Transformations of Hydrazines $RNHNH_2$ (R = Me, Ph) at a Sulfur-Rich Bimetallic Site: Diazene−Diazenido−Isodiazene/Hydrazido(2−) Interconversions

Philippe Schollhammer,[a] Béatrice Didier,[a] Nathalie Le Grand,[a] François Y. Pétillon,*[a] Jean Talarmin,[a] Kenneth W. Muir,*[b] and Simon J. Teat[c]

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The bis(nitrile) compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)_2](BF_4)$ (**1**) (Cp = C_5H_5) reacted with substituted hydrazines $RNHNH_2$ (R = Me, Ph) in acetonitrile at room temperature to give the stable diazene species $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}HN{=}NR)](BF_4)$ [R= Me (**2**), Ph (**3**)]. Compounds **2** and **3** could be readily deprotonated with BuLi to produce neutral diazenido species $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}N{=}NR)]$ [R = Me (**4**), Ph (**5**)]. Photolysis of **4** in THF induced isomerization of the diazenide bridge, affording the complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N{=}NMe)]$ (**8**). This species underwent protonation at the outer nitrogen atom (N_β) to give the stable isodiazene/hydrazido(2–) complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N{=}NHMe)]$-$(BF_4)$ (**9**) which isomerised slowly back into **2** on warming. The molecular structure of the μ-η^2-methyldiazenido complex **4** was established by an X-ray diffraction study.

Introduction

Transition metal complexes containing sulfur ligands have aroused much attention because of their biological and industrial potential.[1] We have been interested in making sulfur-rich dimolybdenum systems in order to relate their reactivity and electrochemical behaviour to their molecular structure.[2] Recently, we have investigated the chemistry of complexes with a tris-thiolato-bridged dimolybdenum(III) core $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}^+$ (Cp = C_5H_5), and have shown that they are extremely suitable candidates for molecular activation.[3−5] In particular, the chloro-bridged complex $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3]$ reacts with hydrazine and phenylhydrazine to give compounds containing nitrogenous functional groups: hydrazine yields the amido (NH_2)[4] group, while phenylhydrazine leads to the formation of diazenido (N=N−Ph)[5] ligands.

The mechanisms that give rise to these products are only poorly understood, but the products themselves are useful structural and chemical models of key intermediates in the reduction of dinitrogenous substrates to ammonia at a binuclear core.[6] In addition, we have demonstrated that the complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N_\alpha N_\beta Ph)]$ unexpectedly undergoes protonation at the outer nitrogen atom (N_β) to give the μ-η^1-isodiazene derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}NNHPh)](BF_4)$, which, upon warming, readily isomerises into the more thermodynamically favoured μ-η^2-diazene $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}HN{=}NPh)](BF_4)$ species.[5] The molecular structure of this derivative showed that the *cis*-diazene Ph−N=N−H unit is stabilized by the $\{Mo_2Cp_2(\mu\text{-}SMe)_3{}^+\}$ dimolybdenum core.

In order to obtain more information on the interaction of hydrazines with Mo_2 systems we investigated the reactions of $RNHNH_2$ (R = Me, Ph) with another tris-thiolato-bridged compound, namely the bis-nitrile derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)_2](BF_4)$ (**1**), in which the labile nitrile groups conferred a reactivity that was quite different from that of the chloride-bridged complex.[3a] We report here the ready formation of *cis*-diazene species $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}HN{=}NR)](BF_4)$ [R= Me (**2**), Ph (**3**)] and their relationships with their η^1-, η^2-diazenido and η^1-isodiazene/hydrazido(2−) parent molecules. Moreover, we show multiple transformations of methyldiazene and methyldiazenido substrates at a bimetallic site and describe the solid-state structure of a rare η^2-methyldiazenido bridged complex.[7−9]

Results

Syntheses and Spectroscopic Characterisation of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}HN{=}NR)](BF_4)$ [R= Me (2), Ph (3)] and $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}N{=}NR)]$ [R= Me (4), Ph (5)]

A red solution of $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)_2](BF_4)$ (**1**) in acetonitrile reacted with an excess of $MeNHNH_2$ at

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[a] UMR CNRS 6521, Chimie, Electrochimie Moléculaires et Chimie Analytique, Faculté des Sciences, Université de Bretagne Occidentale,
BP 809, 29285 Brest-Cédex, France
[b] Department of Chemistry, University of Glasgow,
Glasgow G 12 8QQ, UK
[c] CLRC Daresbury Laboratory,
Daresbury, Warrington WA4 4AD, UK

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room temperature within 1 h to give a mixture of the two compounds $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\eta^2\text{-HN=NMe})](BF_4)$ (**2a**) and $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-NH}_2)]$ (**6**) [Equation (1)]. Precipitation of **6** from the cooled acetonitrile solution and subsequent workup permitted **2a** to be isolated as a spectroscopically and analytically pure brownish powder in 50−60% yields. Under the same conditions, $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\eta^2\text{-HN=NPh})](BF_4)$ (**3a**) was the only product obtained with $PhNHNH_2$. The yields of **2a** and **3a** were occasionally lowered by the formation of a deactivated paramagnetic derivative of the bis-nitrile complex, namely $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\eta^2\text{-NHCO(Me)})](BF_4)$ (**7**), which was formed in low and varying yields and could also be detected in cyclic voltammetry experiments.[3b]

$$\underset{\mathbf{1}}{[Mo_2Cp_2(\mu\text{-SMe})_3(MeCN)_2](BF_4)} \xrightarrow[CH_3CN]{MeNHNH_2\ \text{(excess)}} \underset{\mathbf{2a}}{[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-NH=NMe})](BF_4)} + \underset{\mathbf{6}}{[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-NH}_2)]} \qquad (1)$$

Complexes **2a** and **3a** were unambiguously formulated as dimolybdenum species $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-HN=NR})](BF_4)$ with R = Me and R = Ph, respectively. Their ^1H NMR ($CDCl_3$) spectra exhibit two inequivalent cyclopentadienyl resonances and three SMe resonances, indicating that the $\{Mo_2Cp_2(\mu\text{-SMe})_3\}$ moiety has been retained. The presence of a H−N=N−R ligand is supported by the observation of a low-field signal (at about $\delta = 12$) typical for the proton of the NH group and of the peaks expected for the R substituent.[7] Two-dimensional heteronuclear ^1H-^{15}N inverse-correlation experiments completed the characterisation of **2a**. The ^{15}N chemical shifts (relative to nitromethane) of the NH and NMe groups could be unambiguously assigned to peaks at $\delta = -18.5$ and $\delta = -31.0$, respectively.

On heating, **2a** and **3a** underwent a change in the orientation of the methyl group of one thiolate bridge [Equation (2)]. This isomerization reaction was complete within 24 h and afforded compounds **2b** and **3b**. Complex **2b** is new but it gives rise to ^1H NMR patterns that resemble those of **2a**, suggesting strongly that the two compounds have very similar structures. In particular, the ^1H NMR spectrum of **2b** shows a resonance at $\delta = 12.3$ attributed to the NH group of the diazo bridge. Compound **3b** was identified by comparison of its ^1H NMR spectroscopic data with that of an authentic sample of the species obtained by protonation of the μ-η²-diazenido derivative $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\eta^2\text{-N=NPh})]$. X-ray analysis has established a *syn* orientation of the methyl groups borne by the two sulfur atoms that lie in the equatorial plane of this molecule.[5]

$$\underset{R = Me\ \mathbf{2a},\ Ph\ \mathbf{3a}}{[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-NH=NR})](BF_4)} \xrightarrow{MeCN/\Delta} \underset{R = Me\ \mathbf{2b},\ Ph\ \mathbf{3b}}{[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-NH=NR})](BF_4)} \qquad (2)$$

Deprotonation of **2a−b** and **3a−b** could readily be carried out with Et_3N or BuLi, and gave the η²-diazenido species $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\eta^2\text{-N=NR})]$ [R = Me (**4a−b**), R = Ph (**5a−b**)] [Equation (3)]. Likewise, complexes **4−5** could readily be protonated to regenerate **2−3**. The absence of a resonance at about $\delta = 12$ in the ^1H NMR spectra of **4a−b** and **5a−b** indicates loss of the NH proton. Complexes **5a−b** have been identified as a pair of isomers, which differ in the orientation of the *S*-methyl substituents, by comparison of their ^1H NMR spectra with those of a mixture of the two isomers of the compound $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\eta^2\text{-N=NPh})]$, previously obtained from the reaction of the chloro-bridged derivative $[Mo_2Cp_2(\mu\text{-Cl})(\mu\text{-SMe})_3]$ with $PhNHNH_2$.[5]

$$\underset{\mathbf{2\text{-}3}}{[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-NH=NR})](BF_4)} \underset{HBF_4}{\overset{BuLi}{\rightleftarrows}} \underset{\mathbf{4\text{-}5}}{[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\eta^2\text{-N=NR})]} \qquad (3)$$

Molecular Structure of $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\eta^2\text{-N=NMe})]$ (4b)

Various bonding modes have been observed for the diazenido ligand.[7,8,10] Sutton et al have recently given a helpful summary of these, and we use their terminology in the following discussion.[8] However, very few of the available structural examples relate to the methyldiazenido ligand.[7−9,11−14]

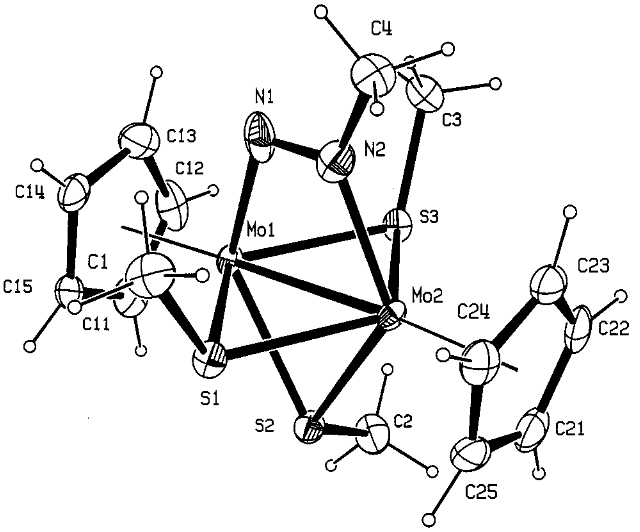


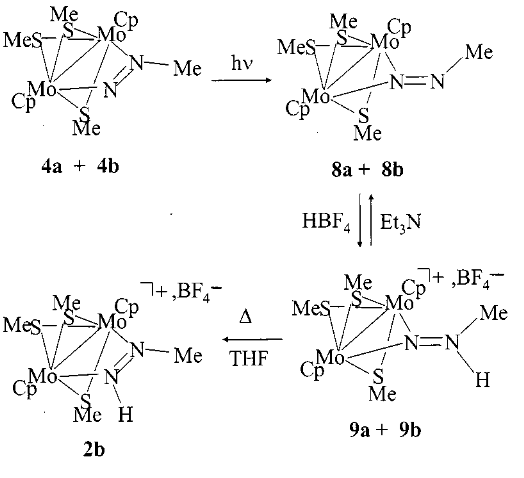
Figure 1. Molecular structure of $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{-}\eta^2\text{-N=NMe})]$ **4b** showing 20% probability ellipsoids; selected bond lengths [Å] and angles [°]: Mo(1)−Mo(2) 2.613(1), Mo(1)−N(1) 2.058(5), Mo(2)−N(2) 2.096(4), N(1)−N(2) 1.202(5), N(2)−C(4) 1.490(6), Mo(1)−S(1) 2.419(1), Mo(1)−S(2) 2.453(1), Mo(1)−S(3) 2.406(1), Mo(2)−S(1) 2.429(1), Mo(2)−S(2) 2.451(1), Mo(2)−S(3) 2.423(1); Mo(1)−S(1)−Mo(2) 65.2(1), Mo(2)−S(2)−Mo(1) 64.4(1), Mo(1)−S(3)−Mo(2) 65.5(1), N(2)−Mo(2)−Mo(1) 68.1(1), N(1)−Mo(1)−Mo(2) 72.2(1), N(2)−N(1)−Mo(1) 107.1(4), N(1)−N(2)−Mo(2) 112.5(4), N(1)−N(2)−C(4) 115.4(4), C(4)−N(2)−Mo(2) 132.0(3)

The structure of **4b** (Figure 1) consists of a tris(μ-thiolato)dimolybdenum unit $\{Mo_2Cp_2(\mu\text{-SMe})_3\}$ bridged by a bidentate, doubly bent N=N−Me group, which is σ-bonded to the Mo_2 unit through both nitrogen atoms [Mo(1)−N(1) = 2.058(5), Mo(2)−N(2) = 2.096(4) Å]. These Mo−N distances differ only slightly from one another. They are shorter than the $Mo-NH_2$ bonds in the amido complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ (**6**) [2.151(2) Å],[4] but not nearly as short as the terminal Mo−NNMe distance of 1.809(3) Å in $[Mo\{N(CH_2CH_2S)_3\}(NNMe)]$, where the Mo−N=N angle is nearly linear.[14] In **4b** the N−N and Mo−Mo bonds are virtually coplanar [N(1)−Mo(1)−Mo(2)−N(2) = 0.1(2)°] and the N(1)−N(2) bond length of 1.202(5) Å is nearly equal to the corresponding value of 1.213(4) Å in $[Mo\{N(CH_2CH_2S)_3\}(NNMe)]$, where the metal-bound N atom is *sp* rather than sp^2-hybridised. The N=N bond lengths in N_2Me ligands in general seem insensitive to the bonding mode of the diazenide: a value of 1.224(11) Å was found in the triply bridging diazenido compound $[\{Mn(CO)_4\}_3(\mu_3\text{-}N_2Me)]$,[11] 1.247(4) Å in the bridging singly bent diazo complex $[CpW(CO)_2(\mu_2\text{-}\eta^2\text{-}N_2Me)Cr(CO)_5]$,[12] and values of 1.215(5) and 1.199(4) Å in the singly bent N_2Me mononuclear complexes $[CpW(CO)_2(N_2Me)]$[13] and $[ReCl(N_2Me)(MeNHNH_2)\{PPh(OEt)_2\}_3][BPh_4]$, respectively.[9]

The endocyclic angles in the Mo_2N_2 ring [72.2(1) and 68.1(1)° at Mo, 107.1(4) and 112.5(4)° at N(1) and N(2)] resemble those in related strained four-membered M_2N_2 ring derivatives such as $[\{C_5Me_5Ir(CO)\}_2(\mu\text{-}\eta^2\text{-}p\text{-}N_2C_6H_4OMe)]$[8] and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}N_2C_6H_5)]$.[10] The Mo(1)−Mo(2) distance [2.613(1) Å] is typical for a quadruply bridged $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ dimolybdenum(III) compound and indicates the bond of unit order required by electron counting rules.[2]

Synthesis and Spectroscopic Characterisation of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N{=}NMe)]$ (8) and $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N{=}NHMe)](BF_4)$ (9)

Photolysis of a red solution of **4** in THF afforded an orange solution of the complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N{=}NMe)]$ (**8**) (Scheme 1). Conversion of **4** into **8** was complete within 48 h. ^1H NMR analysis of **8** revealed the presence of two isomeric species, which are believed to differ only in the orientation of a single SMe group. The ^1H NMR spectrum shows two similar sets of resonances: two peaks between δ = 6 and δ = 5, a single signal at about δ = 3.4 and three peaks between δ = 2 and δ = 1, which can be assigned to inequivalent cyclopentadienyl ligands, the NMe end of the diazo bridge, and the three SMe groups, respectively.



Scheme 1

The mode of coordination of the diazenido bridge in **8** is preserved in the orange cationic complex **9**, which is formed by addition of HBF_4 to a solution of **8** (Scheme 1). Compound **9** could be identified without any ambiguity by ^1H NMR spectroscopy. Its ^1H NMR spectrum displays two sets of characteristic resonances assigned to the $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ cores of two isomers. In addition, two similar patterns consisting of a doublet ($J_{H,H}$ = 4.0 Hz) at δ = 3.56 and 3.64, and a single broad resonance at δ = 11.98 and 12.64 can be attributed to an $H-N-CH_3$ group. Irradiation of the signals at δ = 11.98 and 12.64 gave two singlets at δ = 3.56 and 3.64, which confirms the $^3J_{H,H}$ coupling. Furthermore, variable-temperature ^1H NMR experiments (between 293 and 340 K) show that the line shape is temperature dependent, suggesting that isomer **9a** is fluxional. On warming to 330 K in CD_3CN, broadening and coalescence of the cyclopentadienyl signals of **9a** occurred. The activation barrier of the resulting dynamic process, estimated from the chemical shift difference $\Delta\nu$ and the coalescence temperature of the Cp signals in the ^1H NMR spectrum [$\Delta G^{\neq} = 4.575T_c(9.972 + \log_{10}T_c - \log_{10}\Delta\nu)$], is 71 ± 1 kJ·mol^{-1}.[15] A similar behaviour ($\Delta G^{\neq}$ = 61 ± 1 kJ·mol^{-1}) has previously been reported for the analogous phenyl derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N{=}NHPh)](BF_4)$ (**10**), in which the methyl groups of the equatorial thiolate bridges are in an *anti* configuration.[5] The dynamic behaviour of **9** and **10** is attributable to rotation of the NHR group around the N=N bond axis.

Compound **9** was easily deprotonated to regenerate **8** (Scheme 1), and thermolysis of a mixture of **9a** and **9b** afforded complex **2b** exclusively (Scheme 1).

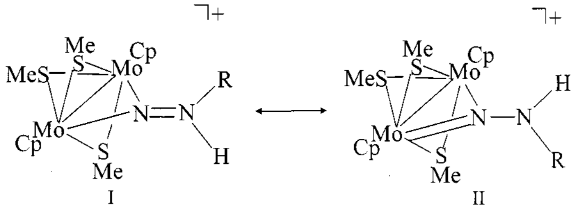
Discussion

Protic diazenes, RN=NH, are reactive species that readily decompose into RH by an N_2 extrusion process.[7,16] Such molecules may be stabilized through coordination to one or two metal centres. There are several reports of the formation of protic diazene complexes by insertion of aryldiazonium reagents ArN_2^+ into a metal-hydride bond or by oxidation of a suitable hydrazine $RNHNH_2$ (R = aryl, alkyl or H), previously coordinated to a metal centre.[7,9,17−19] The latter route has been used to effect the synthesis of methyldiazene derivatives.[9,19] However, it remains unclear precisely how substituted hydrazines $RNHNH_2$ (R = Me, Ph) undergo dehydrogenation upon treatment with $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)_2](BF_4)$ (**1**). It has not been possible to detect the loss of H_2 or the formation of any other side products arising from the eventual disproportionation or deprotonation of hydrazines.[20] The formation of the amido derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ (**6**) from methylhydrazine indicates that the reagent does undergo disproportionation, but **6** has not been isolated from the analogous reaction with phenylhydrazine. We assume that **6** can be formed by reaction of **1** with ammonia at room temperature, but that has no bearing on the formation of **2**−**3** through a disproportionation mechanism.[21] However, the hydrido complex $[HOs(CO)_{10}(\mu\text{-}\eta^2\text{-}N_2Ph)]$ was formed by reaction of phenylhydrazine with the triosmium derivative $[Os_3(CO)_{10}(MeCN)_2]$.[10] This suggests that the protons of the hydrazine can add to a metal centre and that subsequent elimination of H_2 or deprotonation may afford diazenido or diazene species.

The deprotonation of the diazene species **2a** allowed us to compare the behaviour of methyldiazene and methyldiazenido substrates at a bimetallic site with that of the related phenyl ligands that we have described previously.[5,6] $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}N{=}NMe)]$ (**4**) was completely transformed by photolysis into its η^1 isomer $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N{=}NMe)]$ (**8**). It is worth noting that **8** was readily protonated at the outer nitrogen (N_β) atom and that the protonated product $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N{=}NHMe)](BF_4)$ (**9**) was easily isolated as a powder that could be stored for several weeks under a nitrogen atmosphere without isomerizing into **2**. Compound **9** is reasonably stable in solution, and its isomerization into the $\{\mu\text{-}\eta^2\text{-}HN{=}NMe\}$ species **2** was observed only after it had been kept for long periods in solution at ambient temperature (for example, during attempts at recrystallization) or when the solution had been heated. This contrasts with the behaviour of the phenyl analogue **10**, which isomerizes readily at room temperature, and which can be stored in solution only after cooling. The methyl group is evidently more effective than the phenyl group at stabilizing the $\{\mu\text{-}\eta^1\text{-}N{=}NHR\}$ system, and the outer nitrogen atom in $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N{=}NR)]$ complexes is obviously more basic when R = Me. Attempted protonation of the outer nitrogen atom in a doubly bent η^1-N=NR bridge has usually been unsuccessful.[8,10]

In mononuclear complexes containing a terminal doubly bent diazenido ligand it has been shown that the inner nitrogen atom (N_α) is more basic than the N_β atom, and is therefore more easily protonated to give diazene groups.[8] In complexes like $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N{=}NR)]$ the inner nitrogen atom is coordinated to both metal atoms and only the outer nitrogen can be protonated.

The facile $\mu\text{-}\eta^1 \rightarrow \mu\text{-}\eta^2$ rearrangement process observed in $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}N_2HR)]^+$ species, with concomitant migration of the proton from the outer to the inner nitrogen atom to give an η^2-NH=NR species, reveals the flexible nature of the $(\mu\text{-}\eta^1\text{-}N_2HR)$ bridge, especially when R= phenyl. The values of the energy barrier for rotation of the NHR group about the N−N axis in **9** and **10** are in agreement with a greater lability of the diazo bridge when R = Ph than when R = Me. Indeed, replacement of a phenyl by a methyl group increases the energy barrier ($\Delta G^{\neq}$) by about 10 kJ/mol. This suggests that the $\eta^1\text{-}N_2HR$ bridging ligand is better described as an hydrazido(2−) limiting form when R = Ph (II in Scheme 2) and as an isodiazene form when R = Me (I in Scheme 2). The greater electron-withdrawing ability of Ph than Me is consistent with this suggestion. In addition, preliminary electrochemical experiments on the protonated diazenido complexes[22] show that oxidation, which can be compared with the electronic effect of replacing Me by Ph, favours the $\mu\text{-}\eta^1 \rightarrow \mu\text{-}\eta^2$ isomerisation. Moreover, in reactions with bases the cation $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)_2]^+$, ($\mathbf{1}^+$), releases both of its terminal nitrile ligands more easily than $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3]$ loses its bridging chloride group, thus explaining the formation of different products, η^2-diazene derivatives from $\mathbf{1}^+$, but η^1-diazenido species from the μ-chloro complex.



Scheme 2

Experimental Section

General Procedures: All the reactions were performed under nitrogen using standard Schlenk techniques. Solvents were deoxygenated and dried by standard methods. IR spectra were recorded on a Perkin−Elmer 1430 spectrophotometer from KBr pellets. Chemical analyses were performed by the Centre de Microanalyses du CNRS, Vernaison, France. ^1H NMR spectra were recorded on either a Bruker AC300 or AMX3 400 spectrometer and were referenced to $SiMe_4$. $^1H\text{-}^{15}N$ HMBC NMR spectra were recorded on a Bruker 500 and AMX3 400 spectrometer by R. Pichon and N. Kervarec. Literature methods were used for the preparation of $[Cp_2Mo_2(\mu\text{-}SMe)_3(CH_3CN)_2](BF_4)$ (**1**).[23]

Preparation of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}HN{=}NMe)](BF_4)$ (2a): An excess of methylhydrazine (72 μL, 1.36 mmol) was added to a solution of **1** (0.32 mmol, 200 mg) in 15 mL of acetonitrile. The mixture was stirred at room temperature for one hour, whereupon the colour of the mixture changed from red to orange and then a brown solid of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ (**6**) precipitated. Precipitation of **6** was completed by concentration and cooling of the solution (yields: 54 mg, 35%). The solution was then filtered off and the solvents evaporated under vacuum to afford a brown residue that was washed with pentane (2 × 10 mL). Complex **2a** was obtained as a brown powder (yield: 104 mg, 55%). $C_{14}H_{24}BF_4N_2Mo_2S_3$ (595.2): calcd. C 28.3, H 3.9, N 4.7; found C 28.1, H 4.3, N 5.3. Selected spectroscopic data for **2a**: ^1H NMR ($CDCl_3$, 298 K): δ = 1.54 (s, 3 H, SCH_3), 1.63 (s, 3 H, SCH_3), 1.77 (s, 3 H, SCH_3), 3.69 (s, 3 H, $HN{=}NCH_3$), 5.70 (s, 5 H, C_5H_5), 5.88 (s, 5 H, C_5H_5), 12.30 (s, 1 H, $HN{=}NCH_3$). IR (KBr): $\tilde{\nu}$ = 3160 cm^{-1} (w), [ν(N−H)], 1150−950 (s) [ν(B−F)].

Preparation of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}HN{=}NPh)](BF_4)$ (3a): An excess of phenylhydrazine (54 μL, 0.48 mmol) was added at room temperature to an acetonitrile (10 mL) solution of **1** (0.16 mmol, 100 mg). The mixture was stirred for one hour and the solution turned orange. The volume of the mixture was then reduced under vacuum and diethyl ether was added to precipitate the brown-orange product **3a** (yield: 73 mg, 70%). $C_{19}H_{25}BF_4N_2Mo_2S_3$ (656.3): calcd. C 34.8, H 3.8, N 4.3; found C 35.3, H 4.2, N 4.3. Selected spectroscopic data for **3a**: ^1H NMR (CD_2Cl_2, 298 K): δ = 1.71 (s, 3 H, SCH_3), 1.73 (s, 3 H, SCH_3), 1.81 (s, 3 H, SCH_3), 5.85 (s, 5 H, C_5H_5), 6.03 (s, 5 H, C_5H_5), 7.32−6.79 (m, 5 H, $HN{=}NC_6H_5$), 12.0 (s, 1 H, $HN{=}NC_6H_5$). IR (KBr): $\tilde{\nu}$ = 3200 cm^{-1} (w) [ν(N−H)], 1200−900 (s), [ν(B−F)].

Preparation of [Mo_2Cp_2(μ-SMe)$_3$(μ-η^2-HN=NR)](BF_4) [R = Me (2b), R = Ph (3b)]: A solution of **2a** (0.17 mmol, 100 mg) in 10 mL of acetonitrile was warmed to 70 °C for 24 h. The solution turned green. The solution was then concentrated and addition of diethyl ether precipitated a green powder, which was washed twice with pentane (2 × 10 mL). Complex **2b** was obtained as a green powder (yield: 96 mg, 95%). $C_{14}H_{24}BF_4N_2Mo_2S_3$ (595.2): calcd. C 28.2, H 3.9, N 4.7; found C 28.0, H 4.2, N 5.3. Selected spectroscopic data for **2b**: ^1H NMR ($CDCl_3$, 298 K): δ = 1.45 (s, 3 H, SCH_3), 1.58 (s, 3 H, SCH_3), 1.63 (s, 3 H, SCH_3), 3.79 (s, 3 H, $HN{=}NCH_3$), 5.77 (s, 5 H, C_5H_5), 5.91 (s, 5 H, C_5H_5), 12.58 (s, 1 H, $HN{=}NCH_3$). IR (KBr): 3080 cm^{-1} (w), $\tilde{\nu}$ = [ν(N−H)], 1200−950 (s), [ν(B−F)].

In a similar manner, the complex **3b** was obtained as an orange powder (yield: 88 mg, 90%) upon warming **3a** (0.15 mmol, 98 mg). Selected spectroscopic data for **3b**:[5] ^1H NMR (CD_3CN, 298 K): δ = 1.52 (s, 3 H, SCH_3), 1.65 (s, 3 H, SCH_3), 1.72 (s, 3 H, SCH_3), 5.79 (s, 5 H, C_5H_5), 6.11 (s, 5 H, C_5H_5), 7.42−6.93 (m, 5 H, $HN{=}NC_6H_5$), 12.6 (s, 1 H, $HN{=}NC_6H_5$).

Preparation of [Mo_2Cp_2(μ-SMe)$_3$(μ-η^2-N=NMe)](BF_4) (4a−b): 100 μL of a 2.5 M solution of butyllithium in hexane (0.25 mmol) was added to a dichloromethane (10 mL) solution of **2a** or **2b** (100 mg, 0.17 mmol). The solution rapidly turned red. After stirring for a few minutes at ambient temperature, the solvent was evaporated. The residue was extracted with diethyl ether and the extract was purified by chromatography on a silica gel column. Elution with a mixture of THF/Et_3N (90:10) afforded compounds **4a** (yield: 60 mg, 70%) and **4b** (yield: 56 mg, 65%).
4a: ^1H NMR ($CDCl_3$, 298 K): δ = 1.29 (s, 3 H, SCH_3), 1.44 (s, 3 H, SCH_3), 1.69 (s, 3 H, SCH_3), 3.41 (s, 3 H, $N{=}NCH_3$), 5.44 (s, 5 H, C_5H_5), 5.67 (s, 5 H, C_5H_5).
4b: ^1H NMR ($CDCl_3$, 298 K): δ = 1.31 (s, 3 H, SCH_3), 1.38 (s, 3 H, SCH_3), 1.48 (s, 3 H, SCH_3), 3.45 (s, 3 H, $N{=}NCH_3$), 5.45 (s, 5 H, C_5H_5), 5.68 (s, 5 H, C_5H_5).

In similar manner, complexes **5a−b** were obtained as green powders (yield: **5a**: 55 mg, 65%; **5b**: 60 mg 70%) by reacting BuLi with **3a** or **3b** (0.15 mmol, 100 mg).
5a:[5] ^1H NMR ($CDCl_3$, 298 K): δ = 1.49 (s, 3 H, SCH_3), 1.50 (s, 3 H, SCH_3), 1.68 (s, 3 H, SCH_3), 5.31 (s, 5 H, C_5H_5), 5.85 (s, 5 H, C_5H_5), 7.13−6.59 (m, 5 H, $HN{=}NC_6H_5$).
5b:[5] ^1H NMR ($CDCl_3$, 298 K): 1.37 (s, 3 H, SCH_3), 1.45 (s, 3 H, SCH_3), 1.53 (s, 3 H, SCH_3), 5.44 (s, 5 H, C_5H_5), 5.89 (s, 5 H, C_5H_5), 7.20−6.61 (m, 5 H, $HN{=}NC_6H_5$).

Photolysis of [Mo_2Cp_2(μ-SMe)$_3$(μ-η^2-N=NMe)](BF_4) (4a−b): A mixture of **4a** and **4b** (100 mg, 0.20 mmol) was dissolved in 20 mL of THF and irradiated with UV light [Hanau TQ 150 mercury-vapour lamp (300−600 nm)] for 48 h at room temperature. The solution changed from red to orange during this time. THF was removed under vacuum and the residue was purified by chromatography on a silica gel column. Elution with THF/Et_3N (90:10) afforded an orange band containing **8a−b** (yields: 60 mg, 60%).
8a: (80%). ^1H NMR ($CDCl_3$, 298 K): δ = 1.20 (s, 3 H, SCH_3), 1.27 (s, 3 H, SCH_3), 1.90 (s, 3 H, SCH_3), 3.41 (s, 3 H, $N{=}NCH_3$), 5.35 (s, 5 H, C_5H_5), 5.53 (s, 5 H, C_5H_5).
8b: (20%). ^1H NMR ($CDCl_3$, 298 K): δ = 1.18 (s, 3 H, SCH_3), 1.46 (s, 3 H, SCH_3), 1.83 (s, 3 H, SCH_3), 3.43 (s, 3 H, $N{=}NCH_3$), 5.44 (s, 5 H, C_5H_5), 5.62 (s, 5 H, C_5H_5).

Preparation of Complexes [Mo_2Cp_2(μ-SMe)$_3$(μ-η^1-N=NHMe)](BF_4) (9a−b): 1 Equiv. of $HBF_4{\cdot}Et_2O$ was added to a solution of **8** (100 mg, 0.20 mmol) in Et_2O (10 mL). Orange solids of [Mo_2Cp_2(μ-SMe)$_3$(μ-η^1-N=NHMe)](BF_4) (**9**) precipitated from the solution and were collected by filtration and then washed with pentane (yields: 112 mg, 85%). $C_{14}H_{24}BF_4N_2Mo_2S_3$ (595.2): calcd. C 28.3, H 3.9, N 4.7; found C 29.0, H 4.1, N 4.7. Selected spectroscopic data for **9a**: ^1H NMR ($CDCl_3$, 298 K): δ = 1.51 (s, 3 H, SCH_3), 1.64 (s, 3 H, SCH_3), 2.08 (s, 3 H, SCH_3), 3.64 (d, $J_{H,H}$ = 4 Hz, 3 H, $N{=}NHCH_3$), 5.88 (s, 5 H, C_5H_5), 5.97 (s, 5 H, C_5H_5), 12.40 (s, 1 H, $N{=}NHCH_3$). Selected spectroscopic data for **9b**: ^1H NMR ($CDCl_3$, 298 K): δ = 1.47 (s, 3 H, SCH_3), 1.49 (s, 3 H, SCH_3), 1.98 (s, 3 H, SCH_3), 3.56 (d, $J_{H,H}$ = 4 Hz, 3 H, $N{=}NHCH_3$), 5.96 (s, 5 H, C_5H_5), 6.03 (s, 5 H, C_5H_5), 11.97 (s, 1 H, $N{=}NHCH_3$). IR (KBr): $\tilde{\nu}$ = 3220 cm^{-1} (w), [ν(N−H)], 1200−900 (s), [ν(B−F)].

Structure Analysis: Details of the structure analysis of **4b** are summarised in Table 1.[25] The crystals were very thin plates and it was necessary to use synchrotron radiation in conjunction with a Bruker SMART diffractometer to get measurable diffraction patterns. The structure was solved and refined by standard methods.[24] The cyclopentadienyl rings were treated as variable metric rigid groups.

Table 1. Crystallographic data for [Mo_2Cp_2(μ-SMe)$_3$(μ-η^2-N=NMe)] **4b**

	4b
Empirical formula	$C_{14}H_{22}Mo_2N_2S_3$
Fw	506.40
Temperature [K]	160(2)
Wavelength [Å]	0.68490
Cryst system	Orthorhombic
Space group	*Pbca*
a [Å]	11.9830(5)
b [Å]	16.1544(7)
c [Å]	17.5702(7)
V [Å^3]	3401.2(2)
Z	8
$D_{calcd.}$ [Mg/m^3]	1.978
μ [mm^{-1}]	1.837
F(000)	2016
Crystal size [mm]	0.52 × 0.18 × 0.01
θ range [deg]	2.23 to 23.0
Index ranges	$-13 \leq h \leq 14$ $-18 \leq k \leq 20$ $-23 \leq l \leq 22$
No. of rflns collected	14135
No. of indep rflns	2639 [R_{int} = 0.065]
Refinement method	Full-matrix least-squares on F^2
No. of data/params	2639/178
Goodness of fit on F^2	1.10
$R1$, w$R2$ [$I > 2\sigma(I)$]	0.038 0.062
$R1$, w$R2$ (all data)	0.054 0.065
$\Delta\rho$ range, e·A^{-3}	+1.13 to −0.75

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[25] CCDC-170095 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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