positions reflect the tendency of Au(III) to extend its coordination sphere beyond four.[20] As is to be seen from Figure 3, the Au–water interactions occur inside and outside the saddle, respectively, with Ow1 hydrogen bonded to that related by the C_2 axis at a distance of 2.88 (2) Å.

The mean coordination Au–N1 (2.005 (7) Å) and Au–N3 (1.983 (7) Å) bond lengths do not differ from the corresponding ones found in **1**. The mean values are obtained by averaging the values relative to the two crystallographically independent Au(gly-L-his) units. However, the mean Au–N2 distance of 1.995 (8) Å appears slightly longer than the corresponding one in **1** (1.94 (1) Å). This difference could be ascribed to the trans influence of the deprotonated imidazole N donor being greater than that of Cl. The Au1–N42 bond length of 1.987 (7) Å appears shorter than the corresponding Au2–N4 one (2.083 (8) Å). The difference, if significant, may be due to the steric requirements for closing the tetramer structure.

The overall geometry of the Au(gly-L-his) fragments in **2** is similar to that of **1**. The dihedral angles between the mean planes of the imidazole ring and of the metal coordination plane, belonging to the same dipeptide ligand, amount to 24 (2) and 9 (4)° in the two crystallographically independent units of **2**. Comparison with **1** (25.0 (6)°) suggests that the closure of the tetramer slightly alters the conformation of the Au(gly-L-his) units.

In conclusion, $[AuCl_4]^-$ reacts with the dipeptide gly-L-his under acidic conditions to give the mononuclear complex **1**, which displays the expected ligation pattern. **1** readily forms the cyclic tetramer **2** at pH 6–7, which makes Au(III) different from Cu(II), Ni(II), and Pd(II), which reportedly[7] form a cyclic tetramer under alkaline conditions only. The isolation of **1** and **2** is somewhat unexpected considering the instability of Au(III) complexes with amino acids and peptides other than gly-L-his.[21]

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Supplementary Material Available: For **1** and **2**, tables listing crystallographic data and details of refinement, atomic positional and displacement parameters, and bond lengths and angles (9 pages); listings of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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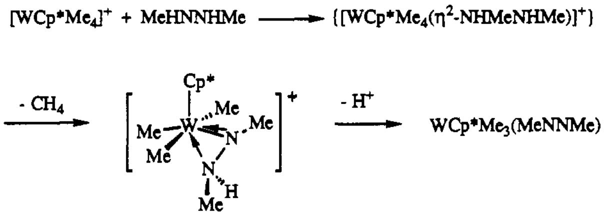
Synthesis and Structure of a Tungsten(IV) η^2-Dimethyldiazene Complex in Which the Diazene Ligand Behaves as a Four-Electron Donor

We have been interested for several years in the chemistry of high-oxidation-state molybdenum and tungsten complexes that is relevant to the reduction of dinitrogen to ammonia, in particular compounds in which N_2H_x ligands are bound to a WCp^*Me_3 core; examples are $WCp^*Me_3(\eta^1\text{-}NNH_2)$,[1] $[WCp^*Me_3(\eta^2\text{-}NHNH_2)]^+$,[1] and $[WCp^*Me_3(\eta^2\text{-}NH_2NH_2)]^+$.[2] A key feature of compounds of this type is the availability of three bonding orbitals on the WCp^*Me_3 fragment, a σ type hybrid orbital, and two orbitals that can be used for either σ or π bonding, the d_{xy} orbital (which lies parallel to the plane of the Cp* ligand between the four basal ligands) and the d_{z^2} orbital.[3] All of the N_2H_x species can be reduced in the presence of protons to give ammonia in high yield and have been shown to reduce hydrazine catalytically to ammonia in high yield in the presence of protons.[2] A type of monomeric complex that is relatively rare in this "high-oxidation-state" chemistry, as well as in the much more extensively studied "low-oxidation-state" chemistry,[4,5] is one that contains a diazene ligand. (*Free* diazene is a relatively high-energy unstable species and therefore an unlikely intermediate in dinitrogen reduction.) In the vast majority of diazene or substituted diazene complexes, the ligand is bound to more than one metal[6–9] or is monodentate.[10] The only structurally characterized examples of monometallic η^2-diazene complexes are diphenyldiazene (azobenzene) complexes[11–17] in which the azobenzene behaves as a two-electron "olefin-like" donor ligand. We report here an example of a monometallic η^2-dimethyldiazene complex in which the diazene behaves as a *four*-electron donor ligand or, alternatively, as a *six*-electron η^2-1,2-dimethylhydrazido(2–) ligand.

Addition of 1,2-dimethylhydrazine to $[WCp^*Me_4]PF_6$[18] in dichloromethane at 25 °C yields lemon yellow, crystalline $[WCp^*Me_3(\eta^2\text{-}NMeNHMe)]PF_6$ (eq 1).[19] We speculate that



(1)

$[WCp^*Me_4(\eta^2\text{-}NHMeNHMe)]PF_6$ is formed first and that it then decomposes rapidly by losing methane. The structure of $[WCp^*Me_3(\eta^2\text{-}NMeNHMe)]PF_6$ is believed to be analogous to that found for $[WCp^*Me_3(\eta^2\text{-}NHNH_2)]^+$ (as shown in eq 1), in which the d_{xy} orbital is used to form the W–N dative π bond and the d_{z^2} orbital the W–N dative σ bond. Unlike the case of $[WCp^*Me_3(\eta^2\text{-}NHNH_2)]^+$, which is deprotonated readily by

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(19) Anal. Calcd for $C_{15}H_{31}F_6N_2PW$: C, 31.71; H, 5.50; N, 4.93. Found: C, 31.84; H, 5.44; N, 4.74.

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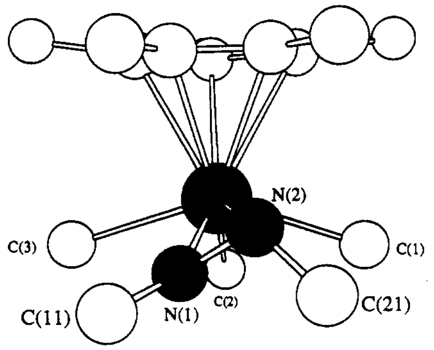
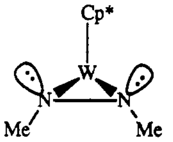


Figure 1. Structure of Cp*WMe$_3$(η^2-MeNNMe). Selected bond distances (Å): W–N(1), 1.860 (8); W–C(3), 2.205 (9); W–N(2), 2.126 (7); N(1)–N(2), 1.38 (1); W–C(1), 2.212 (8); N(1)–C(11), 1.46 (1); W–C(2), 2.225 (9); N(1)–C(21), 1.48 (1). Selected bond angles (deg): N(1)–W–N(2), 39.7 (3); N(2)–W–C(2), 137.8 (3); N(1)–W–C(1), 102.3 (4); N(2)–W–C(3), 114.2 (3); N(1)–W–C(2), 116.0 (4); W–N(1)–N(2), 80.6 (5); N(1)–W–C(3), 76.2 (4); W–N(1)–C(11), 151.7 (7); C(1)–W–C(2), 71.0 (4); N(2)–N(1)–C(11), 118.2 (8); C(1)–W–C(3), 137.8 (4); W–N(2)–N(1), 59.7 (4); C(2)–W–C(3), 72.2 (4); W–N(2)–C(21), 126.5 (6); N(2)–W–C(1), 81.5 (3); N(1)–N(2)–C(21), 110.8 (8).

triethylamine or pyridine to yield WCp*Me$_3$(η^1-NNH$_2$),[1] methylmagnesium chloride (in THF at −40 °C) is required in order to deprotonate [WCp*Me$_3$(η^2-NMeNHMe)]$^+$. The product is a stable, orange-red dimethyldiazene complex, WCp*Me$_3$(MeNNMe), and is isolated in high yield.[20] The proton NMR spectrum of WCp*Me$_3$(MeNNMe) in THF-d_8 at room temperature reveals a very broad peak at 3.01 ppm for the methyl groups of the dimethyldiazene ligand. At −80 °C the two ends of the diazene ligand become inequivalent (methyl resonances at δ(H) 2.70 and 3.17 ppm and δ(C) 38.59 and 40.16 ppm), the activation energy for equilibration being $\Delta G^{*}{}_{5\,°\mathrm{C}}$ = 13.6 kcal/mol. These data are consistent with a structure in which one of the diazene nitrogen atoms forms a π bond to the metal through the d_{xy} or d_{z^2} orbital, and therefore is planar, while the other nitrogen atom is pyramidal.

The structure of WCp*Me$_3$(η^2-MeNNMe)[21] is shown in Figure 1; relevant bond distances and angles are given in the caption. The sp^2-hybridized nitrogen atom (sum of angles around N(1) = 350.5°) is located approximately in a basal position of a square pyramid, while the sp^3-hybridized nitrogen atom (sum of angles around N(2) = 297°) occupies a position above what is roughly the plane formed by the three methyl carbon atoms and N(1). The most attractive explanation is that the bond between N(2) and the metal (W–N(2) = 2.126 (7) Å) involves the d_{xy} orbital, while the d_{z^2} orbital is used to form a π bond (W–N(1) = 1.860 (8) Å). The N(1)–N(2) bond length (1.38 (1) Å) is considerably lengthened from that found for dimethyldiazene itself (1.254 (3) Å)[22] and approximately the same as the N–N bond lengths found in azobenzene complexes,[11,12,15–17] consistent with a considerable amount of reduction to a (η^2-MeNNMe)$^{2-}$ ligand. We propose that the fluxional process that interconverts the two NMe groups in WCp*Me$_3$(η^2-MeNNMe) involves an intermediate having a mirror plane in which the d_{z^2} orbital is nonbonding, as in the azobenzene complexes, viz. (methyl ligands on W omitted)



Addition of 1 equivalent of triflic acid to WCp*Me$_3$(η^2-MeNNMe) at low temperature yields [WCp*Me$_3$(η^2-NMeNHMe)]$^+$, while methylation with methyl triflate yields [WCp*Me$_3$(η^2-NMeNMe$_2$)]$^+$. A preliminary (Cp* disordered) X-ray structure of [WCp*Me$_3$(η^2-NMeNMe$_2$)]$^+$ shows it to have a structure analogous to that known for [WCp*Me$_3$(η^2-NHNH$_2$)]$^+$ (eq 1). Therefore the bonding mode observed in WCp*Me$_3$(η^2-MeNNMe) cannot be ascribed to steric factors alone; i.e., the methyl group on the sp^2 nitrogen atom of the dimethyldiazene ligand *could* point toward the Cp* ligand. We conclude that the d_{xy} and d_{z^2} orbitals in the WCp*Me$_3$ fragment must be roughly equivalent in their ability to form a metal–ligand π bond.

The ability of the metal to form a π bond to one nitrogen atom of the η^2-MeNNMe ligand suggests that an analogous complex that contains a η^2-HNNH ligand might be stable enough to be an intermediate in a hypothetical system in which dinitrogen is reduced and protonated at such a metal site. What is uncertain is whether a η^2-HNNH ligand would be stable toward rearrangement, perhaps most likely to a relatively common η^1-hydrazido(2−) ligand,[4,5] a type of rearrangement that would be analogous to the relatively well-known rearrangement of a terminal acetylene to a vinylidene ligand.[23]

Further studies are under way that are designed to determine the extent to which diazene (or η^2-1,2-hydrazido(2−)) complexes might be accessible intermediates in a system in which the N–N bond in N$_2$H$_x$ or N$_2$H$_x$R$_y$ ligands is cleaved.

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Supplementary Material Available: A textual presentation of experimental details, a labeled ORTEP drawing, and tables of final positional and thermal parameters (5 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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(20) Anal. Calcd for C$_{15}$H$_{30}$N$_2$W: C, 42.67; H, 7.16; N, 6.63. Found: C, 42.87; H, 6.91; N, 6.42.

(21) An orange prismatic crystal of WC$_{15}$H$_{30}$N$_2$ having approximate dimensions of 0.200 × 0.200 × 0.160 mm was mounted on a glass fiber. Data were collected at −72 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. A total of 4060 reflections were collected in the range $3.0° < 2\theta < 55.00°$, with 3835 being unique. No crystal decay was evident during data collection. An empirical absorption correction was applied, using the program DIFABS, which resulted in transmission factors ranging from 0.87 to 1.28. The structure was solved by Patterson methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions and refined isotropically. The final cycle of full-matrix least-squares refinement was based on 2700 reflections ($I > 3.00\sigma(I)$) and 164 variables and used the TEXSAN crystallographic software package from Molecular Structure Corp. The final refinement converged with final R = 0.040 and R_w = 0.041. The maximum and minimum peaks on the final fourier difference map corresponded to 1.10 and −1.40 e/Å^3, respectively. Crystal data: a = 9.392 (4) Å, b = 11.721 (5) Å, c = 14.520 (4) Å, β = 93.67 (3)°, V = 1595 (3) Å^3, space group = $P2_1/a$, Z = 4, MW = 422.27, ρ(calcd) = 1.761 g/cm^3.

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