 12.9 (s, 1H, NH).

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(39) Brauer, G. *Química Inorgânica Preparativa*; Editorial Revertè: Barcelona, 1958; pp 183–188.

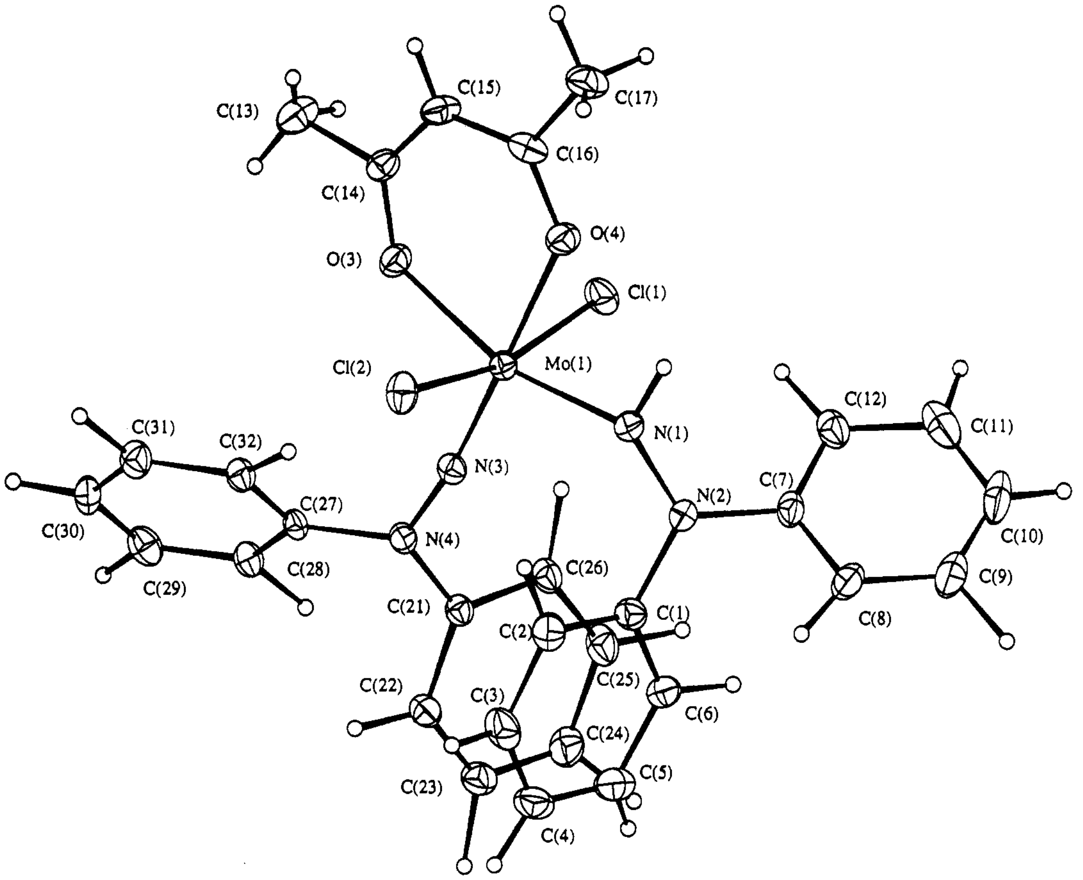

Figure 1. View[40] of the molecular structure of $[Mo(NHNPh_2)(NNPh_2)(acac)Cl_2]$ (**1**) with the atom labeling scheme.

(Acetylacetonato)diiodo{methylphenylhydrazido(1–)}{methylphenylhydrazido(2–)}molybdenum(VI), $[Mo(NHNMePh)(NNMePh)(acac)I_2]$ (6). Yield: 53%. Mp: 171–172 °C dec. Anal. Calcd for $C_{19}H_{24}I_2MoN_4O_2$: C, 33.1; H, 3.50. Found: C, 33.3; H, 3.79. UV–vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 454 nm (4.09), 324 (4.09), 285 (4.48), 234 (4.52). IR (cm^{-1}, KBr): 3239 (w) ν(NH), 1590 (s) ν(NN), 1565 (s) 1545 (s) $\nu(C\cdots O)$, $\nu(C\cdots C)$. ^1H NMR ($CDCl_3$): δ 2.16 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.77 (s, 3H, NCH_3), 4.23 (s, 3H, NCH_3), 5.93 (s, 1H, CH), 7.06–7.67 (m, 10 H, $2C_6H_5$), 13.1 (s, 1H, NH).

Physical Measurements. ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker FT AC/200P spectrometer. IR spectra were obtained as KBr disks with a Perkin-Elmer Model 599 spectrophotometer. Electronic spectra were recorded in CH_2Cl_2 solutions on a Cary Model 219 spectrophotometer. Magnetic measurements were performed at 20 ± 2 °C by the Faraday method using a Cahn Ventron RTL magnetic balance and $[Ni(en)_2]S_2O_3$ as the calibrant. Melting points were determined by using a Kofler apparatus and were corrected. Cyclic voltammetry (CV) studies were carried out with a homemade potentiostat of conventional design. A standard three-electrode cell was used, which consisted of platinum working and auxiliary electrodes and an aqueous saturated calomel electrode (SCE) as the reference. Solution concentrations were 2 mM for the compounds under study and 0.1 M for the supporting electrolyte n-Bu_4NPF_6. All measurements were carried out at room temperature under nitrogen in CH_2Cl_2. Under these experimental conditions the ferrocenium–ferrocene couple was located at +0.50 V.

X-ray Data Collection and Structure Determination of 1 and 4. X-ray data were collected at room temperature with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Lattice parameters were obtained from a least-squares refinements of the setting angles of 25 automatically centered reflections. Crystal data and data collection parameters are summarized in Table 1. The intensities of two standard reflections were monitored every hour; these showed no significant change during data collection. Intensities were corrected for Lorentz and polarization effects. An empirical absorption correction using DIFABS[40] was applied. All computations were performed on a Micro VAX II using the CRYSTALS system.[41] Both structures were solved by conventional heavy-atom methods. Anisotropic thermal parameters were refined for nonhydrogen atoms. All the hydrogen atoms were located on difference electron density maps and were included in the refinements; their coordinates and an overall isotropic thermal parameter were refined. Final refinements gave $R = 0.037$ and $R_w = 0.052$ for **1** and $R = 0.032$ and $R_w = 0.033$ for **4**, respectively. Scattering factors and corrections for anomalous dispersion were taken from ref 42. Atomic positional parameters for nonhydrogen atoms are listed in Tables 2 and 3. Selected intramolecular bond distances and angles are given in Tables 4 and 5. Views[43] of the molecular structure of **1** and **4** with the atom labeling scheme are shown in Figures 1 and 2, respectively.

Results and Discussion

Synthesis of Complexes. In acetonitrile, organohydrazine hydrohalides react readily with $[MoO_2(acac)_2]$ (2:1) at room temperature to yield a series of air-stable diamagnetic crystalline molybdenum complexes containing both organohydrazido(1–) and organohydrazido(2–) ligands (eq 1).

$$[MoO_2(acac)_2] + 2RR'NNH_3{}^+X^- \rightarrow [Mo(NHNRR')(NNRR')(acac)X_2] + Hacac + 2H_2O \quad (1)$$

The complexes are fairly soluble in $CHCl_3$ and CH_2Cl_2, slightly soluble in MeOH, and EtOH, and insoluble in water and hexane. Possible hydrazine hydrohalide impurities can be washed out with water without degradation of the hydrazido complexes. Complexes **1**–**6** appear to be stable both in the solid state and in solution, although the iodo derivatives **3** and **6** undergo slow degradation in solution.

The formulation is consistent with analytical data and with the X-ray crystal studies of **1** and **4** (*vide infra*). Other spectroscopic data also support the view that compounds **1**–**3**

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(41) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. Crystals User Guide, Chemical Crystallography Laboratory. University of Oxford, 1988.

(42) *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

(43) Pearce, L. J.; Watkin, D. J. CAMERON. Chemical Crystallography Laboratory, University of Oxford.

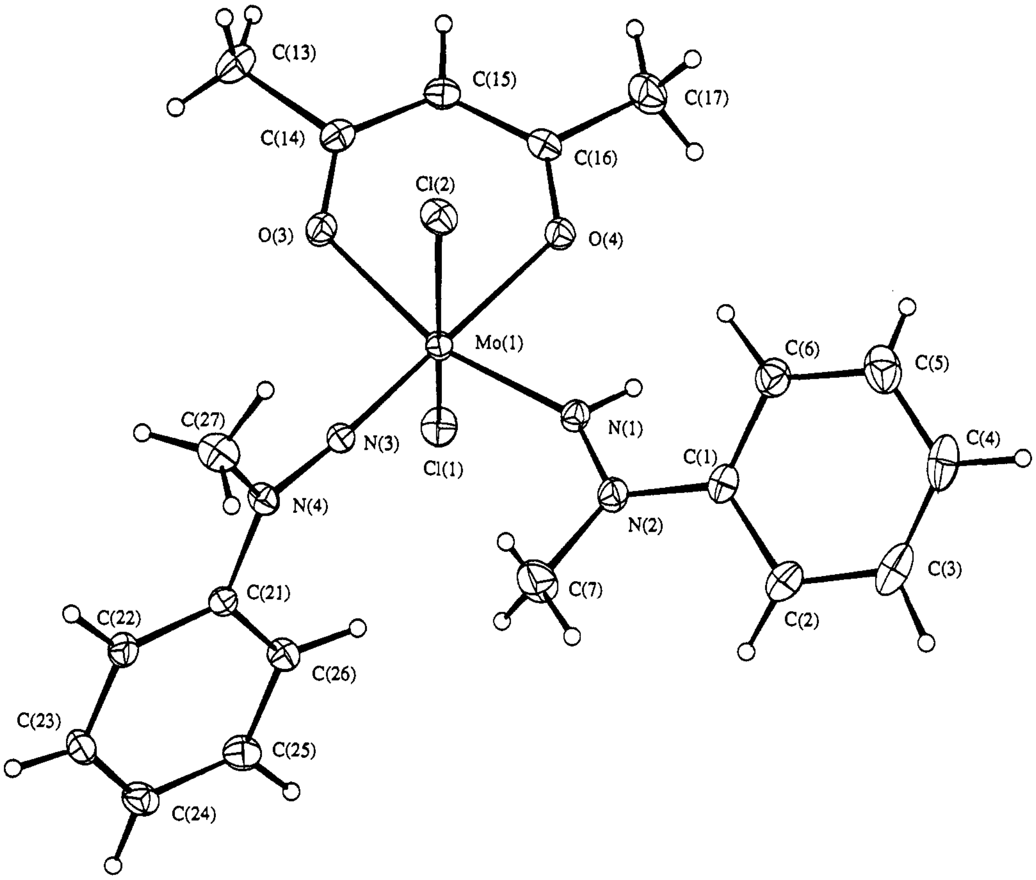

Figure 2. View[40] of the molecular structure of $[Mo(NHNMePh)(NNMePh)(acac)Cl_2]$ (**4**) with the atom labeling scheme.

have virtually identical structures and that the same is true for complexes **4**–**6**. Reaction 1 clearly relies on the lability of the acetylacetonato ligands. The displacement of one acetylacetonato ligand in the course of the reaction of $[MoO_2(acac)_2]$ with organohydrazines has been previously observed.[5–8] Other reactions would occur for dioxo precursors containing kinetically inert ancillary ligands such as bidentate ligands with (N,N), (N,O), (N,S), (O,S), and (S,S) donor sets.[44] For instance,[9] bis[hydrazido(2–)] molybdenum complexes obtained from $[MoO_2(S_2CNR''_2)_2]$ (eq 2) react with 1 equiv of acid to give mixed hydrazido(2–)-hydrazido(1–) complexes (eq 3); while hydrazine hydrochloride is formed with an excess of acid (eq 4).

$$[MoO_2(S_2CNR''_2)_2] + 2RR'NNH_2 \rightarrow [Mo(NNRR')_2(S_2CNR''_2)_2] + 2H_2O \quad (2)$$

$$[Mo(NNRR')_2(S_2CNR''_2)_2] + HX \rightarrow [MoX(NHNRR')(NNRR')(S_2CNR''_2)_2] \quad (3)$$

$$[Mo(NNRR')_2(S_2CNR''_2)_2] + 3HX \rightarrow [MoX_2(NNRR')(S_2CNR''_2)_2] + RR'NNH_3X \quad (4)$$

Up to date organohydrazido(1–) complexes have been obtained by one of the following synthetic routes: (i) protonation of hydrazido(2–) complexes[11] or alkylation of aryldiazene complexes;[18,19] (ii) reaction of dioxomolybdenum complexes with $RNHNH_3^+Cl^-$ [17] or $RNHNH_2$,[20,30] such reactions yielding mixed complexes containing both diazenido and organohydrazido(1–) ligands;[17,30] (iii) displacement of an iodo ligand by mono- or disubstituted hydrazines;[15,16] (iv) reaction of $RNHNH_2$ (R = PhCO or MeOCO) on an acyldiazenido rhenium complex;[10–12] (v) oxidative addition of aryldiazonium halides on iridium hydrides.[13,14] Although the synthetic method described above is unprecedented, it appears to be connected to routes i and ii.

The more salient feature of complexes **1** and **4** is their reactivity towards phosphines to afford mononuclear bis[hydrazido(2–)] complexes formulated as $[Mo(NNRR')_2(PMe_{3-x}Ph_x)_2Cl_2]$ (R = R' = Ph; R = Ph, R' = Me; x = 1, 2, 3) and $[Mo(NNPh_2)_2(acac)I(PPh_3)]$ to be described in a forthcoming publication.[45]

IR, ^1H NMR, and UV–Visible Spectroscopy. The IR spectra show a sharp and weak band in the 3260–3230-cm^{-1} region, which is assigned to the ν(N—H) stretching of the hydrazido(1–) ligand,[10,16,20] and a strong band in the 1595–1585-cm^{-1} region, which is attributed to the ν(N═N) stretching of the hydrazido(2–) ligand.[10] These two bands are present in all complexes. Other noticeable features are the presence of two bands characteristic of the chelated acetylacetonato ligand at 1565 and 1545 cm^{-1} and the absence of any ν(Mo═O) band in the 930–900-cm^{-1} region.

The ^1H NMR spectra of complexes **1**–**6** in $CDCl_3$ at ambient temperature exhibit a NH resonance near 13 ppm, which disappears upon addition of D_2O. In addition, the acetylacetonate ligand gives rise to two different methyl proton resonances at *ca.* 2.0 and 2.3 ppm and a methyne proton resonance at *ca.* 5.9 ppm. As expected, two different methyl proton resonances from the methylphenylhydrazido(2–) and methylphenylhydrazido(1–) ligands are observed at *ca.* 4 ppm for complexes **4**–**6**. The phenyl proton resonances of the hydrazido ligands are observed as complex multiplets.

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[44] See refs 7 and 8 and references therein.

[45] Bustos, C.; Carrillo, D.; Robert, F.; Gouzerh, P. To be submitted for publication.

Table 6. Comparison of Structural Features of "End-on" Coordinated Hydrazido(1−) Ligands

compd	bond lengths, Å M–N$_\alpha$	bond lengths, Å N$_\alpha$–N$_\beta$	bond angles, (°) deg M–N$_\alpha$–N$_\beta$	ref
$[Re(NHNHCOPh)(NNHCOPh)Cl_2(PPh_3)_2]$	2.212(8)	1.44(1)	119.5(4)	10–12
$[Re(NHNHCO_2Me)(NNHCOPh)Cl_2(PPh_3)_2]$	2.206(8)	1.441(8)	121.3(5)	12
$[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(PPh_3)_2(CO)](BF_4)$	1.912(10)	1.388(13)	119.1(8)	14
$[Mo(NHNMe_2)(NO)I\{HB(Me_2pz)_3\}]^a$	1.980(17)	1.33(4)	140.3(15)	16
$[Mo(NHNMePh)(NO)I\{HB(me_2pz)_3\}]^a$	1.88(3)	1.34(3)	144(2)	16
$[Re\{NHNMe(C_6H_4Me\text{-}p)\}(Cp)(CO)_2](BF_4)$	1.949(9)	1.32(1)	139.1(7)	19
$[Mo(NHNHCOPh)(NNCOPh)\{SC(Ph)N(Me)O\}_2]$	1.938(4)	1.361(7)	131.9(3)	20
$[Mo(NHNPh_2)(NNPh_2(acac)Cl_2]$	1.948(5)	1.359(6)	140.5(4)	this work
$[Mo(NHNMePh)(NNMePh(acac)Cl_2]$	1.948(2)	1.339(3)	142.9(4)	this work

[a] $HB(Me_2pz)_3$ = tris(3,4-dimethylpyrazolyl)borate.

Table 7. Cyclic Voltammetric Peak Potential Data (V *vs* SCE) in CH_2Cl_2 Solution

compd	E_p, V I$_c$	E_p, V II$_c$	E_p, V I$_a$
1	−1.11	−1.30	1.16
2	−1.08	−1.22	1.19
3	−0.93	−1.07	1.25
4	−1.14	−1.35	1.12
5	−1.13	−1.28	1.13
6	−1.07	−1.18	1.16

The electronic spectra show four absorption bands in the 220–490-nm region. The bands in the 260–350-nm region have been attributed to the [Mo(NNRR′)] chromophore.[46]

Description of the Structures 1 and 4. These compounds crystallize as discrete molecules. Both complexes display similar distorted octahedral geometries. The chloro ligands occupy two *trans*-axial sites while the equatorial positions are occupied by the two *cis*-hydrazido ligands and the oxygen atoms of the chelated acetylacetonato ligand. Although both hydrazido ligands exhibit "end-on" coordination, they are clearly different: location of the hydrogen atom at N clearly shows up the hydrazido(1−) ligand. The Mo–N–N linkages in the hydrazido(2−)molybdenum moieties, $MoNNPh_2$ and MoNNMePh, display almost linear geometries, 171.9(4) and 173.8(2)°, respectively, while the Mo–N bond lengths, 1.752(4) and 1.750(2) Å, and the N–N bond lengths, 1.313(6) and 1.301(3) Å, respectively, indicate an extensive electronic delocalization throughout the fragments. However, the Mo–N–N linkages in the hydrazido(1−)molybdenum moieties, $MoNHNPh_2$ and MoNHNMePh, exhibit the bent "end-on" geometries instead of the more common[3] "side-on" bonding mode. Steric strain has been put forward for complexes containing bulky ligands[3,16] and could also be effective here. The large angles of the Mo–N–N fragments observed in these complexes, 140.5(4) and 142.9(2)°, respectively, are consistent with a such description.[15] Moreover, the Mo–N bond lengths, 1.948(5) and 1.948(2) Å, and the N–N bond lengths, 1.359(6) and 1.339(3) Å, respectively, are intermediate between single and double bonds. These results are consistent with a significant donation of π-bonding electrons from the α-nitrogen atom to the molybdenum center together with some mesomeric electron drift from the β- to the α-nitrogen atoms.[3] Accordingly, the organohydrazido(2−) ligand may be considered formally as a neutral four-electron donor, while the organohydrazido(1−) ligand would be considered formally as a neutral three-electron donor (Chart 1, form **Ib**). In this manner, the molybdenum center in complexes **1**–**6** would attain a 18-electron configuration. A similar conclusion was derived in $[Re\{NHN(Me)C_6H_4Me\text{-}p\}(Cp)(CO)_2][BF_4]$.[19] Table 6 compares the structural features of "end-on" hydrazido(1−) ligands in molybdenum, rhenium, and iridium complexes. In general, the parameters associated with these moieties are similar to those of complexes **1** and **4**, except in the case of the rhenium complexes $[Re(NHNHR)(NNHCOPh)Cl_2(PPh_3)_2]$ (R = PhCO,[10-12] MeOCO[12]). In these complexes the Re–N bond lengths, 2.212(8) and 2.206(8) Å, and N–N bond lengths, 1.44(1) and 1.441(9) Å, respectively, are consistent with both the presence of single bonds with sp^3 hybridation at N$_\alpha$ and N$_\beta$, and the Re–N–N bond angles, 119.5(4) and 121.3(5)°, respectively, are similar.

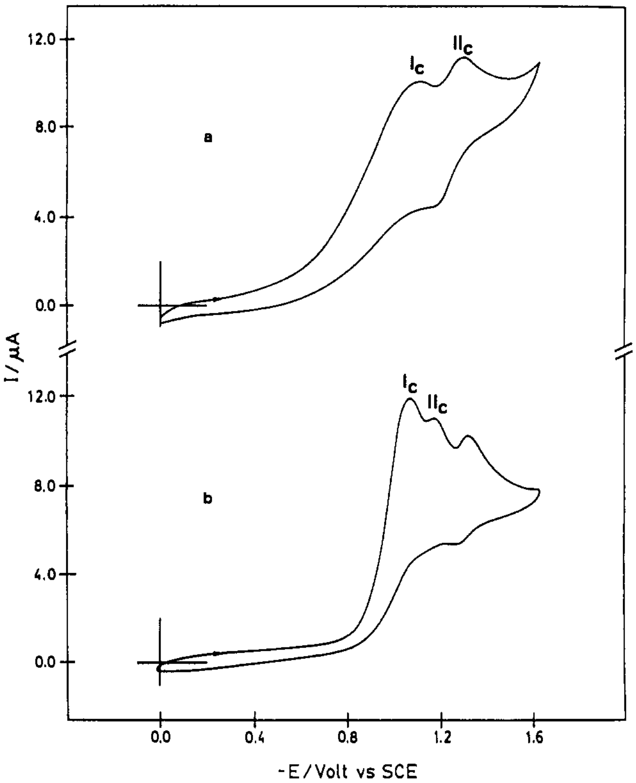

Figure 3. Cyclic voltammograms for the reduction of complexes **1** (a) and **6** (b) in CH_2Cl_2 solution. Concentrations: 2 mM in **1** or **6**; 0.1 M in *n*-Bu_4NPF_6. Scan rate: 0.1 V s^{-1}.

Electrochemical Studies. Cyclic voltammetry (CV) studies of complexes **1**–**6** were carried out in CH_2Cl_2 at a platinum electrode. The CV data are summarized in Table 7 and the voltammograms of complexes **1** and **6** are presented in Figures 3 and 4, respectively. All complexes display two one-electron reduction processes, I$_c$ and II$_c$ in the range from −0.9 to −1.35 V. The first one is irreversible in all cases, while the second appears to be nearly reversible for complexes **1**, **2**, **4**, and **5** according to the peak-to-peak separation (ΔE_p = 90–120 mV) and irreversible for complexes **3** and **6**. The 20-electron species $[Mo(NNPhR)(NHNPhR)(acac)X_2]^{2-}$ generated in the second process should be unstable; its electronic strain could be relieved by elimination of HX or by bending at the inner nitrogen atom of the hydrazido(2−) ligand. Additional cathodic contributions in the CV of the iodo complexes (−1.20 and −1.32 V for **3**; −1.32 V for **6**) might arise from some degradation product of the 20-electron species.

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(46) Shaikh, S. N.; Zubieta, J. *Inorg. Chem.* **1986**, *25*, 4613.

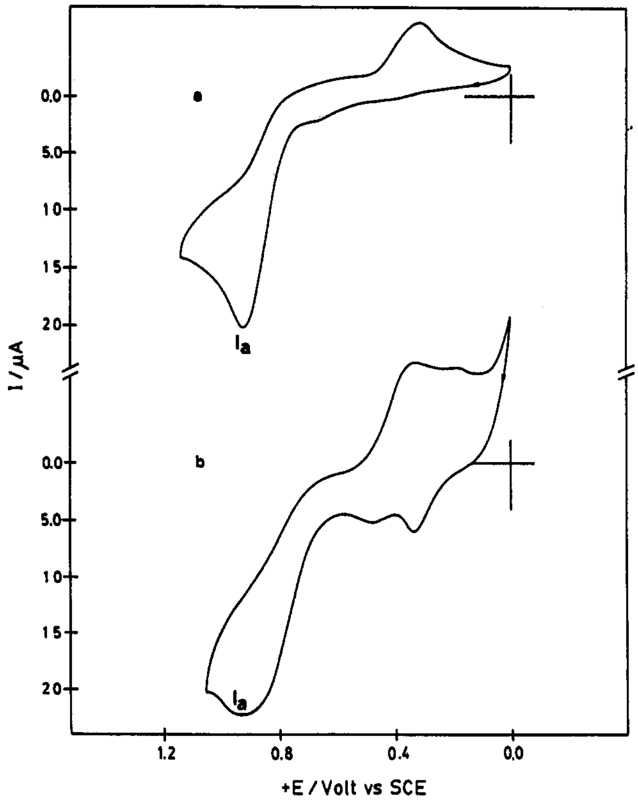

Figure 4. Cyclic voltammograms for the oxidation of complexes **1** (a) and **6** (b) in CH_2Cl_2 solution. Concentrations: 2 mM in **1** or **6**; 0.1 M in *n*-Bu_4NPF_6. Scan rate: 0.1 V s^{-1}.

All complexes exhibit only one irreversible oxidation process (I_a) in the range from +1.12 to +1.25 V. The number of electrons transferred in this process was estimated to be 2 by comparison to the ferrocene oxidation in the same conditions. At least two ill-resolved peaks were observed in the return scan and also appeared in the stabilized E/I profiles. This indicates that [Mo(NHNPhR′)(NNPhR′)(acac)X_2]$^{2+}$, the product of the initial oxidation, is unstable.

The effect of changing R and R′ or X in the CV data of [Mo(NNRR′)(NNRR′)(acac)X_2] shows the expected trend with E less negative (or more positive) in the order R = Me, R′ = Ph < R = R′ = Ph for a given X, and Cl < Br < I. Finally, a plot of II_c *versus* I_a reveals a good correlation of reduction and oxidation potentials. A similar behavior has been observed for the related complexes [Mo(NNRR′)(S_2CNMe_2)$_2$$X_2$] for which it was concluded that the HOMO and LUMO are associated with the Mo(NNRR′) group.[47]

Conclusion. The preparation and characterization of mixed hydrazido(1−)–hydrazido(2−) molybdenum complexes [Mo(NHNRR′)(NNRR′)(acac)X_2] have been described. They offer further examples of the "end-on" ligation of organohydrazido(1−) ligands and provide useful precursors for the synthesis of bis[hydrazido(2−)] complexes.

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Supplementary Material Available: Tables giving crystal data, atomic positional parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and bond lengths and bond angles for compounds 1 and 4 (9 pages). Ordering information is given on any current masthead page.

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[47] Crichton, B. A. L.; Dilworth, J. R.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1981**, 419.