$\eta^1 - \eta^2$ Rearrangement and Protonation of Phenyldiazo Bridging Ligands Attached to the Dimolybdenum System {Mo₂Cp₂(μ -SMe)₃}

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Summary: Rearrangements and protonation reactions of phenyldiazo ligands bound to the bimetallic center, $\{Mo_2-Cp_2(\mu-SMe)_3\}$, are reported.

The organometallic chemistry involved in the transformation $M(N_2) \rightarrow M(N_2R) \rightarrow M(N_2R_2) \rightarrow M(N_2R_3)$, where M is a transition-metal core and R = H, aryl, or alkyl, is relevant to the modeling of N2 reduction by metalloenzymes¹ and to the synthesis of nitrogencontaining organic compounds. The generation of such compounds, either directly from molecular nitrogen or indirectly from diazenido (RN=N⁻) or hydrazido(2-) (RN-NR²⁻) precursors, through C-N bond formation is a currently developing field of organic synthesis.^{1a,2} In this communication we present evidence which gives new insight into catalytic and stoichiometric processes which involve the activation and transformation of dinitrogenous substrates by a *bimetallic* center.³ Α diazenido complex is usually regarded as the first intermediate in the reduction of the dinitrogen molecule; its alkylation or protonation leads to hydrazido(2-) and diazene (RN=NR) species.⁴ The coordination of the diazenido ligand to a single metal atom has been extensively studied and its various modes of bindingsingly bent, doubly bent, or side-on-are well understood.^{1b,5} Much less is known about its behavior as a bridging ligand in di- or polynuclear compounds.⁶ Accordingly, we have studied the reactions of nitrogenous substrates with dimolybdenum systems containing a {Mo₂(μ -SMe)_n} (n = 1-3) core^{3g,7} and now describe the

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formation of μ - η^{1-} and μ - η^{2-} phenyldiazenido complexes [Mo₂Cp₂(μ -SMe)₃(μ - η^{1-} N₂Ph)] (**2**) and [Mo₂Cp₂(μ -SMe)₃(μ - η^{2-} N₂Ph)] (**3**), of the μ - η^{1-} hydrazido(2–) (or isodiazene) compound [Mo₂Cp₂(μ -SMe)₃(μ - η^{1-} NNHPh)]BF₄ (**4**), and of the μ - η^{2-} diazene species [Mo₂Cp₂(μ -SMe)₃(μ - η^{2-} NHN-Ph)]BF₄ (**5**). Some stereochemical aspects of these reactions are also briefly considered.

The thermal reaction of the complex $[Mo_2Cp_2(\mu-SMe)_3 (\mu$ -Cl)] (1) with PhNHNH₂ (2 equiv) in THF at 70 °C for 6 h afforded a red-brown solution from which the complexes 2 and 3 were isolated in 50% and 20% yields as red and green powders (Scheme 1).8 The reaction conditions can be modified to favor formation of 2 (1 week, 20 °C, yield 70%) or 3 (72 h, 70 °C, yield of 2 30%, yield of 3 40%). Thermolysis or photolysis of 2 or 3 gave mixtures containing both isomers, showing that, whatever the initial mode of coordination of the phenyldiazo bridge (η^1 or η^2), it can rearrange to give the alternative isomer (Scheme 2). Compounds 2 and 3 were characterized by elemental analyses and IR and ¹H NMR spectroscopy. The ¹H NMR (in CDCl₃) spectra of **2** and **3** exhibited two inequivalent cyclopentadienyl ligand resonances and three SMe resonances, indicating that the complexes had a $\{Mo_2Cp_2(\mu-SMe)_3\}$ core and that the fourth bridge was not symmetric. Two isomers for 3 differing in the orientation of the S-methyl substituents relative to the Mo-Mo axis were detected in a 85: 15 ratio. The presence of the N₂Ph group was supported

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⁽⁸⁾ Preparation of 2 and 3: A solution of complex 1 (0.2 g, 0.4×10^{-3} mol) and PhNNH₂ (80 μ L, 0.8×10^{-3} mol) in THF (30 cm³) was heated at 70 °C for 6 h. The solution, initially green, became brownish red. After filtration (elimination of NH₄Cl) and evaporation of the solvent, the residue was chromatographed on a silica gel column. Elution with CH₂Cl₂–THF (9:1) afforded a red band containing 2. Complex 3 was then eluted with THF as a green band. Compounds 2 and 3 were washed with pentane and obtained as red and green airstable powders, respectively, with yields depending on the reaction conditions. Compounds 2 and 3 are relatively stable in solution. According to the described conditions the yields are 50% (0.11 g) for 2 and 20% (0.045 g) for 3.2: ¹H NMR (CDCl₃) δ 7.3 (m, 2H, Ph), 7.16 (t, 1H, Ph), 6.45 (d, 2H, Ph), 5.57 (s, 5H, Cp), 4.98 (s, 5H, Cp), 1.87 (s, 3H, SMe), 1.56 (s, 3H, SMe), 1.39 (s, 3H, SMe); IR (KBr, cm⁻¹) 1595 ν (N=N). Anal. Calcd for $Mo_2Cl_3H_2M_2S_3$: C, 40.1; H, 42: N, 4.9. Found: C, 40.8; H, 4.4; N, 5.4.3: ¹H NMR (CDCl₃) for 3a (85%) δ 7.2 (m, 2H, Ph), 7.03 (t, 1H, Ph), 6.61 (d, 2H, Ph), 5.89 (s, 5H, Cp), 5.44 (s, 5H, Cp), 1.53 (s, 3H, SMe), 1.45 (s, 3H, SMe), 1.37 (s, 3H, SMe); ¹H NMR (CDCl₃) for 3b (15%) δ 7.13 (m, 2H, Ph), 7.11 (m, 1H, Ph), 6.59 (m, 2H, Ph), 5.85 (s, 5H, Cp), 5.31 (s, 5H, Cp), 1.68 (s, 3H, SMe), 1.50 (s, 3H, SMe), 1.49 (s, 3H, SMe). Anal. Calcd for $Mo_2Cl_3H_2AN_2S_3$: C, 40.1; H, 4.2; N, 4.9. Found: C, 40.3; H, SMe), 1.49 (s, 3H, SMe), 1.41 (m, 1H, Ph), 6.59 (m, 2H, Ph), 5.53 (s, 5H, Cp), 5.31 (s, 5H, Cp), 1.68 (s, 3H, SMe); 1.50 (s, 3H, SMe), 1.49 (s, 3H, SMe). Anal. Calcd for $Mo_2Cl_3H_2AN_2S_3$: C, 40.1; H, 4.2; N, 4.9. Found: C, 41.1; H, 4.1; N, 5.1.

Scheme 1







by the observation of phenyl resonances in the ¹H NMR spectra and by the elemental analyses.⁸ For **2** a band at 1595 cm⁻¹ in the IR spectrum was assignable to ν (N=N), whereas for **3** such a vibration could not be unambiguously assigned. The coordination mode of the diazenido bridge in **2** was determined by an X-ray analysis (Figure 1).⁹ The molecular structure of **2** is typical of a tetrabridged dinuclear complex of molyb-denum(III): the Cp-Mo-Mo-Cp unit is nearly linear (Cp = C₅H₅ ring centroid), and a four-legged piano-stool geometry around each Mo atom is supplemented by the single metal-metal bond (Mo(1)-Mo(2) = 2.5780(3) Å) required by normal electron counting rules.¹⁰ The phenyldiazenido ligand bridges the two molybdenum atoms in an η^1 fashion. The N(1)-N(2) distance (1.255-



Figure 1. View of a molecule of $[Cp_2Mo_2(\eta^{1}-\mu-NNPh)(\mu-SMe)_3]$ (2) showing 50% probability ellipsoids. Hydrogen atoms are shown as spheres of arbitrary size. Selected distances (Å) and angles (deg): Mo(1)-N(1), 2.084(2); Mo(1)-S(1), 2.474(1); Mo(1)-S(2), 2.458(1); Mo(1)-S(3), 2.476-(1); Mo(1)-Mo(2), 2.5780(3); N(1)-N(2), 1.255(3); Mo(2)-N(1), 2.036(2); Mo(2)-S(1), 2.462(1); Mo(2)-S(2), 2.466(1); Mo(2)-S(3), 2.483(1); N(2)-C(4), 1.440(3); Mo(2)-N(1)-Mo(1), 77.47(7); N(2)-N(1)-Mo(2), 132.6(2); N(2)-N(1)-Mo(1), 149.9(2); N(1)-N(2)-C(4), 116.3(2); Mo(1)-N(1)-N(2)-C(4), -8.0(4); N(1)-N(2)-C(4)-C(5), -60.4(3).

(3) Å) is consistent with a N=N double bond. The slight asymmetry in the Mo-N₂Ph-bridge bond lengths (Mo-(1)-N(1) = 2.084(2) Å, Mo(2)-N(1) = 2.036(2) Å) is most probably attributable to the steric effect of the N-phenyl group. These Mo-N distances are shorter than the 2.151(2) Å found in the amido complex [Mo₂Cp₂(μ -SMe)₃- $(\mu$ -NH₂)], and the Mo(1)-N(1)-Mo(2) angle is slightly more open (cf. 77.5(1) and 73.3(1)°), indicating some π -acceptor character for the diazenido ligand.^{3g} This conclusion is also consistent with the coplanarity of N(1), N(2), Mo(1), Mo(2), and C(4). As has been observed for other bridging aryldiazenido ligands, the orientation of the aromatic ring precludes conjugation between it and the N=N π -bond.⁶ **3** has not yet been characterized by X-ray analysis, but preliminary results¹¹ for its η^2 -MeN=N analogue indicate a strong N=N bond of 1.200-(5) Å and Mo-N and Mo-NMe distances (2.059(5) and 2.097(4) Å) comparable with those in 2.

Protonation of **2** and **3** led respectively to the η^{1} -hydrazido(2–) (or isodiazene) complex [Mo₂Cp₂(μ -SMe)₃- $(\mu-\eta^{1}-NNHPh)$]BF₄ (**4**) and its η^{2} -diazene isomer [Mo₂-Cp₂(μ -SMe)₃($\mu-\eta^{2}$ -NHNPh)]BF₄ (**5**) (Scheme 2).¹² Deprotonation of **4** and **5**, easily effected with Et₃N, gives the starting complexes **2** and **3**. Compounds **4** and **5** were characterized by ¹H NMR, elemental analyses, and IR.¹¹ In the ¹H NMR spectra resonances due to the NH group were detected for **4** and **5** at 12.9 and 12.6 ppm, respectively. The IR spectra of **4** and **5** display ν (NH) bands at 3170 and 3220 cm⁻¹, respectively. The structure of complex **5** has been confirmed by X-ray analysis (Figure 2).¹³ There are three crystallographically independent cations (n = 1-3) which display essentially identical bond lengths and angles. The N=N bonds

⁽⁹⁾ Crystallographic data for $[Cp_2Mo_2(\eta^1,\mu-NNPh)(\mu-SMe)_3]$ (2): C_{19} -H₂₄Mo₂N₂S₃, M_r = 568.46, monoclinic, space group $P2_1/c$, a = 9.1807-(3) Å, b = 13.9964(7) Å, c = 16.8168(12) Å, $\beta = 96.859(4)^\circ$, V = 2145.4(2) Å³, Z = 4, $D_c = 1.760$ g cm⁻³, μ (Mo K α) = 1.467 mm⁻¹. The intensities of 8182 reflections with θ (Mo K α) < 30.4° were corrected for minor (2.9%) crystal decomposition and for absorption (transmission factors 0.656-0.856). Refinement of 236 parameters on F^2 using all 6472 unique reflections ($R_{int} = 0.017$; 5227 with $I > 2\sigma(I)$ gave $R[I > 2\sigma(I)]$ = 0.028 and wR2(all data) = 0.076; $|\Delta\rho| < 0.65$ e Å⁻³. (10) Schollhammer, P.; Guénin, E.; Poder-Guillou, S.; Pétillon, F.

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Figure 2. View of one of the $[Cp_2Mo_2(\eta^2-\mu-NHNPh)(\mu-SMe)_3]$ cations in **5** with 50% probability ellipsoids. Hydrogen atoms are shown as spheres of arbitrary size. Selected distances (Å) and angles (deg) for the three independent cations n = 1-3: Mo(n1)-N(n1), 2.018(9), 2.029(9), 2.011(9); Mo(n1)-S(n3), 2.434(4), 2.439(4), 2.435-(4); Mo(n1)-S(n1), 2.443(4), 2.446(4), 2.444(4); Mo(n1)-S(n2), 2.456(4), 2.457(4), 2.460(3); Mo(n1)-Mo(n2), 2.650-(2), 2.657(2), 2.644(2); Mo(n2)-N(n2), 2.137(8), 2.128(8), 2.101(9); Mo(n2)-S(n3), 2.431(4), 2.438(4), 2.434(4); Mo(n2)-S(n1), 2.440(4), 2.444(4), 2.445(4); Mo(n2)-S(n2), 2.476(4), 2.471(4), 2.467(4); N(n1)-N(n2), 1.324(11), 1.307-(11), 1.309(12); N(n2)-C(n14), 1.424(10), 1.432(10), 1.438-(11); N(n2)-N(n1)-Mo(n1), 112.2(6), 112.0(7), 113.4(7); N(n1)-N(n2)-Mo(n2), 105.1(6), 105.9(6), 104.6(7).

(mean 1.313(7) Å) are slightly longer than in **2**, as are the Mo–Mo bonds (mean 2.650(4) Å). Unsurprisingly, the Mo(n1)–N bonds (mean 2.02(1) Å) are shorter than the Mo(n2)–N bonds (mean 2.12(1) Å).

Complex **4** exhibits dynamic behavior attributable to rotation of the NHPh group around the N=N bond axis with $\Delta G^{\ddagger} = 61.3 \pm 1 \text{ kJ mol}^{-1}$ (Scheme 3), which

(13) Crystallographic data for {[Cp₂Mo₂(η^2 - μ -NHNPh)(μ -SMe)₃]-[BF₄]₃·2CH₂Cl₂·1/₂OEt₂(5): C₆₁H₈₄B₃Cl₄F₁₂Mo₆N₆O_{1/2}S₉, M_r = 2175.75, triclinic, space group *P*1, a = 12.509(3) Å, b = 17.052(3) Å, c = 21.170. (4) Å, α = 66.67(3)°, β = 86.02(3)°, γ = 75.34(3)°, *V* = 4009.0(14) Å³, *Z* = 2, D_c = 1.802 g cm⁻³, μ (Mo K α) = 1.348 mm⁻¹. The intensities of 15 886 reflections with θ (Mo K α) < 25.0° were corrected for absorption (transmission factors 0.58–0.88). Refinement of 784 parameters on F^2 using all 14 038 unique reflections ($R_{\rm int}$ = 0.128; 5612 with $I > 2\sigma(I)$] = 0.064 and wR2(all data) = 0.168; $|\Delta \rho| < 0.96$ e Å⁻³. The asymmetric unit contains three ordered dimolybdenum cations, three BF₄⁻ anions (all disordered), two CH₂Cl₂ solvates (one disordered), and a diethyl ether molecule disordered over an inversion center. Solvate and anion disorder, together with the small size of the specimen (0.21 × 0.15 × 0.06 mm), have adversely affected the precision of the analysis.



indicates that the contribution of the hydrazido(2–) resonance form of the NNHPh bridge is significant. Complex **4** in solution at room temperature or on mild heating gives the μ - η^2 -NHNPh complex **5**. The intermediate **6** was observed but not isolated. Its ¹H NMR spectrum in CD₂Cl₂ showed a resonance at 12.0 ppm for the NH group, phenyl resonances between 7.32 and 6.79 ppm, two inequivalent cyclopentadienyl groups at 6.03 and 5.85 ppm, and three peaks for the SMe bridges at 1.71, 1.73, and 1.81 ppm. Evidently the rearrangement involves inversion of one SMe group and $\eta^1 \rightarrow \eta^2$ isomerization of the diazo bridge accompanied by transfer of a proton across the N–N bond. Complete identification of **6** will allow us to confirm the order of these steps.

In summary, we have synthesized new μ - η^{1-} and μ - η^{2-} diazenido complexes and the corresponding protonated cations which contain μ - η^{1-} hydrazido(2–) (isodiazene) and μ - η^{2-} diazene ligands. These species readily undergo $\eta^{1} \rightarrow \eta^{2}$ isomerizations which are critical to understanding the stepwise reduction of NNR ligands bound to a thiopolymetallic system. We are now investigating how **2** and **3** are formed and the mechanism of reactions in which their diazo ligands are reduced.

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Supporting Information Available: Tables of atomic parameters and all bond distances and angles for **2** and **5** (14 pages). Ordering information is given on any current masthead page. The structures will be deposited in the Cambridge Structural Database.

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⁽¹²⁾ Preparation of 4 and 5: To a solution of 2 or 3 (0.2 g, 0.35×10^{-3} mol) in THF (5 cm³) was added 1 equiv of HBF₄–Et₂O. The solution turned instantly from red to orange or from green to yellow for compound 2 or 3, respectively. Addition of pentane (10 cm³) precipitated compound 4 or 5 as an orange or yellow air-stable solid, respectively. 4 and 5 were washed with pentane and obtained with ca. 90% yields (0.21 g). 4 transformed into 5 in solution at room temperature. 4: ¹H NMR (CD₃CN) δ 12.9 (s, 1H, NH), 7.54 (m, 2H, Ph), 7.45 (t, 1H, Ph), 6.97 (d, 2H, Ph), 6.01 (s, 5H, Cp), 5.64 (s, 5H, Cp), 2.05 (s, 3H, SMe), 1.66 (s, 3H, SMe), 1.56 (s, 3H, SMe); IR (KBr, cm⁻¹) 3220 ν (NH), 1150–950 ν (BF). Anal. Calcd for Mo₂BC₁₉H₂₅F₄N₂-S₃: C, 34.8; H, 3.8; N, 4.3. Found: C, 34.5; H, 3.9; N, 3.8. 5: ¹H NMR (CD₃CN) δ 12.6 (s, 1H, NH), 7.42 (m, 2H, Ph), 7.32 (t, 1H, Ph), 6.93 (d, 2H, Ph), 6.11 (s, 5H, Cp), 5.79 (s, 5H, Cp), 1.72 (s, 3H, SMe), 1.65 (s, 3H, SMe), 1.52 (s, 3H, SMe); IR (KBr, cm⁻¹) 3170 ν (NH), 1150–950 ν (BF). Anal. Calcd for Mo₂BC₁₉H₂₅F₄N₂S₃: C, 34.8; H, 3.8; N, 4.3. Found: C, 34.5; H, 3.8; N, 4.3. Found: C, 35.2; H, 4.0; N, 4.4.