# Reactions of Dioxo[N-(salicylidene)-2-aminophenolato-N,O,O'](hexamethylphosphoramide)molybdenum(VI) Complexes with Substituted Hydrazines and Chemistry of Molybdenum(VI)-Hydrazido Complexes

Mikael Retbøll, Eval Rud Møller, Rita G. Hazell and Karl Anker Jørgensen[†]

Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

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The reaction of dioxo[N-(salicylidene)-2-aminophenolato-N,O,O'](hexamethylphosphoramide)molybdenum(VI), **4a**, and its C-imine substituted derivatives, **4b,c** with different mono- and di-substituted hydrazines has been investigated. The reaction of **4a** with 1,1-dimethylhydrazine leads to decomposition of the complex. When complex **4b** is treated with 1,1-dimethylhydrazine an $\eta^1$-coordinated hydrazido(2 – ) molybdenum complex, **8a**, is formed. The 2-aminophenolato-N,O ligand present in **8a** originates from cleavage of the salicylidene ligand in **4b**. The structure of **8a** is determined by an X-ray crystallographic investigation. The electronic structure of **4b** and **8a** is investigated using extended Hückel calculations and based on the results for **4a**, a mechanism for the formation of **8a** is postulated. The chemical properties of **8a** are discussed on the basis of its electronic structure. A general method for the preparation of a series of complexes similar to **8a** has been developed. A minor product is also formed in the reaction of methylhydrazine with **4b** and the possible structures of this complex are discussed; it is postulated that the hydrazido ligand in this complex might coordinate to the molybdenum atom in an $\eta^2$-fashion. The chemical properties of the $\eta^1$-coordinated hydrazido(2 – ) molybdenum complex, **8a**, have been investigated and reactions with e.g. hydrogen chloride, dimethyl sulfate, benzaldehyde and benzoyl chloride have been performed.

One of the fundamental processes in nature is the reduction of molecular nitrogen by the nitrogenase enzymes.[1] As molecular nitrogen is exceedingly unreactive, the understanding of the enzymatic activation has been, and still is, a great challenge to chemists.[1] In an attempt to gain insight into the chemistry of the enzymatic activation of molecular nitrogen, several transition-metal complexes resembling the enzymatic system have been prepared.[1] The metals in these complexes have various oxidation states, and different nitrogen fragments are coordinated, bound through single or multiple bonds to the metal centre.[2]
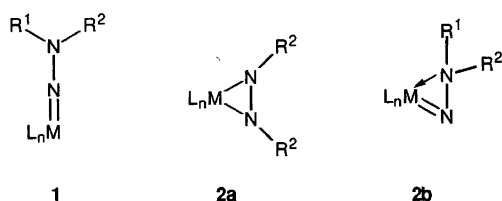
The enzymatic reduction of molecular nitrogen producing ammonia is generally accepted to be a stepwise reduction/protonation reaction,[1,3] in which the most likely intermediate dinitrogen ligands are dinitrogen (NN),

diazenido (NNR), diazeno (RNNR), hydrazido(2 – ) (NNR₂), hydrazido(1 – ), (NRNR₂) and hydrazino (R₂NNR₂) (where R signifies an organic group or a hydrogen atom).[3] It is believed that molybdenum is an important part of the active site in the nitrogenase enzyme.[1e] Therefore the dinitrogen ligands above have been especially studied in connection with the group-VI transition metals molybdenum and tungsten.

One class of dinitrogen ligands which has gained attention is hydrazido(2 – ), as these, by interaction with a transition metal, resemble some of the final steps in the proposed enzymatic reduction of molecular nitrogen to ammonia.[1,3] The main subject in these studies has been the structural determination of these complexes,[4,5] whereas their chemistry has received less attention. The structural reports have revealed, that the hydrazido(2 – ) ligand can bind to a transition metal in two ways, either end-on, as an $\eta^1$-ligand, **1**, or side-on, as an $\eta^2$-ligand,

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[†] Author to whom correspondence should be addressed.

**2a,b.** The latter types are, in principle, a metal diazeno- and a hydrazido complex, **2a** and **2b**, respectively.



1          2a          2b



3a: $R^1$ = H          4a: $R^1$ = H
3b: $R^1$ = Me          4b: $R^1$ = Me
3c: $R^1$ = Ph          4c: $R^1$ = Ph

Molybdenum and tungsten complexes of type **1** and **2** can be prepared by different procedures: reaction of molybdenum and tungsten complexes with the metal in different oxidation states, with molecular nitrogen combined with protonation and reduction[4a–g,t,5a,b] or by reaction with hydrazines,[4g–q,5a,e] diazonium salts,[5n] or azo compounds.[4y]
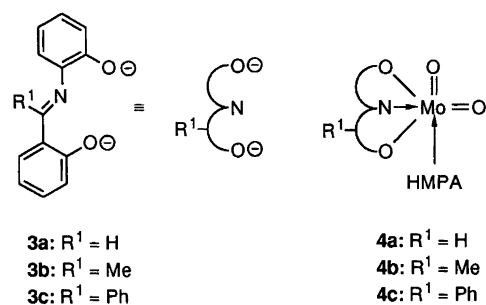
The vast majority of structurally characterised molybdenum hydrazido(2 − ) complexes are of type **1**,[4a–x] and according to our knowledge only few examples of type **2a,b** complexes containing molybdenum have been assigned.[4y,u] For the tungsten hydrazido(2 − ) complexes the structures are predominantly **1**, but a few examples of **2a,b** have been characterised.[5p–r] Chemical knowledge of the molybdenum- and tungsten hydrazido(2 − ) complexes **1** and **2a,b** is very limited: protonation reactions have been investigated,[4a–c,z,aa,5a,e] and recently alkylation reactions have also been studied.[4g]

This paper presents new chemical information on molybdenum hydrazido(2 − ) complexes: First the reactions of dioxo[$N$-(salicylidene)-2-aminophenolato-$N,O,O'$]-(hexa-methylphosphoramide)molybdenum(VI), **4a**, and its $C$-imine substituted derivatives, **4b,c**, with various mono-, 1,1- and 1,2-disubstituted hydrazines forming hydrazido(2 − ) complexes are presented. This is followed by the presentation of an investigation of the chemical properties of some of the molybdenum hydrazido(2 − ) products.

ligand **3a**, followed by a decomposition of the molybdenum complex (*vide infra*).



6a

However, treatment of complex **4b**, where the imino carbon atom is methyl substituted, with 1,1-dimethylhydrazine, **5a**, in $CH_2Cl_2$ led to the reaction of eqn. (1).

Complex **8a** was isolated in 31% yield and characterised by spectroscopic methods and X-ray structural determination (*vide infra*). It was also observed that treatment of **4c** with **5a** or 1-methyl-1-phenylhydrazine, **5b**, led to a similar type of reaction, but in these cases **8e** and **8f** were isolated in 15% and <5% yields, respectively. These low yields are probably due to the presence of the phenyl substituent in **4c**, which might cause more steric hindrance compared with the methyl substituent in **4b**.

Because of the unexpected product in eqn. (1) the crystal structure of **8a** was determined (see the Experimental section). The crystal structure of **8a** is shown in Fig. 1. Table 1 gives the crystallographic data for the X-ray diffraction study of **8a**, while Table 2 presents some selected bond lengths and bond angles for **8a**.
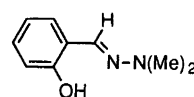
## Results and discussion

The dioxo molybdenum complexes, **4a–c**, which are the starting compounds for the present study, are prepared in good yields by reaction of $Mo(O)_2(acac)_2$ with hexamethylphosphoramide (HMPA) and $N$-(salicylidene)-2-aminophenol, **3a**, (often referred to as the SAP-ligand) or its $C$-imine substituted derivatives, **3b,c**. For further details see the Experimental section.

Treatment of complex **4a** with 1,1-dimethylhydrazine, **5a**, caused the cleavage of the imine bond of ligand **3a** rather than reaction at the molybdenum centre. The main detectable products were the hydrazone (>60% yield), **6a**, 2-aminophenol, **7**, and some unidentified molybdenum complexes. The formation of **6a** takes place by a nucleophilic attack of **5a** on the imine carbon atom in



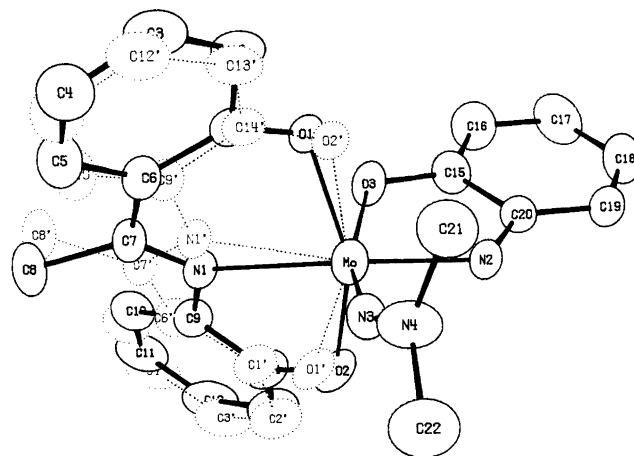*Fig. 1.*

Table 1. Crystallographic data for (mer-2-[1-(2-oxo-phenyliminato)ethyl]phenolato-N,O,O')(2-aminophenolato-O,N)(N,N-dimethylhydrazido)molybdenum(VI), **8a**.

## Crystal data

Chemical formula: $C_{22}H_{22}MoN_4O_3$
$M_r$ 486.39 g mol$^{-1}$
$a$/Å 10.7238(12)
$b$/Å 11.6098(13)
$c$/Å 10.3910(11)
$Z$ 2
$V$/Å$^3$ 1063.54( )
Radiation: Mo K$\alpha$
$\lambda$/Å 0.70169
Absorption coefficient (mm$^{-1}$): 0.630
Crystal source: from own lab.
Crystal colour dark red
Crystal size (mm): 0.35×0.20×0.09

Crystal system: triclinic
Space group $P\bar{1}$.
$\alpha°$ 110.8645(65)
$\beta°$ 110.2361(60)
$\gamma°$ 100.4568(59)

$D_x$/Mg m$^{-3}$ 1.519
No. of reflections for lattice parameters 50×4
$\theta$ range for lattice parameters (°): 20–30
$T$/K 293

Crystal description: flat

## Data collection

Diffractometer type: 4 circle
Absorption correction type
Integration
No. of reflections measured 5179
No. of independent reflections 4288
No. of observed reflections 2270
Criterion for observed $I > 3\sigma(I)$
$h_{min}$ 0
$k_{min}$ −14
$l_{min}$ −12

Collection method $\omega/2\theta$
Absorption correction:
$T_{min} = 0.865$; $T_{max} = 0.928$
$R_{int}$ 0.0329
$\theta_{max}$ 25°
No. of standard reflections (and interval): 2 (50)
Variation of standard: 10%
$h_{max}$ 13
$k_{max}$ 14
$l_{max}$ 11

## Refinement

Treatment of H atoms: no ref.
$R$ 0.055
$wR$ 0.055
$S$ 1.276
$(\Delta/\sigma)$max 2.2 (for $S_{11}$)
Extinction correction: none

Refined on $F$
No. of parameters refined 207
No. of reflections used in refinement 2270
Weighting scheme $w = [(\sigma F^2 + 1.02\ F^2)^{1/2} - |F|]^{-2}$
$(\Delta\rho)_{min}$ e Å$^{-3}$ −0.8
$(\Delta\rho)_{max}$ e Å$^{-3}$ 0.9
Source of atomic scattering factors
International Tables Vol. IV

To the best of our knowledge, this is the first structure solved containing a hydrazido(2 − ) ligand in combination with a SAP ligand, moreover it is the only structure with

ligand **3b**.[6] The X-ray analysis revealed that two diastereomeric units of **8a**, shown in Fig. 1, were present in the crystal in a ratio close to 2:1.[7a] Fig. 1 shows that ligand

Table 2. Selected bond lengths and angles for {mer-2-[1-(2-oxo-phenyliminato)ethyl]phenolato-N,O,O'}(2-aminophenolato-O,N)(N,N-dimethylhydrazido)molybdenum(VI), **8a**.

| Bond lengths | | Bond angles | | | | | |
|---|---|---|---|---|---|---|---|
| Mo—O1 | 2.015(5) | O1—Mo—N3 | 95.5(3) | O2'—Mo—N3 | 84.1(5) | Mo—O1'—C1' | 123.9(7) |
| Mo—O1' | 1.928(8) | O2—Mo—N3 | 103.3(3) | N1'—Mo—N3 | 98.4(3) | Mo—O1'—C14' | 117.6(7) |
| Mo—O2 | 2.022(6) | N1—Mo—N3 | 108.2(3) | O2'—Mo—N2 | 98.9(3) | Mo—N1−C7 | 124.3(5) |
| Mo—O2' | 1.988(8) | N2—Mo—N3 | 87.6(2) | N1'—Mo—N2 | 170.2(3) | Mo—N1−C9 | 110.8(5) |
| Mo—N1 | 2.242(6) | O3—Mo—N3 | 161.2(2) | O1'—Mo—N2 | 104.4(4) | Mo—N1'—C7' | 126.2(6) |
| Mo—N1' | 2.240(6) | O1—Mo—N2 | 107.9(2) | O1'—Mo—O3 | 95.0(6) | Mo—N1'—C9' | 109.1(6) |
| Mo—O3 | 2.045(6) | O2—Mo—N2 | 94.3(3) | N1'—Mo—O3 | 95.1(3) | Mo—O3—C15 | 115.9(4) |
| Mo—N2 | 1.964(5) | N1—Mo—N2 | 161.7(2) | O2'—Mo—O3 | 87.1(5) | Mo—N3—N4 | 152.9(5) |
| Mo—N3 | 1.771(6) | O3—Mo—N2 | 77.4(2) | O1'—Mo—O2' | 156.5(4) | N3—N4—C21 | 119.5(6) |
| C7—N1 | 1.289(9) | O1—Mo—O2 | 151.5(3) | O1'—Mo—N1' | 82.4(4) | N3—N4—C22 | 120.9(6) |
| N1—C9 | 1.449(13) | O1—Mo—O3 | 78.7(3) | N1'—Mo—O2' | 74.1(3) | C21—N4—C22 | 119.6(7) |
| O3—C15 | 1.338(8) | O1—Mo—N1 | 80.5(2) | O2—Mo—O1' | 10.8(6) | | |
| N2—C20 | 1.377(8) | O2—Mo—O3 | 89.2(3) | O1—Mo—O2' | 14.2(4) | | |
| N3—N4 | 1.296(8) | N1—Mo—O2 | 73.4(3) | N1—Mo—N1' | 19.5(4) | | |
| N4—C21 | 1.461(10) | N1—Mo—O3 | 88.7(2) | Mo—O1−C1 | 118.2(7) | | |
| N4—C22 | 1.445(19) | O1'—Mo—N3 | 99.8(5) | Mo—O2−C14 | 118.5(7) | | |

(1)

**4b**          **5a**                    **8a**
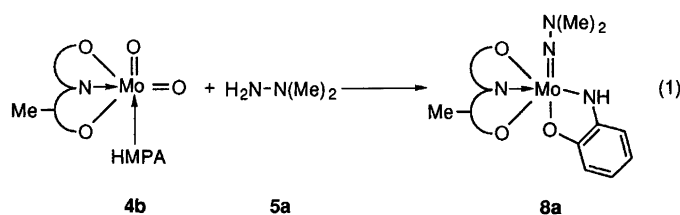
3b is *mer* bound to the molybdenum centre. Ligand 3b is a substituted SAP ligand, which can bind either *mer*[7a,b] or *fac*[7c] to a molybdenum centre. The two reported *mer*-structures[7a,b] consist of a tridentate SAP ligand and three mono-dentate ligands, while the *fac*-complex[7c] contains a tri-, a bi- and a mono-dentate ligand.
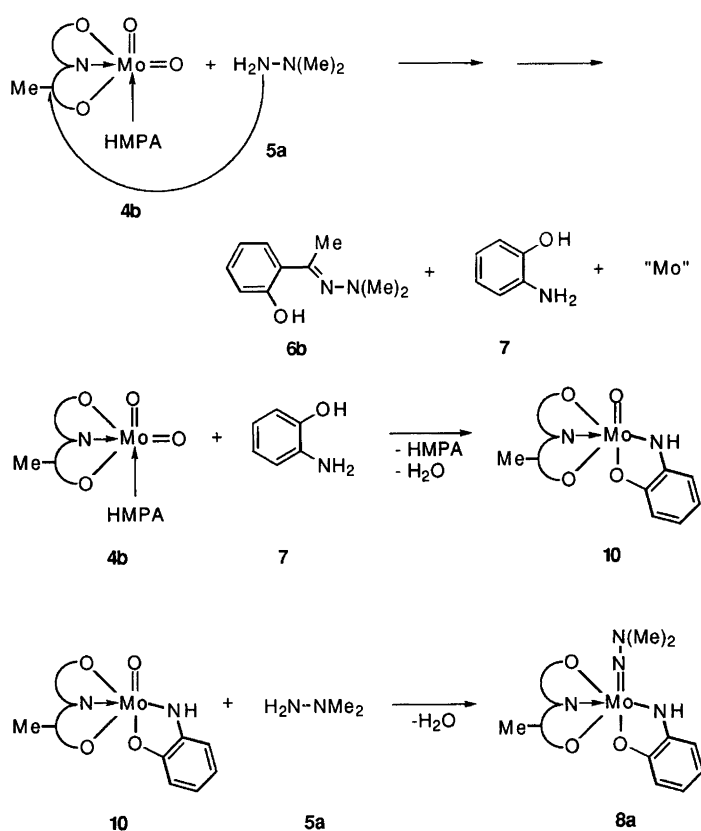
Complex 8a can be regarded as a distorted octahedral complex, with the apical positions occupied by the hydrazido(2 − ) ligand and the oxygen atom of the bidentate 2-aminophenolato ligand. The $N,O,O'$ atoms of the 3b ligand and the nitrogen atom of the 2-aminophenolato ligands constitute the equatorial positions. If the hydrazido(2 − ) ligand is regarded as a two-electron donor, complex 8a is formally an unfavoured 14e⁻ complex. In order to compensate for the formally low electron count, the nitrogen lone pair electrons of the hydrazido(2 − ) ligand interact with the molybdenum centre.[8] This is seen from the Mo = $N^3$–$N^4$ bonding angle, equal to 152.9(5)°, which is a significant increase from an ideal 120° angle for an $sp^2$-hybridised nitrogen atom. Moreover, the X-ray analysis revealed that the hydrazido(2 − ) β-nitrogen atom and the 2-aminophenolato nitrogen atom are $sp^2$-hybridised, which for the latter is also a strong indication of interaction between the lone pair electrons at this atom with the molybdenum centre. This also increases the electron count at the molybdenum centre. The molybdenum–nitrogen and the nitrogen–nitrogen bond lengths in the hydrazido(2 − ) ligand are 1.771(6) Å and 1.296(8) Å, respectively. Other bond lengths and angles are given in Table 2. A series of $N,N$-dimethylhydrazido(2 − ) molybdenum complexes have been characterised: the molybdenum–nitrogen and the nitrogen–nitrogen bond lengths in these hydrazido(2 − ) ligands are in the range 1.752–1.821 Å and 1.24–1.30 Å, respectively, while the Mo = N–N angle is found in the range 152.5–178°.[4g,i–l] It appears thus that the Mo = N bond length for 8a [1.771(6) Å] is among the shorter of the Mo = N bond lengths characterised, while the N–N bond length in 8a [1.296(8) Å] is among the longer N–N bond lengths characterised. The N–N bond length in 8a corresponds to a bond order of about 1.6–1.7.[9] It is interesting to note that the N–N bond length for hydrazine is reduced from 1.45 Å,[9] which is a typical N–N bond length between $sp^3$ hybridised nitrogen atoms, to 1.296(8) Å when bound to the molybdenum atom in 8a. This reduction in N–N bond length is, to a certain extent, probably due to the change in hybridisation of the nitrogen atoms from $sp^3$ in 5a to $sp^2$ in 8a. With regard to the Mo = N–N bond angle

the one found for 8a [152.9(5)°C] is among the smallest bond angles found for $N,N$-dimethylhydrazido(2 − ) molybdenum complexes.[4q,i–l] It should be noted that the complexes with Mo = N–N bond angles of 152.5°[4l] and 155.5°[4q] are also electron deficient complexes as in 8a. The hydrazido(2 − ) ligand in 8a is thus best described as Mo = N–NMe₂, rather than an isodiazene (Mo←N = NMe₂), as the latter type of complexes have the following characteristic bond lengths and angles for the Mo←N = NMe₂ fragment: Mo–N ~2.1 Å,N–N ~ 1.15 Å and <MoNN ~ 165°.[4q]

In order to understand the presence of the 2-aminophenolato ligand in 8a and the electronic structure of this complex a series of extended Hückel calculations were performed.[10] First the electronic structure of 4b was investigated: the HOMO of 4b, located at − 11.9 eV, as well as the next four occupied MOs of 4b are located on the phenyl rings of ligand 3b and are not discussed further. The LUMO is also found on the 3b ligand, but exclusively at the imine functionality, perpendicular to the $xy$-plane of the ligand as the $\pi^*_{C=N}$ orbital with the largest amplitude at the carbon atom as shown in 9. This orbital energy is calculated to be − 9.98 eV. The two next unoccupied MO are $\pi^*_{Mo=O}$.

**4b**

**9**

281
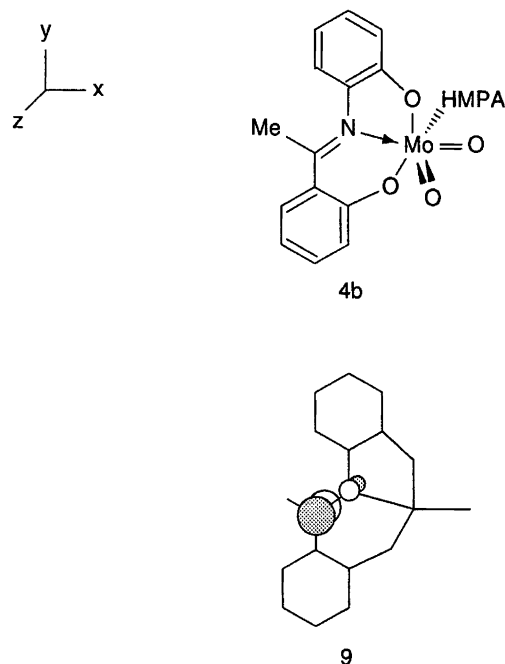
The formation of **8a** can be envisaged from the frontier orbitals of **4b** and is outlined in Scheme 1. Because of the location of the LUMO (**9**) at the carbon atom of the imine functionality of the **4b** ligand, 1,1-dimethylhydrazine, **5a**, acting as a nucleophile, attacks this carbon atom. This leads to cleavage of the ligand (and the complex) and formation of the hydrazone, **6b**, and 2-amino-phenol, **7**. In the next step 2-aminophenol reacts with another molecule of **4b** to give the molybdenum complex, **10**, from which **8a** is formed by reaction with **5a**. Support for the mechanism outlined in Scheme 1 is (*i*) the molybdenum complex, **10**, is observed by $^1$H NMR spectroscopy during the reaction and (*ii*) **10** reacts with **5a** to give **8a** (see the Experimental section).

$- 9.62$ eV, and the second lowest unoccupied MO at $- 9.31$ eV, are combinations of a molybdenum $d_{xy}$ orbital and the $\pi^*_{C=N}$ orbital on ligand **3b**. The third and fourth lowest unoccupied MOs are at $- 8.87$ eV and $- 8.68$ eV, respectively, and are mainly found as $\alpha^*_{Mo=N}$. The latter orbital is shown in **12**. Although the HOMO is located on the $\beta$-nitrogen atom in the Mo = N–N fragment, the largest negative charge is found on the $\alpha$-nitrogen atom with a charge of $- 1.00$, while the $\beta$-nitrogen atom has a charge of $- 0.23$. The electronic structure of **8a** indicates that both nitrogen atoms can be attacked by electrophiles depending on the electronic nature of the electrophile. But, the oxygen atom at the 2-aminophenolato ligand may also be susceptible to attack by electrophiles owing to the



*Scheme 1.*

The electronic structure of **8a** was also studied using extended Hückel calculation.[10] In the following the electronic structure of mainly the Mo = N–N(Me)$_2$ fragment of **8a** is discussed. The HOMO, at $- 11.20$ eV, is a $d_{xz}$ orbital at the molybdenum atom, mixed in with a $p_x$ orbital at the nitrogen atoms and is $\pi_{Mo=N}$ and $\pi^*_{N-N}$ as shown in **11**, with the largest amplitude at the $\beta$-nitrogen atom. The next four occupied MOs are found at the ligands of which the second HOMO, at $- 11.88$ eV, is located on the 2-aminophenolato ligand and mainly on the nitrogen and oxygen atoms; the atomic charge at the nitrogen and oxygen atoms of this ligand are calculated to be $- 0.89$ and $- 1.17$, respectively. The LUMO at
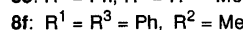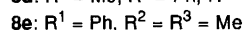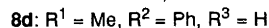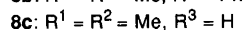
presence of a high-lying occupied MO on this ligand and a relatively high negative charge on the oxygen atom. The reactions of **8a** are presented later.

In order to gain more insight into the formation and the chemistry of complexes with a structure similar to **8**, a general procedure for the formation of 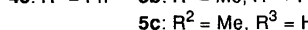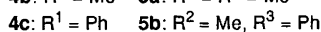these complexes was developed by reaction of **4b,c** and 2-aminophenol, **7**, with 1,1-dimethylhydrazine, **5a**, 1-methyl-1-phenylhydrazine, **5b**, methylhydrazine, **5c**, and phenylhydrazine, **5d** [eqn. (2)]:

The results for the reaction of **4b,c** and **7** with **5a–d** giving **8a–f** are presented in Table 3.

The results in Table 3 show that **8a–f** can be prepared

8a



11          12

8a presented as the last reaction steps in Scheme 1. For the reaction of 4b with 1,1-dimethylhydrazine, 5a, 1-methyl-1-phenylhydrazine, 5b, and methylhydrazine, 5c, the following reactivity is observed: 5a > 5c > 5b.

In the reaction of 4b with 5c in the presence of 7 another minor product of a molybdenum–hydrazido complex was also found. This product can be isolated as a solid material, but unfortunately we have not been able to grow crystals for X-ray analysis which would allow a structural determination, but based on spectroscopic investigations it is suggested to be 13a or 14a.

The structure of 13a/14a is unusual as the hydrazido(2 –) (azo/diazeno) ligand is $\eta^2$-coordinated to the molybdenum atom. Very few examples of side-on coordinated hydrazines to early transition-metal complexes are known or have been postulated. Deprotonation of $[(Mo(NHNHCO_2Me)(NNCO_2Me)(S_2CNMe_2)_2]$ and $[(Mo(NHNMePh)(NNMePh)(S_2CNMe_2)_2]-[BPh_4]^{4u}$ has been proposed to give an $\eta^2$-coordinated hydrazido(2 –) ligand to the molybdenum atom, corresponding to 14a, and azobenzene has been postulated to



(2)

**4b**: $R^1$ = Me    **5a**: $R^2$ = $R^3$ = Me    **8a**: $R^1$ = $R^2$ = $R^3$ = Me
**4c**: $R^1$ = Ph    **5b**: $R^2$ = Me, $R^3$ = Ph    **8b**: $R^1$ = $R^2$ = Me, $R^3$ = Ph
                      **5c**: $R^2$ = Me, $R^3$ = H    **8c**: $R^1$ = $R^2$ = Me, $R^3$ = H
                      **5d**: $R^2$ = Ph, $R^3$ = H    **8d**: $R^1$ = Me, $R^2$ = Ph, $R^3$ = H
                                                       **8e**: $R^1$ = Ph, $R^2$ = $R^3$ = Me
                                                       **8f**: $R^1$ = $R^3$ = Ph, $R^2$ = Me

in good yields by the procedure outlined in eqn. (2). The structural elucidations of 8b–f are based on the X-ray structure of 8a, discussed above, and their $^1$H and $^{13}$C NMR spectra. The mechanism for the formation of 8a–f in eqn. (2) is probably closely related to the formation of
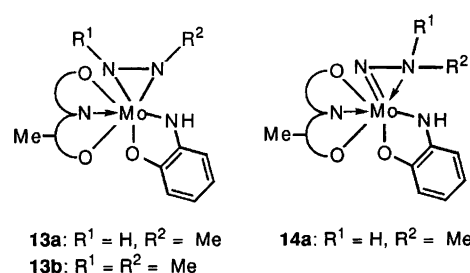
*Table 3.* Preparation of complexes, 8a–f, by the reaction of 4b, c, and 2-aminophenol, 7, with 1,1-dimethylhydrazine, 5a, 1-methyl-1-phenylhydrazine, 5b, methylhydrazine, 5c, and phenylhydrazine, 5d.

| Entry | 4 | 5 | Reaction time/h | Yield (%)[a] |
|---|---|---|---|---|
| 1 | 4b | 5a | 24 | 8a (77) |
| 2 | 4b | 5b | 108 | 8b (74) |
| 3 | 4b | 5c | 20 | 8c (66) |
| 4 | 4b | 5d | 20 | 8d (65) |
| 5 | 4c | 5a | 24 | 8e (79) |
| 6 | 4c | 5b | 24 | 8f (74) |

[a] Isolated yield.



**13a**: $R^1$ = H, $R^2$ = Me          **14a**: $R^1$ = H, $R^2$ = Me
**13b**: $R^1$ = $R^2$ = Me

coordinate to $Cp_2Mo^{4y}$ to give a complex similar to 13a. For the tungsten complexes both systems having unsubstituted, monosubstituted and 1,1-dimethylhydrazine ligands have been observed.[5p–r] The structural assignment of the 13a/14a is based primarily on $^1$H NMR and IR spectroscopic data. The $^1$H NMR spectrum of 13a/14a is significantly different from that of 8c. (*i*) Two signals [$\delta$(H)] at 1.8 ppm and 4.24 ppm of the methyl group of the hydrazido ligand are observed at room temperature

in $C_6D_6$ in the ratio 0.8:1. The presence of two signals for the methyl substituent is due to the methyl group occupying different environments, depending on the orientation of the hydrazido ligand relative to the other ligands in **13a/14a**. This could indicate that two forms of the complex are present in solution, and that the difference of these two systems is the orientation of the hydrazido ligand relative to the rest of the organic ligands. Similar splitting of the ^{1}H NMR signal of the methyl groups has been observed for a tungsten complex.[5p-r] If the solvent is changed to $CDCl_3$ the ratio between the two isomers of **13a/14a** is found to be 0.1:1. (*ii*) The ^{1}H NMR signal of the amino proton in the 2-aminophenolato ligand is shifted downfield by 2.1 ppm in **13a/14a** compared with **8c**. This could be due to hydrogen bonding of the amine hydrogen atom to one of the hydrazine nitrogen atoms as these might be expected to be closer to the 2-amino-phenolato ligand in **13a/14a** compared with **8c**. (*iii*) The N–N stretching frequency at 1390 cm$^{-1}$ observed for **8c** is not observed for **13a/14a**, indicating that the latter complex has another binding mode of the methylhydrazine fragment compared with **8c**. However, a new frequency at 950 cm$^{-1}$ is present, which could indicate a complex with a hydrazine N–N single bond character.[11] (*iv*) The IR spectrum for **13a/14a** shows two strong bands for N–H stretching frequencies at 3280 cm$^{-1}$ and 3360 cm$^{-1}$.

At the present stage we are not able to evaluate the stability of **8c** relative to **13a/14a**, but it is found that by reaction of **4b** with **5c** in the presence of **7** complex **8c** is formed first, followed by a slow formation of **13a/14a**. It has also been observed that addition of an excess of **5c** to this reaction causes an increase in the yield of **13a/14a**, and that addition of **5c** to **8c** dissolved in $CH_2Cl_2$ leads to the transformation of **8c** into **13a/14a**. We are not yet able to account for these observations.

Reaction of **4b** and 2-aminophenol, **7**, with 1,2-dimethylhydrazine also leads to a complex which, based on ^{1}H NMR spectroscopy, has been assigned as **13b**. The isolated yield of **13b** is very low (< 5 %) and the remaining part of the crude product is mainly starting materials.

In an attempt to obtain insight into the chemistry of the molybdenum hydrazido(2 − ) complexes studied here several reactions of **8a** have been performed.

Complex **8a** reacts with HCl in $CH_2Cl_2$ at room temperature within few minutes to give a green complex[12] and NMR spectroscopy shows the presence of ligand **3b** bound to the molybdenum atom and Mo = N–N(Me)$_2$. Based on ^{1}H NMR, ^{13}C NMR and IR spectroscopic
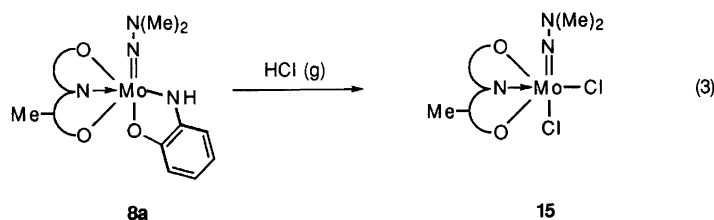
data (see the Experimental section) the structure of the green complex is proposed to be **15** [eqn. (3)]. Further evidence for **15** is its reaction with $AgNO_3$ from which AgCl precipitates.
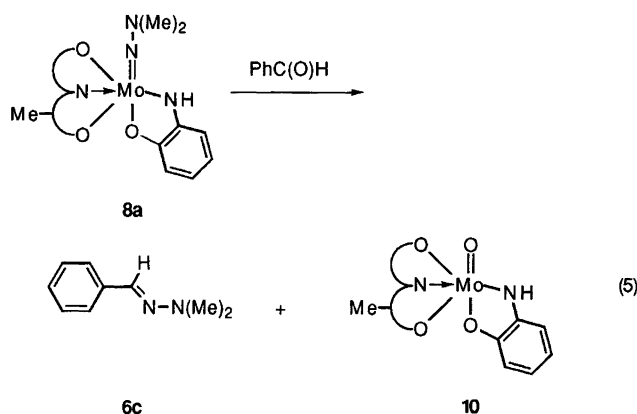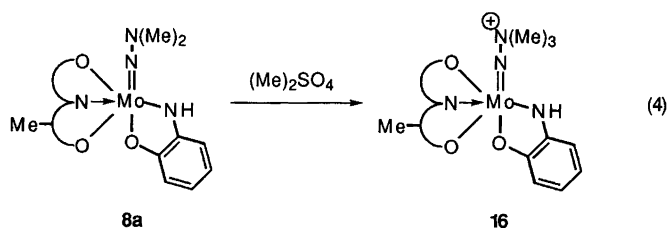
The reaction of **8a** with hydrogen chloride takes place by initial protonation of probably the oxygen atom of the 2-aminophenolato ligand, as this atom possesses a high negative atomic charge and relatively high amplitude among the occupied frontier MOs (see above). This protonation is followed by a nucleophilic attack of chloride ion at the molybdenum atom with substitution of the 2-aminophenolato ligand by two chloride ions. It is notable that the protonation takes place at the 2-aminophenolato ligand to give 2-aminophenol, leaving the hydrazido(2 − ) ligand unaffected under these reaction conditions. In related hydrazido(2 − ) metal complexes protonation and cleavage of the N–N bond and ligand cleavage were found to be very dependent on the proton source and the solvent used.[4a-c,i,q,z,aa]

Complex **8a** is methylated at the β-nitrogen atom in the Mo = N–N(Me)$_2$ fragment by $(Me)_2SO_4$ to give **16** as observed by ^{1}H NMR spectroscopy [eqn. (4)]. But methylation of **8a** is very dependent on the methylation reagents as no reaction is observed by treatment with MeI under similar conditions. The methylation at the β-nitrogen atom of the Mo = N–N(Me)$_2$ fragment of **8a** is similar to the methylation site of $CpMoMe_3NNMe_2$,[4g] where the β-nitrogen atom is methylated by MeOTf. The methylation at the β-nitrogen atom in the Mo = N–N(Me)$_2$ fragment of **8a** corresponds to an interaction of the electrophile with the HOMO (**11** see above) of **8a**.

The reaction of **8a** with organic carbonyl compounds has also been investigated; in the case of benzaldehyde as the substrate the following reaction takes place, where the hydrazone, **6c**, was isolated was 54 % yield [eqn. (5)]. The reaction probably takes place by a 'Wittig-like' mechanism. It should be noted that only very few reactions involving a reaction with a hydrazido(2 − ) molybdenum complex and an aldehyde leading to a hydrazone have been reported.[13]

Because of the reluctance of the N–N bond in the Mo = N–N(Me)$_2$ fragment of **8a** to be cleaved by hydrogen chloride, several other attempts to break this bond were made. We succeeded in cleaving the N–N bond in **8a** only by reaction with benzoyl chloride in the presence of 0.5–1.0 equivalent of $H_2O$ (in the absence of $H_2O$ no reaction took place) in $CH_2Cl_2$. This reaction led to a cleavage of the N–N bond and *N,N*-dimethylbenzamide, **17**, is formed in 20 % yield [eqn. (6)], and some molyb-



**8a**       HCl (g)       (3)       **15**

N(Me)2

(Me)2SO4

8a

⊕N(Me)3

16 (4)

N(Me)2

PhC(O)H

8a

H

N−N(Me)2 +

6c

Me−

N→Mo−NH

10 (5)

denum compounds, among which **15** was identified. We are not at present able to give a mechanism for the N−N bond cleavage in **8a**.

shifts are relative to TMS and are given as δ values. All spectra were recorded at room temperature (rt). IR spectra were recorded on a Nicolet 5MX-IR spectrometer.

N(Me)2

PhC(O)Cl
—————→
H2O

8a

O
‖
Ph−C−N(Me)2 (6)

17
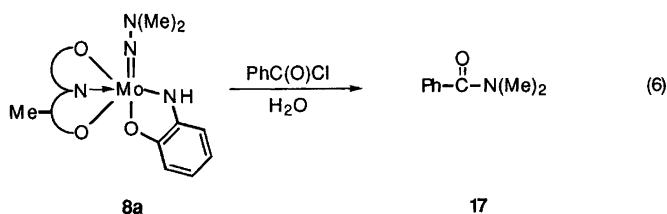
In another attempt to cleave the N−N bond in **8a** with other Lewis acids, the reaction of **8a** with benzoic anhydride was performed. But, in this case **10** was isolated as the major product in 72% yield and no products indicating N−N bond cleavage were observed.

Only very few successful examples are known in which the N−N bond in hydrazido(2 − )molybdenum complexes is cleaved. In one example it was found that photolysis of a bis[(*N,N*-dimethyldithiocarbamato)bis(*N*-alkyl-*N*-phenylhydrazido(2 − )]molybdenum(VI) complex in halogenated solvents causes predominantly the transfer of the hydrazido group to the solvent with formation of dichloroacetohydrazines, and a small amount of the corresponding dichloroacetamides.[14] The latter product was formed by N−N bond cleavage and N(R)Ph transfer.[14]

**Experimental**

*Apparatus.* ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 or Varian Gemini 300. Chemical

The calculations were performed on a Macintosh Quadra 700 using the CAChe® work system.

*Chemicals and solvents.* Solvents [$CH_2Cl_2$, $Cl(CH_2)_2Cl$, $C_2H_5OC_2H_5$ and petroleum ether] were dried prior to use by distillation over $P_2O_5$ and stored over molecular sieves. Mo (VI) (O)$_2$(acac)$_2$, HMPA (**WARNING**: suspected carcinogen), 2-aminophenol, 2-hydroxyacetophenone, 2-hydroxybenzophenone, methylhydrazine, phenylhydrazine (distilled and stored below −18°C), 1,1-dimethylhydrazine, 1-methyl-1-phenylhydrazine and methylamine·H$_2$O (40%) were purchased from Aldrich and used without further purification. 1,2-dimethylhydrazine,[4s] ligands **3a**[8b] and **4a**[15] were prepared according to the literature.

*Preparation of* **4b**. 2-Hydroxyacetophenone methylimine (24.69 g, 165 mmol), prepared by condensation of 2-hydroxyacetophenone and methylamine, was added to a solution of 2-aminophenol (17.94 g, 165 mmol) in 200 ml Cl(CH$_2$)$_2$Cl. The reaction was refluxed under a nitrogen

atmosphere for 48 h with the evolution of methylamine. Upon cooling of the reaction mixture, yellow crystals of protonated **3b** precipitated (25.89 g, 69%). The crystals were added to a solution of $Mo(O)_2(acac)_2$ (37.02 g, 114 mmol) in 400 ml $Cl(CH_2)_2Cl$ and the mixture stirred at rt. After 45 min HMPA (20.41 g, 114 mmol) dissolved in 10 ml $CH_2Cl_2$ was added and the reaction mixture was stirred at rt for 60 min. The reaction mixture was filtered and the filtrate was dried on a rotary evaporator. $C_2H_5OC_2H_5$ (400 ml) was added and the solution was stirred for 60 min. Then a yellow powder of **4b** was filtered off. Yield: 40.62 g (67%). The powder can be crystallised from hot $Cl(CH_2)_2Cl$. IR (KBr): $v(Mo = O)$ 910 cm$^{-1}$ (s), $v(Mo = O)$ 935 cm$^{-1}$ (s). $^1H$ NMR (DMSO): δ 2.53 (d, $J = 9.4$ Hz, 18 H), 2.90 (s, 3 H), 6.84 (dd, $J = 8.1$ Hz, $J = 1.2$ Hz, 1 H), 6.88–6.90 (m, 2 H), 7.04 (dd, $J = 7.7$ Hz, $J = 1.2$ Hz, 1 H), 7.16 (ddd, $J = 8.0$ Hz, $J = 7.4$ Hz, $J = 1.4$ Hz, 1 H), 7.20 (dd, $J = 8.0$ Hz, $J = 1.4$ Hz, 1 H), 7.97 (dd, $J = 8.2$ Hz, $J = 1.6$ Hz, 1 H). $^{13}C$ NMR (DMSO): δ 21.2, 36.4 (d, $J = 3.4$ Hz), 116.6, 119.1, 119.1, 120.5, 123.5, 124.8, 128.6, 131.7, 134.1, 136.1, 160.2, 161.7, 171.2.

*Preparation of* **4c**. 2-Hydroxybenzophenone (24.75 g, 4.0 mmol) was dissolved in $Cl(CH_2)_2Cl$ at rt and $NH_3$ was bubbled through the solution in the presence of molecular sieves (4 Å). After removal of the solvent 95% of the corresponding 2-hydroxybenzophenone imine was isolated and used without further purification. 2-Hydroxybenzophenone imine (335 mg, 1.7 mmol) and 2-aminophenol (164 mg, 1.5 mmol) were dissolved in $Cl(CH_2)_2Cl$ and refluxed under nitrogen for 48 h with the evolution of $NH_3(g)$. The reaction mixture was filtered and the solvent evaporated off. The crude material was washed with petroleum ether and protonated **3c** (81%) was obtained after filtration. The protonated **3c** (1.2 mmol, 347 mg) was dissolved in $Cl(CH_2)_2Cl$ and added to a solution of $Mo(O)_2(acac)_2$ (1.2 mmol) in 10 ml $Cl(CH_2)_2Cl$ and the mixture was stirred for 30 min at rt. HMPA (1.2 mmol, 215 mg) was added and the reaction mixture was stirred for another 30 min. The volume of the solvent was reduced to 3 ml on a rotary vaporator and the by-products precipitated by the addition of $C_2H_5OC_2H_5$ and then filtered off. The organic phase was reduced to 3 ml and **4c** precipitated after the addition of petroleum ether. Yield: 77%. IR (KBr): $v(Mo = O)$ 910 cm$^{-1}$ (s), $v(Mo = O)$ 935 cm$^{-1}$ (s). $^1H$ NMR (CDCl$_3$): δ 2.51 (d, $J = 9.8$ Hz, 18 H), 5.85 (dd, $J = 8.3$ Hz, $J = 1.3$ Hz, 1 H), 6.15 (dt, $J = 8.5$ Hz, $J = 7.1$ Hz, $J = 1.6$ Hz, 1 H), 6.65–6.96 (m, 5 H), 7.29–7.52 (m, 6 H). $^{13}C$ NMR (CDCl$_3$): δ 36.5 (d, $J = 5.2$ Hz), 117.8, 118.1, 118.9, 119.4, 122.3, 126.2, 126.6, 128.5, 128.6, 129.3, 129.5, 133.6, 134.0, 136.1, 137.4, 162.1, 166.0, 166.2.

*Reaction of* **4b** *with 1,1-dimethylhydrazine,* **5a**. The complex **4b** (0.5 mmol, 266 mg) was dissolved in 20 ml $CH_2Cl_2$ and 1.0 mmol (60 mg) of **5a** was added. The

reaction mixture was stirred for 3 h at rt. The solvent was removed and the crude material dissolved in $CH_2Cl_2$. Petroleum ether was added and crystals precipitated. The crystals were dissolved in $CH_2Cl_2$ and purified on a column using silica and $CH_2Cl_2$ as the eluent. By this procedure 31% of **8a** was isolated. The spectroscopic data for **8a** are given below.

*General procedure for formation of* **8a, b–f**. The complex, **4b** or **4c** (130 mg, 0.25 mmol) was dissolved in 5 ml $CH_2Cl_2$ using the standard Schlenk technique and the appropriate hydrazine (**5a, b, d, f**) (0.50 mmol) and 2-aminophenol (27 mg, 0.25 mmol) were added. The reaction mixture was stirred at rt for the period of time given in Table 3. The solvent was removed and the crude material was dissolved in $CH_2Cl_2$ and separated by flash column chromatography (fcc) using silica and 1% $CH_3OH$–99% $CH_2Cl_2$. The isolated yields of **8a, b, d–f** are given in Table 3.

Spectroscopic data for **8a, b, d–f**: **8a**: $^1H$ NMR (CDCl$_3$): δ 2.89 (s, 3 H), 3.10 (s, 6 H), 6.66–6.89 (m, 8 H), 7.02–7.76 (m, 1 H), 7.13–7.19 (q, 1 H), 7.27–7.35 (m, 1 H), 7.76–7.80 (q, 1 H), 11.3 (br s, 1 H). $^{13}C$ NMR (CDCl$_3$): δ 20.6, 43.2, 43.4, 115.0, 115.8, 117.0, 117.2, 117.8, 119.1, 120.0, 123.0, 125.8, 126.1, 129.5, 130.2, 134.4, 137.6, 147.4, 154.5, 163.1, 164.2, 169.5. IR (KBr): $v(N-N)$ 1390 cm$^{-1}$ (m). **8b**: $^1H$ NMR (CDCl$_3$): δ 2.80 (s, 3 H), 3.51 (s, 3 H), 6.63–7.09 (m, 13 H), 7.22–7.36 (m, 3 H), 7.72 (d, $J = 8.2$ Hz, 1 H), 11.36 (br s, 1 H). $^{13}C$ NMR (CDCl$_3$): δ 20.7, 38.9, 114.0, 114.9, 115.1, 115.3, 116.6, 117.1, 117.8, 119.0, 119.7, 122.6, 123.6, 123.9, 125.1, 126.0, 129.0, 130.1, 133.5, 137.1, 142.0, 146.9, 161.5, 162.5, 163.8, 169.7. IR (KBr): $v(N-N)$ 1395 cm$^{-1}$ (m). **8d**: $^1H$ NMR (DMSO): δ 2.93 (s, 3 H), 6.38–7.44 (m, 16 H), 7.95 (d, $J = 7.9$ Hz, 1 H), 9.00 (br s, 1 H), 13.5 (br s, 1 H). IR (KBr): $v(N-H)$ 3260 cm$^{-1}$ (s), $v(N-N)$ 1400 cm$^{-1}$ (m). **8e**: $^1H$ NMR (CDCl$_3$): δ 3.02 (s, 6 H), 6.00 (dd, $J = 1.4$ Hz, 8.2 Hz, 1 H), 6.16 (dt, $J = 1.4$ Hz, 7.2 Hz, 8.3 Hz, 1 H), 6.58–6.90 (m, 10 H), 7.22–7.51 (m, 5 H), 11.4 (br s, 1 H). $^{13}C$ NMR (C$_6$D$_6$): δ 115.1, 115.8, 117.0, 117.5, 117.8, 118.4, 118.8, 122.9, 126.0, 127.6, 127.6, 128.9, 129.4, 129.5, 129.6, 130.3, 133.6, 134.3, 137.4, 137.4, 147.9, 162.9, 163.3, 166.7, 168.1. IR (KBr): $v(N-N)$ 1395 cm$^{-1}$ (m). **8f**: $^1H$ NMR (CDCl$_3$): δ 3.50 (s, 3 H), 6.05 (dd, $J = 1.3$ Hz, 8.4 Hz, 1 H), 6.23 (dd, $J = 1.3$ Hz, 8.4 Hz, 1 H), 6.65–7.55 (m, 20 H), 11.4 (br s, 1 H). IR (KBr): $v(N-N)$ 1390 cm$^{-1}$ (m).

*Procedure for the formation of* **8c**. The complex, **4b** (133 mg, 0.25 mmol) and 2-aminophenol (27 mg, 0.25 mmol) were dissolved in 5 ml $CH_2Cl_2$ using the standard Schlenk technique. The reaction mixture was stirred at rt and 1-methylhydrazine, **5c**, dissolved in 2 ml of $CH_2Cl_2$ was added dropwise over 8 h to the solution and the reaction mixture was stirred for the period of time given in Table 3. The reaction mixture was separated using fcc as described above. The yield of **8c** is given in Table 3.

Spectroscopy data for **8c**: $^1$H NMR (CDCl$_3$): δ 2.81 (s, 3 H), 2.88 (s, 3 H), 6.69–7.17 (m, 10 H), 7.33 (dt, $J$ = 1.7 Hz, 7.2 Hz, 8.5 Hz, 1 H), 7.6 (br s, 1 H), 7.78 (dt, $J$ = 1.7 Hz, 7.2 Hz, 8.5 Hz, 1 H), 11.4 (br s, 1 H). IR (KBr): v(N–H) 3250 cm$^{-1}$ (m), v(N–N) 1395 cm$^{-1}$ (m).

*Preparation of* **10**. The complex **8a** (244 mg, 0.50 mmol) was dissolved in 10 ml Cl(CH$_2$)$_2$Cl and benzoic anhydride (226 mg, 1.0 mmol) was added. The reaction mixture was refluxed with stirring for 16 h. The solvent was removed and the crude material dissolved in CH$_2$Cl$_2$ and separated by fcc using silica and 2% CH$_3$OH–98% CH$_2$Cl$_2$: After recrystallization in hot Cl(CH$_2$)$_2$Cl 72% of **10** was isolated.

Spectroscopic data for **10**: $^1$H NMR (CDCl$_3$): δ 2.99 (s, 3 H), 6.68–7.26 (m, 10 H), 7.50 (t, $J$ = 8.4 Hz, 1 H), 7.86 (d, $J$ = 6.8 Hz, 1 H), 12.4 (br s, 1 H). $^{13}$C NMR (CDCl$_3$): δ 21.8, 115.3, 115.8, 117.3, 118.5, 120.3, 120.7, 120.7, 123.0, 129.9, 130.6, 130.7, 135.8. IR (KBr): v(Mo = O) 940 cm$^{-1}$ (s).

*Reaction of* **10** *with* **5a**. The reaction was performed in an NMR tube. The complex **10** (22 mg, 0.05 mmol) was dissolved in 0.7 ml CDCl$_3$ and 1,1-dimethylhydrazine, **5a**, (9 mg, 0.15 mmol) was added. After 9 h the only product detectable by $^1$H NMR spectroscopy was **8a** which was formed almost quantitatively.

*Preparation of* **13a/14a**. Reaction conditions similar to those used for the preparation of **8a** were used, except the solvent was changed to C$_6$H$_6$. The reaction mixture was stirred for 20 h at rt. Isolation: fcc: First on silica using 2% CH$_3$OH–98% CH$_2$Cl$_2$ where the violet compound was collected and the solvent evaporated. The violet compound was then loaded onto a new flash column using silica and eluting initially with 100% CH$_2$Cl$_2$ followed by a slow increase of the polarity of the eluent by the addition of CH$_3$OH up to a ratio of 1% CH$_3$OH–99% CH$_2$Cl$_2$. At this polarity the red band on the column was removed (the end-on compound). Then the polarity was increased to 3% CH$_3$OH–97% CH$_2$Cl$_2$ and **13a/14a** was isolated in 27% yield. The complex was dissolved in CH$_2$Cl$_2$ and was precipitated by the addition of petroleum ether.

**13a/14a**: $^1$H NMR (CDCl$_3$): δ 1.98, 2.81 (s, 3 H), 2.66 (s, 3 H), 2.89, 2.94 (s, 1 H), 6.15–6.96 (m, 12 H), 13.5 (br s, 1 H). $^{13}$C NMR (CDCl$_3$): δ 29.7, 45.8, 115.2, 115.7, 115.8, 116.7, 117.4, 118.7, 119.4, 121.1, 125.5, 126.7, 128.4, 128.8, 134.7, 144.2, 146.2, 160.5, 161.6. IR (KBr): v(N–N) 950 cm$^{-1}$ (s), v(N–H) 3280 cm$^{-1}$ (s), v(N–H) 3360 cm$^{-1}$ (s).

*Preparation of* **13b**. The complex **4b** (1.0 mmol, 532 mg) and 2-aminophenol (1.0 mmol, 104 mg) were dissolved in 10 ml CH$_2$Cl$_2$ and 1,2-dimethylhydrazine (1.0 mmol, 60 mg) dissolved in 1 ml C$_2$H$_5$OC$_2$H$_5$ was added under a nitrogen atmosphere at rt. The reaction mixture was stirred for 31 h. The solvent was evaporated off and the

crude material was separated on a silica plate using 2% CH$_3$OH–98% CH$_2$Cl$_2$ as the eluent. The complex **13b** was isolated as a violet compound in 3% yield. The remaining part of the crude material was mainly unchanged starting materials.

**13b**: $^1$H NMR (CDCl$_3$): δ 2.18 (s, 3 H), 2.94 (s, 3 H), 3.07 (s, 3 H), 6.69–7.87 (m, 12 H), 12.9 (s, 1 H).

*Reaction of* **8a** *with HCl*. Complex **8a** (266 mg, 0.50 mmol) was dissolved in 15 ml CH$_2$Cl$_2$. HCl(g) was bubbled through the solution for 3 min during which time a colour change from red to green took place. The solution was filtered and 5 ml petroleum ether were added. Upon cooling green crystals precipitated. Yield: 85% of **15**. $^1$H NMR (CDCl$_3$): δ 2.81 (s, 3 H), 4.10 (s, 6 H), 6.44 (d, $J$ = 7.7 Hz, 1 H), 6.55 (d, $J$ = 8.0 Hz, 1 H), 6.84–7.33 (m, 5 H), 7.55 (d, $J$ = 8.0 Hz, 1 H). $^{13}$C NMR (CDCl$_3$): δ 23.5, 43.4, 116.5, 119.2, 124.3, 124.6, 124.6, 127.4, 130.2, 132.8, 135.9, 137.8, 159.1, 162.5, 174.4.

*Reaction of* **8a** *with Me$_2$SO$_4$*. The reaction with Me$_2$SO$_4$ was performed in an NMR tube. Complex **8a** (49 mg, 0.10 mmol) was dissolved in 0.7 ml CDCl$_3$. Me$_2$SO$_4$ (15 mg, 0.12 mmol) dissolved in 0.1 ml CDCl$_3$ was added. After 15 h only **8a** and **16** could be detected, together with decomposition products from Me$_2$SO$_4$. $^1$H NMR (CDCl$_3$): δ 2.98 (s, 3 H), 3.68 (s, 9 H), 6.51–7.79 (m, 8 H).

*Reaction of* **8a** *with PhC(O)H*. The complex **8a** (0.25 mmol, 22 mg) was dissolved in 5 ml Cl(CH$_2$)$_2$Cl and 0.25 mmol (27 mg) benzaldehyde was added. The reaction mixture was stirred for 20 h at rt. The hydrazone, **6c**, could be separated from the reaction mixture on a silica plate using CH$_2$Cl$_2$ as the eluent. **6c**: $^1$H NMR (CDCl$_3$): δ 2.97 (s, 6 H), 7.22–7.35 (m, 4 H), 7.57 (d, 2 H, $J$ = 7.7 Hz).

*Reaction of* **8a** *with PhC(O)Cl*. Complex **8a** (266 mg, 0.50 mmol) was dissolved in 5 ml CH$_2$Cl$_2$. Benzoyl chloride (140 mg, 1.0 mmol) dissolved in 5 ml CH$_2$Cl$_2$ was added dropwise over 10 min. Addition of H$_2$O (14 μl, 0.25 mmol) caused a change of the colour of the solution to green. The reaction mixture was stirred for 36 h. The reaction mixture was filtered. The solvent from the filtrate was evaporated and the crude material was filtered. A clear oil of N,N-dimethylbenzamide was collected after filtration of the solvent. Yield 20% of **17**. In order to establish the nature of the oil, N,N-dimethylbenzamide was prepared by an independent procedure and found to be identical with **17**.

*Reaction of* **8c** *with H$_2$NNHMe*. The reaction was performed in an NMR tube. Complex **8c** (49 mg, 0.10 mmol) was dissolved in C$_6$D$_6$, and methylhydrazine (8 μl, 0.11 mmol) was added. After 6 h the only detectable products were **8c**, **13a/14a** and salicylaldehyde methylhydrazone. It should be noted that slow decomposition

of **8c** takes place when it is dissolved in $C_6D_6$ within 6–10 h, but **13a/14a** could not be detected.

*X-ray investigation.* Crystals suitable for X-ray crystallography were grown from benzene. The space group of the crystal was determined from precession photographs to be triclinic, $P\bar{1}$. Standard reflections monitored every 50 reflections showed a 10% decrease in intensity and this was corrected for.

The X-ray analysis revealed that two diastereomeric units, shown in Fig. 1, were present in the crystal in a ratio close to 2:1. The initial refinements gave unreasonable geometry around the imine bond. A disordered model where N1, C7 and C8 were split into two could be

refined to $R = 0.051$, but the geometry was still not satisfactory. A similar model where soft restraints were introduced to give reasonable geometry led to a poorer agreement, $R = 0.053$. A constrained refinement where two partially occupied **3b** ligands were kept identical, except for rotation around the C–N bond gave still poorer agreement ($R = 0.055$), probably because it was necessary to constrain the thermal parameters, too. The parameters refined were three Euler angles and centre coordinates for two **3b** ligand units, coordinates of one **3b** ligand in an inertial system; one twist angle; an occupation factor; an angle for positioning the hydrogens of each methyl group; coordinates and anisotropic thermal parameters for the rest of the complex, giving a total of 207 variables; all

*Table 4.* Atomic coordinates.

| Atom | x | y | z | $U_{eq}$ |
|------|------|------|------|------|
| Mo | 0.89382(7) | 0.24277(6) | 0.34507(7) | 0.039 |
| O1 | 0.8820(7) | 0.0645(5) | 0.3354(8) | 0.030 |
| C1 | 0.9159(15) | −0.0162(13) | 0.2347(14) | 0.034 |
| C2 | 0.9956(14) | −0.0877(13) | 0.2921(18) | 0.040 |
| C3 | 1.0341(19) | −0.1739(16) | 0.1970(18) | 0.055 |
| C4 | 0.9922(18) | −0.1947(16) | 0.0466(19) | 0.066 |
| C5 | 0.9085(16) | −0.1351(13) | −0.0128(17) | 0.058 |
| C6 | 0.8670(14) | −0.0444(11) | 0.0786(13) | 0.040 |
| C7 | 0.7683(10) | 0.0136(9) | 0.0082(10) | 0.038 |
| C8 | 0.6891(12) | −0.0489(11) | −0.1698(11) | 0.055 |
| N1 | 0.7515(8) | 0.1159(7) | 0.0931(7) | 0.032 |
| C9 | 0.6488(12) | 0.1728(12) | 0.0354(12) | 0.036 |
| C10 | 0.5163(12) | 0.1129(14) | −0.0878(14) | 0.044 |
| C11 | 0.4290(17) | 0.1810(14) | −0.1181(18) | 0.051 |
| C12 | 0.4693(16) | 0.3116(15) | −0.0223(20) | 0.053 |
| C13 | 0.6017(15) | 0.3739(16) | 0.1052(19) | 0.049 |
| C14 | 0.6893(17) | 0.3049(13) | 0.1321(16) | 0.039 |
| O2 | 0.8153(9) | 0.3606(7) | 0.2618(8) | 0.041 |
| O1' | 0.8202(16) | 0.3344(9) | 0.2310(14) | 0.038 |
| C1' | 0.6885(22) | 0.2873(15) | 0.1174(19) | 0.038 |
| C2' | 0.6265(23) | 0.3848(19) | 0.1098(26) | 0.049 |
| C3' | 0.4924(24) | 0.3464(20) | −0.0036(29) | 0.054 |
| C4' | 0.4205(23) | 0.2165(22) | −0.1120(27) | 0.053 |
| C5' | 0.4813(17) | 0.1245(20) | −0.1131(21) | 0.047 |
| C6' | 0.6173(16) | 0.1566(15) | 0.0008(16) | 0.037 |
| C7' | 0.6847(12) | 0.0555(11) | −0.0085(13) | 0.037 |
| C8' | 0.6171(15) | −0.0737(15) | −0.1608(13) | 0.054 |
| N1' | 0.7950(11) | 0.0734(9) | 0.1089(10) | 0.032 |
| C9' | 0.8672(18) | −0.0204(14) | 0.1110(15) | 0.037 |
| C10' | 0.8850(22) | −0.1082(19) | −0.0054(21) | 0.053 |
| C11' | 0.9663(27) | −0.1822(26) | 0.0205(25) | 0.064 |
| C12' | 1.0375(29) | −0.1674(25) | 0.1659(28) | 0.057 |
| C13' | 1.0238(23) | −0.0769(19) | 0.2864(26) | 0.041 |
| C14' | 0.9394(21) | −0.0056(17) | 0.2580(18) | 0.033 |
| O2' | 0.9317(15) | 0.0904(9) | 0.3748(11) | 0.030 |
| O3' | 0.7227(5) | 0.1987(9) | 0.3867(5) | 0.036 |
| N2 | 0.9650(6) | 0.3696(5) | 0.5615(6) | 0.028 |
| C15 | 0.7403(8) | 0.2727(7) | 0.5279(8) | 0.035 |
| C16 | 0.6391(8) | 0.2571(8) | 0.5802(9) | 0.050 |
| C17 | 0.6713(10) | 0.3406(9) | 0.7310(10) | 0.056 |
| C18 | 0.8007(10) | 0.4389(8) | 0.8253(9) | 0.051 |
| C19 | 0.9023(8) | 0.4561(7) | 0.7770(8) | 0.037 |
| C20 | 0.8732(7) | 0.3721(6) | 0.6272(8) | 0.030 |
| N3 | 1.0710(7) | 0.2884(5) | 0.3715(6) | 0.035 |
| N4 | 1.2055(7) | 0.3139(7) | 0.4467(8) | 0.052 |
| C21 | 1.2530(9) | 0.2468(8) | 0.5395(10) | 0.058 |
| C22 | 1.3089(9) | 0.4070(9) | 0.4394(10) | 0.063 |

*Table 5.* Atomic parameters.

| Atom | Orbital | $H_{ij}/\text{eV}$ | $\zeta_1$ | $\zeta_2$ | $c_1{}^a$ | $c_2{}^a$ |
|------|---------|--------|------|------|------|------|
| Mo | 5s | −8.34 | 1.96 | | | |
| | 5p | −5.24 | 1.90 | | | |
| | 4d | −10.50 | 4.45 | 1.90 | 0.6097 | 0.6097 |
| O | 2s | −32.3 | 2.275 | | | |
| | 2p | −14.8 | 2.275 | | | |
| P | 3s | −18.6 | 1.75 | | | |
| | 3p | −14.2 | 1.30 | | | |
| N | 2s | −26.00 | 1.95 | | | |
| | 2p | −13.40 | 1.95 | | | |
| C | 2s | −21.40 | 1.625 | | | |
| | 2p | −11.40 | 1.625 | | | |
| H | 1s | −13.60 | 1.300 | | | |

$^a$ Coefficients used in a double-zeta expansion of the metal d orbitals.

hydrogens were in calculated positions, at N2 three hydrogen positions were calculated and the one corresponding to the $sp^2$ hybridization corresponds to a peak in the difference map, its temperature factor was refined and remained small. The crystallographic data for **8a** is given in Table 1 and atomic coordinates in Table 4.

*Theoretical calculations.* The extended Hückel[11] calculations were performed using the structures published for **4** and **8a**. The parameters are given in Table 5.

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