$\eta^1-\eta^2$ Rearrangement and Protonation of Phenyldiazo Bridging Ligands Attached to the Dimolybdenum System $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$

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Summary: Rearrangements and protonation reactions of phenyldiazo ligands bound to the bimetallic center, $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$, 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 N_2 reduction by metalloenzymes[1] and to the synthesis of nitrogen-containing organic compounds. The generation of such compounds, either directly from molecular nitrogen or indirectly from diazenido ($RN{=}N^-$) or hydrazido(2−) ($RN{-}NR^{2-}$) 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] A 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 binding—singly 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 $\{Mo_2(\mu\text{-}SMe)_n\}$ ($n = 1-3$) core[3g,7] and now describe the formation of μ-η^1- and μ-η^2-phenyldiazenido complexes $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N_2Ph)]$ (**2**) and $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}N_2Ph)]$ (**3**), of the μ-η^1-hydrazido(2−) (or isodiazene) compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}NNHPh)]BF_4$ (**4**), and of the μ-η^2-diazene species $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}NHNPh)]BF_4$ (**5**). Some stereochemical aspects of these reactions are also briefly considered.

The thermal reaction of the complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ (**1**) with $PhNHNH_2$ (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 $CDCl_3$) spectra of **2** and **3** exhibited two inequivalent cyclopentadienyl ligand resonances and three SMe resonances, indicating that the complexes had a $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ 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 N_2Ph 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 $PhNNH_2$ (80 μL, 0.8×10^{-3} mol) in THF (30 cm^3) was heated at 70 °C for 6 h. The solution, initially green, became brownish red. After filtration (elimination of NH_4Cl) and evaporation of the solvent, the residue was chromatographed on a silica gel column. Elution with CH_2Cl_2−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 air-stable 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 ($CDCl_3$) 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 $\nu(N{=}N)$. Anal. Calcd for $Mo_2C_{19}H_{24}N_2S_3$: C, 40.1; H, 4.2; N, 4.9. Found: C, 40.8; H, 4.4; N, 5.4. **3**: ^1H NMR ($CDCl_3$) 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 ($CDCl_3$) 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 $Mo_2C_{19}H_{24}N_2S_3$: C, 40.1; H, 4.2; N, 4.9. Found: C, 41.1; H, 4.1; N, 5.1.

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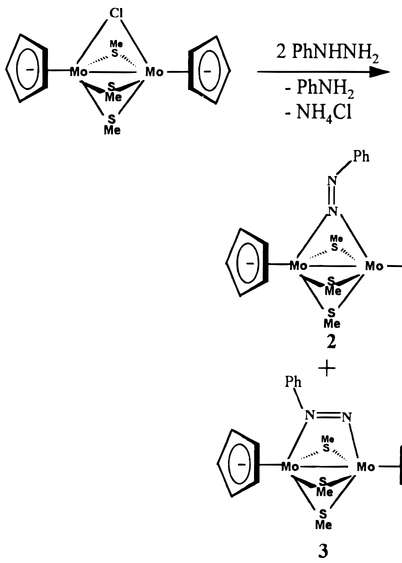
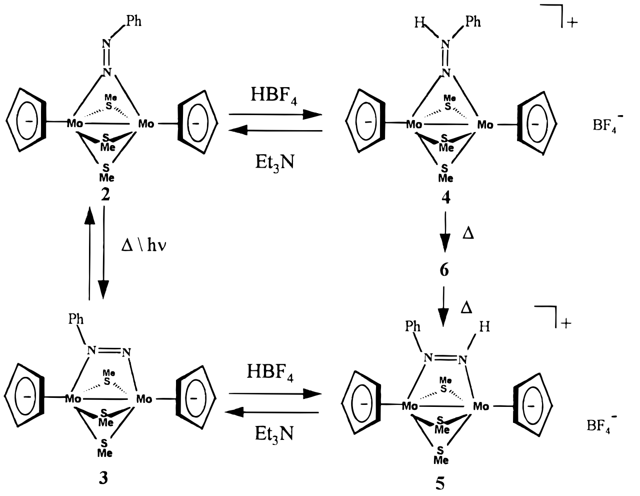
Scheme 1



Scheme 2



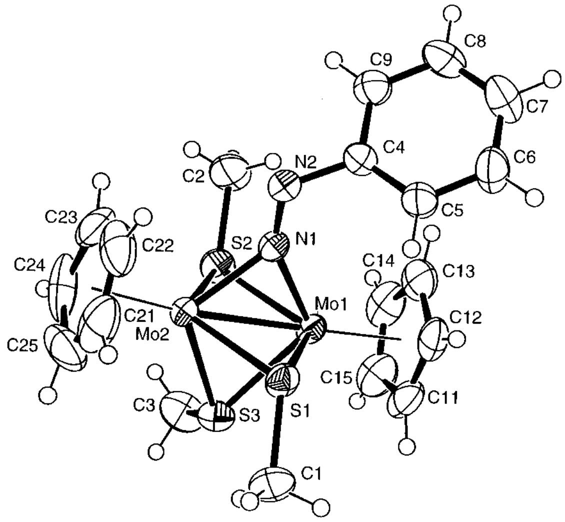


Figure 1. View of a molecule of $[\mathrm{Cp_2Mo_2}(\eta^1\text{-}\mu\text{-NNPh})(\mu\text{-SMe})_3]$ (**2**) showing 50% probability ellipsoids. Hydrogen atoms are shown as spheres of arbitrary size. Selected distances (Å) and angles (deg): Mo(1)–N(1), 2.084(2); Mo(1)–S(1), 2.474(1); Mo(1)–S(2), 2.458(1); 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).

by the observation of phenyl resonances in the ^{1}H 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 molybdenum(III): the Cp–Mo–Mo–Cp unit is nearly linear (Cp = C_5H_5 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(3) Å) is consistent with a N=N double bond. The slight asymmetry in the Mo–N$_2$Ph-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 $[\mathrm{Mo_2Cp_2}(\mu\text{-SMe})_3(\mu\text{-NH}_2)]$, 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 results[11] 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 $[\mathrm{Mo_2Cp_2}(\mu\text{-SMe})_3(\mu\text{-}\eta^1\text{-NNHPh})]\mathrm{BF_4}$ (**4**) and its η^2-diazene isomer $[\mathrm{Mo_2Cp_2}(\mu\text{-SMe})_3(\mu\text{-}\eta^2\text{-NHNPh})]\mathrm{BF_4}$ (**5**) (Scheme 2).[12] Deprotonation of **4** and **5**, easily effected with Et$_3$N, gives the starting complexes **2** and **3**. Compounds **4** and **5** were characterized by ^{1}H NMR, elemental analyses, and IR.[11] In the ^{1}H 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

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[9] Crystallographic data for $[\mathrm{Cp_2Mo_2}(\eta^1\text{-}\mu\text{-NNPh})(\mu\text{-SMe})_3]$ (**2**): $\mathrm{C_{19}H_{24}Mo_2N_2S_3}$, 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, β = 96.859(4)°, V = 2145.4(2) Å^3, Z = 4, D_c = 1.760 g cm^{-3}, μ(Mo Kα) = 1.467 mm^{-1}. The intensities of 8182 reflections with θ(Mo Kα) < 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}.

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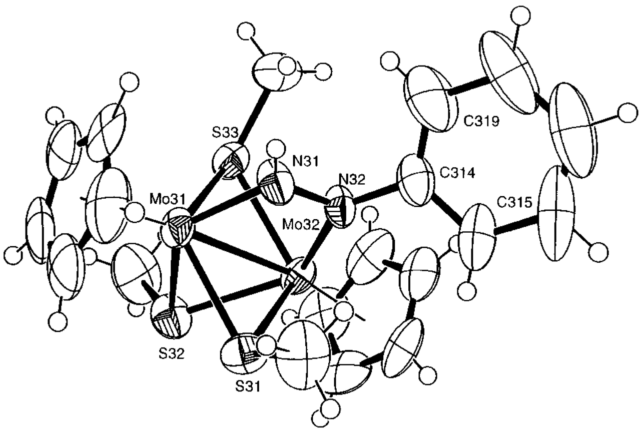
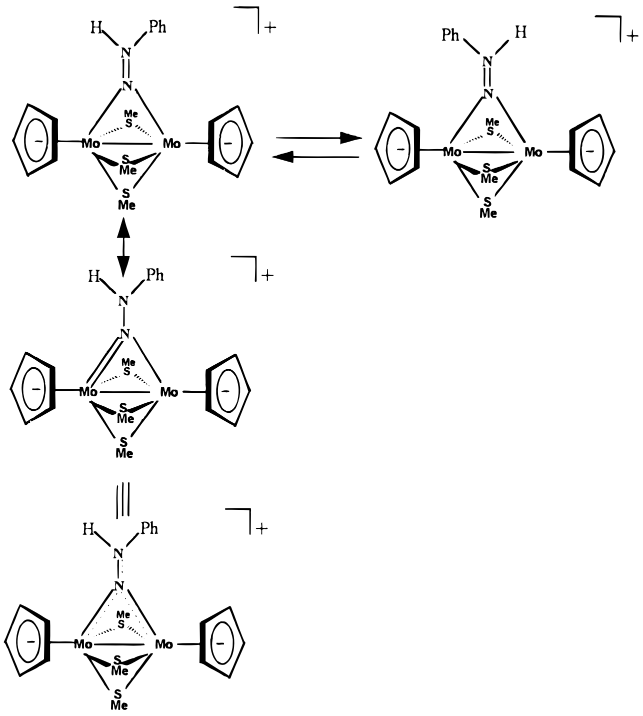


Figure 2. View of one of the [$Cp_2Mo_2(\eta^2$-μ-NHNPh)(μ-SMe)$_3$] cations in **5** with 50% probability ellipsoids. Hydrogen atoms are shown as spheres of arbitrary size. Selected distances (Å) and angles (deg) for the three independent cations $n = 1-3$: Mo(n1)−N(n1), 2.018(9), 2.029(9), 2.011(9); 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).

Scheme 3



Complex **4** exhibits dynamic behavior attributable to rotation of the NHPh group around the N=N bond axis with $\Delta G^{\ddagger} = 61.3 \pm 1$ kJ mol^{-1} (Scheme 3), which 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 ^{1}H NMR spectrum in CD_2Cl_2 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 cm^3) was added 1 equiv of HBF_4−Et_2O. The solution turned instantly from red to orange or from green to yellow for compound **2** or **3**, respectively. Addition of pentane (10 cm^3) 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**: ^{1}H NMR (CD_3CN) 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 $Mo_2BC_{19}H_{25}F_4N_2S_3$: C, 34.8; H, 3.8; N, 4.3. Found: C, 34.5; H, 3.9; N, 3.8. **5**: ^{1}H NMR (CD_3CN) 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 $Mo_2BC_{19}H_{25}F_4N_2S_3$: C, 34.8; H, 3.8; N, 4.3. Found: C, 35.2; H, 4.0; N, 4.4.

(13) Crystallographic data for {[$Cp_2Mo_2(\eta^2$-μ-NHNPh)(μ-SMe)$_3$][BF_4]}$_3$·$2CH_2Cl_2$·$^1/_2OEt_2$ (**5**): $C_{61}H_{84}B_3Cl_4F_{12}Mo_6N_6O_{1/2}S_9$, $M_r = 2175.75$, triclinic, space group $P1$, $a = 12.509(3)$ Å, $b = 17.052(3)$ Å, $c = 21.170(4)$ Å, $\alpha = 66.67(3)°$, $\beta = 86.02(3)°$, $\gamma = 75.34(3)°$, $V = 4009.0(14)$ Å^3, $Z = 2$, $D_c = 1.802$ g cm^{-3}, μ(Mo Kα) = 1.348 mm^{-1}. The intensities of 15 886 reflections with θ(Mo Kα) < 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 ($R_{int} = 0.128$; 5612 with $I > 2\sigma(I)$) gave $R[I > 2\sigma(I)] = 0.064$ and wR2(all data) = 0.168; $|\Delta\rho| < 0.96$ e Å^{-3}. The asymmetric unit contains three ordered dimolybdenum cations, three BF_4^- anions (all disordered), two CH_2Cl_2 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.