Organometallic Compounds Containing the *cis*-$[MoO(NNPhR)]^{2+}$ Core (R = Me, Ph) – X-ray Structures of $[MoO(NNPh_2)Me_2(o\text{-phen})]$ and $[MoO(NNPh_2)Ph_2(o\text{-phen})]$

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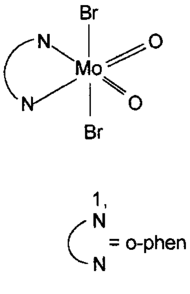
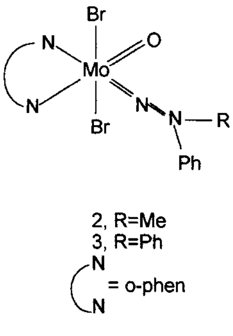
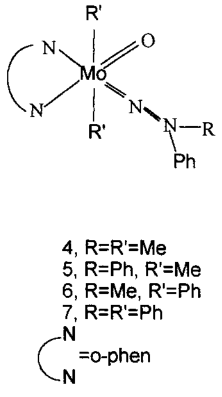
New organometallic compounds containing the *cis*-$[MoO(NNPhR)]^{2+}$ core have been synthesized by means of a two-step procedure involving: (i) functionalization of the precursor $[MoO_2Br_2(o\text{-phen})]$ (**1**) with $MePhNNH_2$ and Ph_2NNH_2 to afford the intermediates $[MoO(NNMePh)Br_2(o\text{-phen})]$ (**2**) and $[MoO(NNPh_2)Br_2(o\text{-phen})] \cdot MeCN$ (**3**), respectively, and (ii) reaction of these intermediates with Grignard reagents to give $[MoO(NNPhR)Me_2(o\text{-phen})]$ [R = Me (**4**), R = Ph (**5**)], $[MoO(NNPhMe)Ph_2(o\text{-phen})]$ (**6**), and $[MoO(NNPh_2)Ph_2(o\text{-phen})] \cdot CH_2Cl_2$ (**7**). These compounds have been characterized by ^1H-NMR, IR, and UV/Vis spectroscopy and the crystal and molecular structures of **5** and **7** have been determined by X-ray diffraction analysis.

Much of the current interest in coordination of the hydrazido ligand, NNH_2, at transition-metal centers stems from the expectation that its geometric and electronic structure, as well as its reactivity, may provide some insight into the mechanism of metal-catalysed reduction of dinitrogen into ammonia.[1−6] Organohydrazido ligands, NNRR′ (RR′ = alkyl and/or aryl; H and alkyl/aryl), are considered as potential models of NNH_2 because of their structural similarities. Accordingly, in the last few years increasing attention has been paid to transition-metal complexes containing NNRR′ ligands and, consequently, several studies have been carried out involving chemical and electrochemical cleavage of the N−N bond,[7−11] *N*-alkylation,[10,12] protonation−deprotonation reactions,[13,14] and hydrolysis of the Mo−NNRR′ group.[15] Very recently, we have studied the electronic structures of hydrazido and organohydrazido ligands using Extended Hückel Molecular Orbital (EHMO) and ab initio calculations, with the aim of resolving uncertainties regarding the assignment of hydrazido(2−) or isodiazene character to NNH_2 and NNRR′ groups (RR′ = alkyl and/or aryl) in coordination compounds.[16]

As part of an ongoing investigation into (organohydrazido)molybdenum complexes, we have previously described the synthesis, characterization, and the chemical properties of a number of inorganic complexes containing the *cis*-$[Mo(NNPhR)_2]^{2+}$ and *cis*-$[MoO(NNPhR)]^{2+}$ cores with a wide range of ancillary ligands, e.g. acetylacetonate,[14,17−21] tertiary phosphanes,[14,21,22] 2,2′-bipyridine,[15] 1,10-phenanthroline,[15] hydridotris(pyrazolyl)borate,[23,24] hydridotris(3,5-dimethylpyrazolyl)borate,[23] and mercaptobenzoate.[25] However, recent work in our laboratories has focused on the synthesis of organometallic molybdenum compounds containing these cores; the new piano-stool compounds formulated as $[(\eta^5\text{-}C_5H_5)Mo(NNPhR)_2(PPh_3)]^+CF_3SO_3^-$ (R = Me, Ph) represent the first two members of this new class of organometallic compounds.[26] This paper deals with a convenient synthesis of the first members of a new class of organometallic molybdenum compounds containing the *cis*-$[MoO(NNPhR)]^{2+}$ core. Functionalization of the novel precursor $[MoO_2Br_2(o\text{-phen})]$ (**1**) with neutral organohydrazines leads to the stable intermediates $[MoO(NNMePh)Br_2(o\text{-phen})]$ (**2**) and $[MoO(NNPh_2)Br_2(o\text{-phen})] \cdot MeCN$ (**3**). Subsequent reaction of these with Grignard reagents affords the organometallic compounds formulated as $[MoO(NNPhR)Me_2(o\text{-phen})]$ [R = Me (**4**), R = Ph (**5**)], $[MoO(NNPhMe)Ph_2(o\text{-phen})]$ (**6**), and $[MoO(NNPh_2)Ph_2(o\text{-phen})] \cdot CH_2Cl_2$ (**7**). We also report the X-ray crystal and molecular structures of compounds **5** and **7**.


1,


2, R=Me
3, R=Ph


4, R=R′=Me
5, R=Ph, R′=Me
6, R=Me, R′=Ph
7, R=R′=Ph

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Results and Discussion

The preparations of the organometallic compounds **4**−**7** were carried out starting from the inorganic precursor [MoO_2Br_2(*o*-phen)] (**1**), according to a two-step procedure: (i) functionalization of complex **1** with neutral 1,1-disubstituted hydrazines, $PhRNNH_2$ (R = Me, Ph), to obtain the inorganic intermediates [MoO(NNMePh)Br_2(*o*-phen)] (**2**) and [MoO($NNPh_2$)Br_2(*o*-phen)] · MeCN (**3**), and (ii) reaction of the intermediate complexes **2** and **3** with Grignard reagents R′MgBr (R′ = Me, Ph), to afford the organometallic compounds formulated as [MoO(NNPhR)Me_2(*o*-phen)] [R = Me (**4**), R = Ph (**5**)], [MoO(NNMePh)Ph_2(*o*-phen)] (**6**), and [MoO($NNPh_2$)Ph_2(*o*-phen)] · CH_2Cl_2 (**7**).

Precursor **1** was synthesized in excellent yield (86%) by oxidation of [$Mo(CO)_6$] with bromine in the presence of 1,10-phenanthroline, using a mixture of CH_2Cl_2/EtOH (1:1) as solvent (for further details, see Experimental Section). This one-pot procedure, developed in our laboratories, is essentially a modification of that described in the literature for obtaining [MoO_2Br_2(bpy)][27] (bpy = 2,2′-bipyridine) through: (i) photochemical reaction of [$Mo(CO)_6$] with bpy in hexane[28] to generate the precursor [$Mo(CO)_4$(bpy)], and (ii) oxidation of this precursor with an excess of bromine in CH_2Cl_2/EtOH (1:1).

Step 1. Synthesis and Characterization of the Intermediate Complexes [MoO(NNMePh)Br_2(*o*-phen)] (2) and [MoO($NNPh_2$)Br_2(*o*-phen)]·MeCN (3)

The syntheses of complexes **2** and **3** were performed in acetonitrile by reaction of precursor **1** with the neutral 1,1-disubstituted hydrazines $PhRNNH_2$ (R = Me, Ph), respectively, in a 1:2 molar ratio (Equation 1).

$$[MoO_2Br_2(o\text{-phen})] + PhRNNH_2 \rightarrow [MoO(NNPhR)Br_2(o\text{-phen})] + H_2O \quad (1)$$

We have found that the use of an excess of organohydrazine in these reactions does not lead to the bis(organohydrazido) complexes, but rather the yields of **2** and **3** are increased somewhat. We have observed that in similar molybdenum complexes the *cis*-$[Mo(NNPhR)_2]^{2+}$ group undergoes hydrolysis with loss of one NNPhR ligand if water is present.[15] As is apparent from Equation 1, the formation of the *cis*-$[MoO(NNPhR)]^{2+}$ group is accompanied by the elimination of one water molecule.

Complexes **2** and **3** were obtained as orange, air-stable crystalline solids in yields of 91% and 80%, respectively, and were characterized by ^{1}H-NMR, IR, and UV/Vis spectroscopy (see Experimental Section). The ^{1}H-NMR spectra of both complexes feature a complex multiplet in the range $\delta = 6.85-10.20$, attributable to the phenyl and phenanthroline proton resonances. The spectrum of complex **2** containing the NNMePh ligand, which had to be recorded in [D_6]DMSO solution owing to the low solubility of this complex in $CDCl_3$, CD_3COCD_3, and CD_3NO_2, exhibits three proton resonances in the region $\delta = 3.65-4.50$. These resonances may be attributed to the unmodified complex, [MoO(NNMePh)Br_2(*o*-phen)], and the cationic species $[MoO(NNMePh)Br(Me_2SO)(o\text{-phen})]^+$ and $[MoO(NNMePh)(Me_2SO)_2(o\text{-phen})]^{2+}$, formed by successive substitutions of the Br^- ligands by Me_2SO solvent molecules.

Step 2. Synthesis and Characterization of the Organometallic Compounds [MoO(NNPhR)Me_2(*o*-phen)] [R = Me (4), R = Ph (5)], [MoO(NNMePh)Ph_2(*o*-phen)] (6), and [MoO($NNPh_2$)Ph_2(*o*-phen)]·CH_2Cl_2 (7)

The syntheses of the organometallic compounds **4**−**7** were carried out at 0°C in dry THF by reaction of the inorganic intermediates **2** and **3** with the corresponding Grignard reagents, R′MgBr (R′ = Me, Ph; Equation 2). Under the experimental conditions used, an excess of the Grignard reagent was added to the solution in order to solubilize the inorganic intermediates **2** and **3**.

$$[MoO(NNPhR)Br_2(o\text{-phen})] + 2R'MgBr \rightarrow [MoO(NNPhR)R'_2(o\text{-phen})] + 2MgBr_2 \quad (2)$$

Compounds **4**, **5** and **7** were obtained in yields of 41−80%, while compound **6** was isolated in only 17% yield. All compounds were obtained as orange, air-stable crystalline solids, and were characterized by ^{1}H-NMR, IR, and UV/Vis spectroscopy. The ^{1}H-NMR spectra each feature a complex multiplet in the range $\delta = 6.65-10.15$, attributable to the phenyl proton resonances of the NNMePh ligand and the proton resonances of the *o*-phenanthroline ligand. The spectra of compounds **6** and **7** are more complicated than those of **4** and **5** owing to the proton resonances of the phenyl ligands bonded to the molybdenum center in *trans* positions (vide infra). The spectra of compounds **4** and **6** also feature methyl proton resonances due to the NNMePh ligand at $\delta = 4.00$ and $\delta = 4.23$, respectively. In addition, the spectra of **4** and **5** exhibit methyl proton resonances at $\delta = 0.17$ and $\delta = 0.19$, attributable to the methyl ligands bonded to the molybdenum center in *trans* positions. The spectrum of compound **7**, which crystallizes with a CH_2Cl_2 solvent molecule, exhibits a methylene proton resonance at $\delta = 5.30$.

Structural Results

ORTEP drawings of [MoO($NNPh_2$)Me_2(*o*-phen)] (**5**) and [MoO($NNPh_2$)Ph_2(*o*-phen)] (**7**), in similar perspectives for the sake of comparison, are presented in Figures 1 and 2. In both compounds, the molybdenum center displays distorted octahedral geometry, with the two methyl and two phenyl ligands occupying mutually *trans* positions, and with the equatorial plane being defined by the oxo group, the N(1) and N(2) atoms of the *o*-phenanthroline, and the N(3) atom of the organohydrazido ligand. The geometric parameters observed in the *cis*-$[MoO(NNPhR)]^{2+}$ cores of these compounds are quite similar to those reported in the literature for other (organohydrazido)oxomolybdenum complexes.[16,29] An extensive delocalization of the electron density throughout the Mo($NNPh_2$) units is supported by (i) the short Mo−N(3) and N(3)−N(4) bond lengths of 1.770(3) and 1.330(4) Å in **5**, and of 1.770(6) and 1.307(9) Å in **7**; (ii) the almost linear Mo−N(3)−N(4) bond angles of 171.7(2)° and 173.6(5)° in **5** and **7**, respectively, and (iii) the almost planar Mo−N(3)−N(4)C(31)C(41) moiety, the sum of the bond angles about N(4) being 358.7(3)° and 360.0(5)° in **5** and **7**, respectively. On the other hand, the Mo−O bond lengths of 1.711(2) and 1.711(4) Å in **5** and **7**, respectively, fall within the normal range[29] and, in line with expectation,[15] the *trans* influence exerted by this group is clearly far more important than that exerted by the organohydrazido ligands, e.g. Mo−N(2) = 2.361(3) Å vs. Mo−N(1) = 2.302(3) Å for **5**, and Mo−N(2) = 2.368(5) Å vs. Mo−N(1) = 2.302(6) Å for **7**. Finally, one more salient feature of the structures of these compounds is the preferential inclination of the two methyl (**5**) and the two phenyl (**7**) ligands toward the N(2) atom of the *o*-phenanthroline ligand; thus, in **5** the C(51)−Mo−N(2) and C(61)−Mo−N(2) bond angles are 74.5(1) and 76.1(1)° while the C(51)−Mo−N(1) and C(61)−Mo−N(1) bond angles are 84.7(1) and 79.8(1)°; likewise, in **7** the C(51)−Mo−N(2) and C(61)−Mo−N(2) bond angles are 76.7(2) and 78.6(2)° while the C(51)−Mo−N(1) and C(61)−Mo−N(1) bond angles are 89.5(2) and 81.5(2)°. These differences can most probably be ascribed to repulsions between the methyl and phenyl ligands and the oxo group. As a further consequence of these repulsions, the C(51)−Mo−C(61) bond angles are 149.9(1) and 155.3(2)° in compounds **5** and **7**, respectively. For comparison purposes, it is noteworthy that the methyl and *p*-anisyl ligands in the related organometallic compounds $[MoO_2R_2(bpy)]$ (R = Me,[30] C_6H_4OMe[31]) are also bent toward the midpoint of the N,N vector of the bpy ligand, the C−Mo−C bond angles in these cases amounting to 149.03(10) and 153.6(1)°, respectively. On the other hand, in the related inorganic complexes $[MoO(NNPh_2)Cl_2(o\text{-phen})]$ and $[MoO(NNPh_2)Cl_2(bpy)]$, this folding effect is less pronounced and the Cl−Mo−Cl bond angles are found to be 161.5(1)° and 160.2(1)°, respectively.[15]

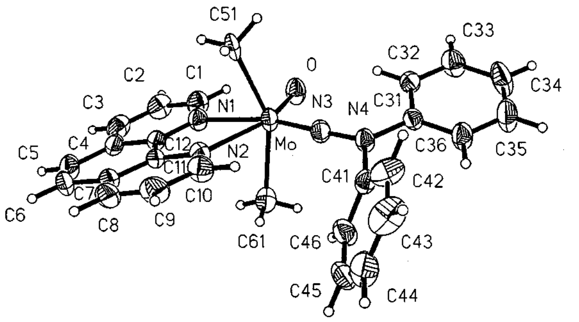

Figure 1. Molecular structure of compound **5** with thermal ellipsoids drawn at a 40% probability level; selected bond lengths (Å) and angles (°): Mo−O 1.711(2), Mo−N(1) 2.302(3), Mo−N(2) 2.361(3), Mo−N(3) 1.770(3), Mo−C(51) 2.331(3), Mo−C(61) 2.226(4), N(3)−N(4) 1.330(4); Mo−N(3)−N(4) 171.7(2), N(3)−N(4)−C(31) 119.4(2), N(3)−N(4)−C(41) 117.5(3), C(31)−N(4)−C(41) 121.8(3), C(51)−Mo−C(61) 149.9(1)

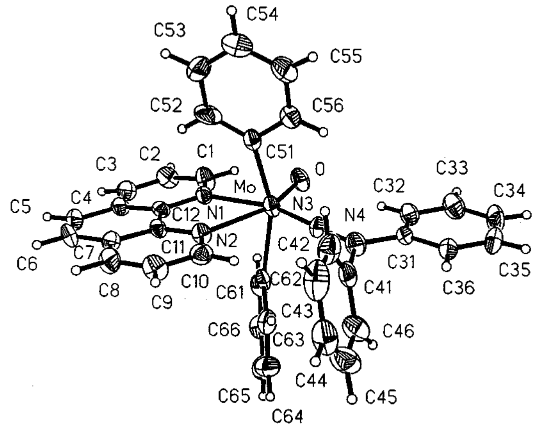

Figure 2. Molecular structure of compound **7** with thermal ellipsoids drawn at a 40% probability level; selected bond lengths (Å) and angles (°): Mo−O 1.711(4), Mo−N(1) 2.302(6), Mo−N(2) 2.368(5), Mo−N(3) 1.770(6), Mo−C(51) 2.240(7), Mo−C(61) 2.220(8), N(3)−N(4) 1.307(9); Mo−N(3)−N(4) 173.6(5), N(3)−N(4)−C(31) 121.3(5), N(3)−N(4)−C(41) 119.1(5), C(31)−N(4)−C(41) 119.6(6), C(51)−Mo−C(61) 155.3(2)

With reference to our recent study concerned with molecular orbital analysis of hydrazido(2−)−metal bonding in coordination chemistry,[16] if formally considered as a dianion, the hydrazido ligand represents a six-electron donor when it is coordinated in a linear mode in monohydrazido complexes. Accordingly, the molybdenum center in the organometallic compounds described herein attains an 18-electron configuration.

Conclusion

The present study highlights the potential utility of the new inorganic precursor $[MoO_2Br_2(o\text{-phen})]$ (**1**) for the preparation of organometallic *trans*-dialkyl and *trans*-diaryl compounds containing the *cis*-[MoO(NNPhR)]$^{2+}$ core, where R = Me, Ph. The readiness with which the *cis*-MoO_2^{2+} fragment can be monofunctionalized with neutral 1,1-disubstituted hydrazines opens a facile synthetic route for the preparation of stable inorganic intermediates, further reaction of which with Grignard reagents, as in the present investigation, allows access to organometallic compounds formulated as $[MoO(NNPhR)Me_2(o\text{-phen})]$ and $[MoO(NNPhR)Ph_2(o\text{-phen})]$ (R = Me, Ph). These derivatives containing the *cis*-[MoO(NNPhR)]$^{2+}$ core represent the first members of a new class of organometallic molybdenum compounds, the chemical and electrochemical properties of which, associated with cleavage of the N−N bond, will be the subject of further investigations in our laboratories.

Experimental Section

General: All operations were performed under inert atmosphere using standard vacuum/nitrogen line (Schlenk) techniques. Hexacarbonylmolybdenum, bromine, 1-methyl-1-phenylhydrazine, 1,1-

diphenylhydrazine hydrochloride, methylmagnesium bromide (3.3 M in diethyl ether), phenylmagnesium bromide (0.79 M in THF), and 1,10-phenanthroline, were purchased from commercial sources and used as received. Solvents were dried and distilled under nitrogen by standard methods prior to use. − Microanalytical data were obtained with a Perkin-Elmer Model 2400 elemental analyzer. − IR spectra were obtained from KBr disks with a Perkin-Elmer Model 1600 FT-IR spectrophotometer. − Electronic spectra were recorded in CH_2Cl_2 solutions with a Hewlett Packard 8452A spectrophotometer. − ^{1}H-NMR spectra were recorded in $CDCl_3$ or $[D_6]$DMSO with a Bruker FT AC/200P spectrometer; chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonances as internal standards. − Melting points were determined using a Kofler apparatus.

Preparation of [MoO$_2$Br$_2$(*o*-phen)] (1): To a vigorously stirred solution of $[Mo(CO)_6]$ (3.95 g, 15.0 mmol) and 1,10-phenanthroline (2.70 g, 15.0 mmol) in 200 mL of CH_2Cl_2/EtOH (1:1), excess bromine was added dropwise. Following the addition, the mixture was warmed to 40°C and stirred for 45 min, whereupon a microcrystalline orange solid was deposited. The crude material was filtered off, washed with diethyl ether, dried in vacuo, and finally recrystallized from CH_3CN. Yield before recrystallization: 6.04 g (86%), m.p. 195°C (dec.). − $C_{12}H_8Br_2MoN_2O_2$ (467.96): calcd. C 30.80, H 1.72, N 5.99; found C 29.83, H 1.76, N 5.89. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 266 nm (4.47). − IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1} (vw), ν(CH); 2921 (vw), ν(CH); 2818 (vw), ν(CH); 935 (vs) and 901 (vs), ν(MoO_2). − ^{1}H NMR ($CDCl_3$): δ = 9.90 (dd, 2 H, $^3J_{HH}$ = 8.2 Hz), 8.67 (dd, 2 H, $^3J_{HH}$ = 4.9 Hz), 8.12 (s, 2 H), 8.06 (dd, 2 H, $^3J_{HH}$ = 1.4 Hz).

Preparation of [MoO(NNMePh)Br$_2$(*o*-phen)] (2): To 1.83 g (3.91 mmol) of **1**, dissolved in 180 mL of acetonitrile, was added 0.96 g (7.82 mmol) of 1-methyl-1-phenylhydrazine, $MePhNNH_2$. The mixture was stirred vigorously under reflux for 2 h, in the course of which a microcrystalline solid was deposited. The pink solid was filtered off, washed with acetonitrile and diethyl ether, and dried in vacuo. Yield 2.04 g (91%), m.p. 315°C (dec.). − $C_{19}H_{16}Br_2MoN_4O$ (572.11): calcd. C 39.89, H 2.81, N 9.79; found C 38.66, H 2.70, N 9.76. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 535 (4.13), 388 (4.60), 298 sh (5.13), 276 (5.40). − IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1} (w), ν(CH); 2932 (w), ν(CH); 2856 (vw), ν(CH); 1583 (m), ν(NN); 902 (s), ν(MoO). − ^{1}H NMR ($[D_6]$DMSO): δ = 10.17−6.87 (m, 13 H, $C_{12}H_8N_2$ and C_6H_5), 4.47, 4.42, 3.67 (s, 3 H, CH_3).

Preparation of [MoO(NNPh$_2$)Br$_2$(*o*-phen)]·MeCN (3): The procedure adopted was similar to that described for **2**, using in this case 1.34 g (6.08 mmol) of 1,1-diphenylhydrazine hydrochloride, $Ph_2NNH_3^+Cl^-$, previously neutralized with triethylamine, and 1.42 g (3.04 mmol) of **1**. The product was obtained as a red microcrystalline solid. Yield 2.16 g (80%), m.p. 290°C. − $C_{26}H_{21}Br_2MoN_5O$ (675.23): calcd. C 46.25, H 3.13, N 10.37; found C 46.44, H 3.10, N 9.38. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 520 nm (3.28), 388 (3.70), 298 sh (4.19), 278 (4.48). − IR (KBr): $\tilde{\nu}$ = 3044 cm^{-1} (w), ν(CH); 2922 (vw), ν(CH); 2856 (vw), ν(CH); 1585 (m), ν(NN); 899 (s), ν(MoO). − ^{1}H NMR ($CDCl_3$): δ = 10.19−6.99 (m, 18 H, $C_{12}H_8N_2$ and 2 C_6H_5 hydrazido), 2.01 (s, 3 H, CH_3CN).

Preparation of [MoO(NNMePh)Me$_2$(*o*-phen)] (4): To 0.30 g (0.52 mmol) of **2** suspended in 20 mL of dry THF at 0°C, 0.38 g (3.15 mmol) of methylmagnesium bromide in Et_2O was added dropwise. After stirring for 1 h, the reaction mixture was allowed to warm to room temperature and then concentrated to dryness in vacuo. The residue was partitioned between 20 mL of CH_2Cl_2 and 20 mL of saturated aqueous ammonium chloride solution, the aqueous phase was extracted with further CH_2Cl_2, and the combined organic extracts were dried with magnesium sulfate. After concentrating the dried extract to a volume of 10 mL, it was allowed to stand at −18°C, resulting in the deposition of an orange microcrystalline solid. This was filtered off, washed with diethyl ether, dried in vacuo, and finally recrystallized from CH_2Cl_2 layered with diethyl ether. Yield before recrystallization: 0.094 g (41%), m.p. 173°C. − $C_{21}H_{22}MoN_4O$ (442.37): calcd. C 56.96, H 4.97, N 12.65; found C 56.11, H 5.09, N 12.19. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 380 nm br (3.83), 326 (4.24), 270 (4.60). − IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1} (w), ν(CH); 2945 (m), ν(CH); 2878 (w), ν(CH); 1592 (s), ν(NN); 886 (vs), ν(MoO). − ^{1}H NMR ($CDCl_3$): δ = 10.17−6.97 (m, 13 H, $C_{12}H_8N_2$ and C_6H_5 hydrazido), 4.00 (s, 3 H, CH_3 hydrazido), 0.17 (s, 6 H, $2CH_3$).

Preparation of [MoO(NNPh$_2$)Me$_2$(*o*-phen)] (5): The synthesis of this yellow crystalline complex was carried out using a procedure similar to that described for complex **4**, adding in this case 0.56 g (4.66 mmol) of methylmagnesium bromide to 0.49 g (0.73 mmol) of **3** in 20 mL of dry THF. Suitable single crystals for X-ray diffraction studies were obtained from CH_2Cl_2 layered with diethyl ether. Yield 0.58 g (80%), m.p. 215°C. − $C_{26}H_{24}MoN_4O$ (504.44): calcd. C 61.91, H 4.80, N 11.11; found C 61.22, H 4.70, N 10.98. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 380 nm br. (4.32), 310 (4.92), 270 (5.32). − IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1} (vw), ν(CH); 2951 (w), ν(CH); 2889 (w), ν(CH); 1586 (m), ν(NN); 892 (vs), ν(MoO). − ^{1}H NMR ($CDCl_3$): δ = 10.20−7.20 (m, 18 H, $C_{12}H_8N_2$ and 2 C_6H_5 hydrazido), 0.19 (s, 6 H, 2 CH_3).

Preparation of [MoO(NNMePh)Ph$_2$(*o*-phen)] (6): To 0.31 g (0.54 mmol) of **2**, dissolved in 20 mL of dry THF, 0.59 g (3.20 mmol) of phenylmagnesium bromide in THF was added dropwise. After stirring for 1 h at 0°C, the reaction mixture was allowed to warm to room temperature and then concentrated to dryness in vacuo. The residue was partitioned between 20 mL of CH_2Cl_2 and 20 mL of saturated aqueous ammonium chloride solution. The CH_2Cl_2 solution containing the product was dried with magnesium sulfate and concentrated to a volume of 10 mL. On leaving the concentrated solution to stand at −18°C, a brown crystalline solid was deposited, which was filtered off, washed with diethyl ether, and dried in vacuo. Yield 0.052 g (17%), m.p. 165°C. − $C_{31}H_{26}MoN_4O$ (566.51): calcd. C 65.73, H 4.63, N 10.07; found C 64.85, H 4.48, N 9.82. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 420 nm br. (4.27), 334 (4.90), 270 (5.33). − IR (KBr): $\tilde{\nu}$ = 3041 cm^{-1} (w), ν(CH); 2964 (vw), ν(CH); 2922 (vw), ν(CH); 1592 (m), ν(NN); 896 (s), ν(MoO). − ^{1}H NMR ($CDCl_3$): δ = 10.48−6.67 (m, 23 H, $C_{12}H_8N_2$, C_6H_5 hydrazido and 2 C_6H_5), 4.23 (s, 3 H, CH_3 hydrazido).

Preparation of [MoO(NNPh$_2$)Ph$_2$(*o*-phen)]·CH$_2$Cl$_2$ (7): This yellow crystalline complex was synthesized according to the procedure described above, adding in this case 1.08 g (5.95 mmol) of phenylmagnesium bromide to 0.31 g (0.46 mmol) of **3** in 20 mL of dry THF. Suitable single crystals for X-ray diffraction studies were obtained from CH_2Cl_2 layered with hexane. Yield before recrystallization: 0.22 g (67%), m.p. 185°C. − $C_{37}H_{30}Cl_2MoN_4O$ (713.52): calcd. C 62.28, H 4.24, N 7.85; found C 61.46, H 4.23, N 7.99. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 368 nm br. (4.07), 332 (4.45), 256 (4.75). − IR (KBr): $\tilde{\nu}$ = 3047 cm^{-1} (w), ν(CH); 3000 (vw), ν(CH); 2956 (vw), ν(CH); 1586 (m), ν(NN); 889 (vs), ν(MoO). − ^{1}H NMR ($CDCl_3$): δ = 10.52−6.68 (m, 28 H, $C_{12}H_8N_2$, 2 C_6H_5 hydrazido and 2 C_6H_5), 5.30 (s, 2 H, CH_2Cl_2).

X-ray Structure Determination for 5: $C_{26}H_{24}MoN_4O$, M_r = 504.4 g mol^{-1}, unit cell dimensions: a = 9.346(2), b = 20.936(4), c = 12.389(2) Å, β = 106.26(2)°, V = 2327(1) Å^3, monoclinic, $P2_1/n$, Z = 4, $D_{calcd.}$ = 1.440 g cm^{-3}, μ(Mo-K_α) = 0.589 mm^{-1}, F(000) =

Table 1. Crystal data for [MoO(NNPh$_2$)Me$_2$(*o*-phen)] (**5**) and [MoO(NNPh$_2$)Ph$_2$(*o*-phen)]·CH$_2$Cl$_2$ (**7**)

	5	**7**
Empirical formula	$C_{26}H_{24}MoN_4O$	$C_{37}H_{30}Cl_2MoN_4O$
Crystal size [mm]	0.50 × 0.28 × 0.20	0.20 × 0.18 × 0.06
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	9.346(2)	11.951(2)
b [Å]	20.936(4)	19.850(3)
c [Å]	12.389(3)	14.135(2)
β [°]	106.26(2)	100.97(1)
Volume [Å^3]	2327(1)	3292(1)
Z	4	4
Molecular mass	504.4	713.5
Density (calcd.) [Mg/m^3]	1.440	1.440
F(000)	1032	1456
Absorption coefficient [mm^{-1}]	0.589	0.597
max./min. transmission factors	0.6708/0.5782	0.9518/0.9053
Reflections collected	4338	4562
2θ range [°]	3 → 50	3 → 45
Index ranges	$0 \le h \le 11$	$0 \le h \le 12$
	$0 \le k \le 24$	$0 \le k \le 21$
	$-14 \le l \le 14$	$-15 \le l \le 14$
Independent reflections	4077	4324
R_{int}	0.0245	0.0229
Observed reflections [$F > 4\sigma(F)$]	3435	2261
Weighting scheme g [$w^{-1} = \sigma^2(F) + gF^2$]	0.0014	0.0006
Number of parameters refined	289	406
Final R indices [R/(obsd. data) wR]	0.0355/0.0526	0.0387/0.0378
Goodness-of-fit S	1.19	0.81
Residual ρ_{max}/ρ_{min} [eÅ^{-3}]	0.70/−0.34	0.32/−0.31

1032, crystal size [mm]: 0.50 × 0.28 × 0.20. Siemens R3m/V four-circle diffractometer; Mo-K_α radiation (λ = 0.71073, graphite monochromator), 2θ range 3.0−50.0° at 298 K, scan type θ-2θ, reflections collected 4338, independent reflections 4077 (R_{int} = 2.45%), observed reflections 3435 [$F > 4.0\sigma(F)$]. Convergence at R = 0.0355, R_w = 0.0526, $w^{-1} = \sigma^2(F) + gF^2$. Cell parameters were determined from least-squares fits of 25 reflections with 15° ≤ 2θ ≤ 30°. Two standard reflections, monitored every 98 reflections, showed no significant variation of intensity during data collection. Intensities were corrected for Lorentz and polarization effects, and semiempirical corrections based on ψ scans were applied for absorption.

X-ray Structure Determination for 7: $C_{37}H_{30}Cl_2MoN_4O$, M_r = 713.5 g mol^{-1}, unit cell dimensions: a = 11.951(2), b = 19.850(3), c = 14.135(2) Å, β = 100.97(1)°, V = 3292(1) Å^3, monoclinic, $P2_1/n$, Z = 4, $D_{calcd.}$ = 1.440 g cm^{-3}, μ(Mo-K_α) = 0.597 mm^{-1}, F(000) = 1456, crystal size [mm]: 0.20 × 0.18 × 0.06. Siemens R3m/V four-circle diffractometer; Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator), 2θ range 3.0−45.0° at 298 K, scan type θ-2θ, reflections collected 4562, independent reflections 4324 (R_{int} = 2.29%), observed reflections 2261 [$F > 4.0\sigma(F)$]. Convergence at R = 0.0387, R_w = 0.0378, $w^{-1} = \sigma^2(F) + gF^2$. Cell parameters were determined from least-squares fits of 30 reflections with 15° ≤ 2θ ≤ 30°. Two standard reflections, monitored every 98 reflections, showed no significant variation of intensity during data collection. Intensities were corrected for Lorentz and polarization effects, and semiempirical corrections based on ψ scans were applied for absorption.

Both structures were solved by direct methods and refined on F by full-matrix least-squares calculations (see Table 1). The function minimized was $\Sigma w(F_o - F_c)^2$. All non-H atoms were refined anisotropically. A riding model was applied to H atoms, which were 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.[32] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102552 (**5**) and -102553 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int. code) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

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