4b was thermally stable, but the decomplexation with trimethylamine *N*-oxide or by irradiation with a high-pressure mercury lamp in the presence of triphenylphosphine gave the liberated fulvene **5** in low yield.

In contrast to the above results, intramolecular cyclotrimerization of 3,3,5,5,8,8,10,10-octamethyl-4,9-dioxa-3,5,8,10-tetrasiladodeca-1,6,11-triyne (**6**), the corresponding acyclic triyne to **1**, gave a benzene derivative, **7**, in the reaction with $Cr(CO)_6$. The reaction of **6** with $Mo(CO)_6$ afforded a complex (**8**), which was also obtained by the reaction of **7** and $Mo(CO)_6$.

The mechanism and further extension of the reaction will be reported later.

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Registry No. 1, 91269-65-7; **2**, 53170-83-5; **3a**, 93304-56-4; **3b**, 93304-57-5; **4a**, 93304-58-6; **4b**, 93304-59-7; **4c**, 93304-60-0; **5**, 497-20-1; **6**, 93304-55-3; **7**, 53170-80-2; **8**, 93304-61-1; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

Supplementary Material Available: Physical and spectroscopic data of all new compounds and tables of atomic parameters, anisotropic temperature parameters, list of distances, list of angles, and observed and calculated structure factors for **4b** (26 pages). Ordering information is given on any current masthead page.

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(7) Several interesting facts can be pointed out. The Mo atom has a distorted octahedral configuration and is bonded to six carbons of the fulvene ligand and three carbonyl groups. Similar to previously reported structure of diphenylfulvene complex,[6a] the C1–C6 double bond of **4b** is inclined by 30.47° to the planar cyclopentadiene ring in spite of a presumed loss of conjugation. An increased bond length of C1–C6 (1.447 Å) from values of diphenylfulvene complex (1.40 Å) or parent uncoordinated fulvene (1.349 Å)[8] should be noted. For a fulvene–$Cr(CO)_3$, an analysis of the bending of the exocyclic methylene group has been discussed recently by Hoffmann and his co-workers with the extended Hückel method.[9] The OC–Mo–CO bond angles (81.3°, 83.6°, and 97.5°) are unequal, while the respective Mo–CO bond lengths are approximately equal (1.99, 2.01, and 2.03 Å). The effect of substituents of the fulvene ligands on the details of the structure has been reported recently.[6b]

(8) (a) A value obtained by microwave spectroscopy: Barton, P. A.; Brown, R. D.; Burden, F. R.; Domaille, P. J.; Kent, J. E. *J. Mol. Spectrosc.* **1972**, *43*, 401. (b) Bond lengths and ^{13}C NMR of several fulvenes and their metal complexes have been discussed: Watts, W. *J. Organomet. Chem.* **1981**, *220*, 165.

(9) Albright, T. A.; Hoffmann, R.; Hofmann, P. *Chem. Ber.* **1978**, *111*, 1591.

Preparation and Some Chemistry of a Molecule Containing a μ-η^2,η^2-$NHNH^{2-}$ and a μ-η^1,η^1-NH_2NH_2 Ligand Bound between Two Tungsten(VI) Centers

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It is now thought that a pivotal intermediate in the reduction of dinitrogen by nitrogenase may be a complex of molybdenum containing an NHNH ligand.[1] There are only two structurally characterized molecules containing the NHNH unit. In $[Cr(CO)_5]_2(\mu$-η^1,η^1-NHNH$)$[2] the NHNH ligand appears to be most like diimide, and the metal therefore Cr(0), while in $W(\eta^5$-C_5Me_4-t-Bu$)(CCMe_3)I]_2$ $(\mu$-η^1,η^1-NHNH$)$[3] it appears to be a 1,2-hydrazido^{2-} ligand, and the metal therefore W(6+). Here we report a molecule containing the hitherto unknown μ-η^2,η^2-$NHNH^{2-}$ ligand, as well as a μ-η^1,η^1-NH_2NH_2 ligand, that we think raises some interesting new questions concerning the chemistry of molecular nitrogen and partially reduced molecular nitrogen bound to relatively high oxidation state Mo or W centers.

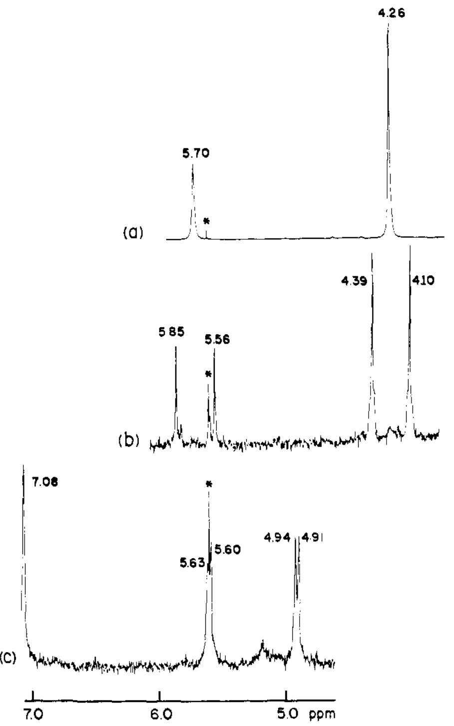

Figure 1. Signals for protons attached to nitrogen atoms in (a) **1** in acetone-d_6, (b) **1** prepared from $^{15}N_2H_4$, and (c) **2** in acetone-d_6 (* unidentified impurity).

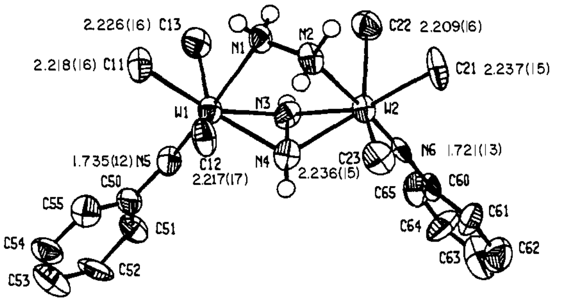

Figure 2. View of $[W(NPh)Me_3]_2(\mu$-η^1,η^1-$NH_2NH_2)(\mu$-η^2,η^2-NHNH$)$ (hydrogen atoms included on nitrogen atoms only; ORTEP II, 40% ellipsoids). The included bond lengths refer to W–C or W═N bonds. Others can be found in the text or in the complete table in the supplementary material.

Addition of methyllithium to $W(NPh)Me_3Cl$[4] in ether at −30 °C generates what we believe to be thermally unstable, yellow $W(NPh)Me_4$ (cf. $W(NPh)(CH_2SiMe_3)_4$[4]). Addition of 1 equiv of hydrazine to a solution of $W(NPh)Me_4$ generated in this fashion yields a yellow solution from which a pale yellow solid (**1**) can be isolated in ~80% yield.[5] The ^1H NMR spectrum of **1** in acetone–d_6 shows (inter alia) two signals in the ratio of 1:2 at 5.70

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(1) (a) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589. (b) Pombeiro, A. J. L. In "New Trends in the Chemistry of Nitrogen Fixation"; Chatt, J., da Camara Pina, L. M., Richards, R. L., Eds.; Academic Press: London, 1980; Chapter 6.

(2) Huttner, G.; Gartzke, W.; Allinger, K. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 822.

(3) Churchill, M. R.; Li, Y.-J.; Blum, L.; Schrock, R. R. *Organometallics* **1984**, *3*, 109.

(4) Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483.

(5) Methyl lithium (10 mL, 1.14 M, 5.6 mmol) was added to a saturated solution of 2.0 g (5.6 mmol) of $W(NPh)Me_3Cl$ in ether at -30 °C. The resulting yellow solution was warmed until LiCl precipitated (at approximately -25 °C). The solution was then cooled again to -30 °C and transferred via cannula to a solution containing 0.18 mL (5.6 mmol) of anhydrous (98%) N_2H_4 in 50 mL of ether. The reaction was stirred at -30 °C for 20 min and then warmed to room temperature. The solution was filtered and the salts were washed with ether. The solvent was removed in vacuo leaving 1.60 g (80%) of yellow **1**. The compound can be recrystallized from dichloromethane by adding toluene. These crystals contain 0.5 equiv of toluene by ^1H NMR.

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and 4.26 ppm (Figure 1a). The ^1H NMR spectrum of a sample of **1** prepared[6] using $^{15}NH_2{}^{15}NH_2$ (Figure 1b) confirms that these signals can be ascribed to protons attached to nitrogen atoms originally in the added hydrazine. Other features of the ^1H and ^{13}C NMR spectra[8] are consistent with a molecule with the formula $W(NPh)Me_3(NHNH_2)$ containing two types of methyl groups. Curiously, however, the ^{15}N NMR spectrum[9] of **1**-$^{15}N_2$ did *not* show two distinct ^{15}N signals expected for an imido-like sp^2-hybridized α-nitrogen atom and sp^3-hybridized β-nitrogen atom in an $NHNH_2$ ligand, but what appeared to be a doublet at ~57.0 ppm ($J_{NH} \approx 68$ Hz) overlapping with a triplet at ~54.9 ppm ($J_{NH} \approx 68$ Hz). Since no $NHNH_2{}^{1-}$ complex is known, we were compelled to determine the structure of **1**.[10]

Figure 2 shows **1** to be a dimer containing a μ-η^2,η^2-hydrazido^{2-} ligand and a μ-η^1,η^1-hydrazine ligand. Each metal has pseudooctahedral geometry; three methyl groups and the hydrazido^{2-} ligand occupy the four "equatorial" sites with the linear phenylimido groups trans to the hydrazine nitrogen atoms in the "axial" positions. Chemically the metal centers are equivalent and the molecule has noncrystallographic C_{2v} symmetry. No W–W bond is present since the W(1)–W(2) distance is long (3.731 (1) Å) and the dihedral angle between the $W(1)N_2$ and $W(2)N_2$ planes is large (~135°). This result is consistent with the complex containing W(6+) and $NHNH^{2-}$. The hydrazido^{2-} ligand is essentially symmetrically bound between W(1) and W(2) (W(1)–N(3) = 2.106 (12), W(1)–N(4) = 2.115 (11), W(2)–N(3) = 2.157 (11), W(2)–N(4) = 2.170 (12)Å) with an N–N distance of 1.391 (15) Å. The N(1)–N(2) distance of 1.434 (14) Å is close to that found in free hydrazine, the W(1)–N(1)–N(2)–W(2) linkage forms a zigzag arrangement, and W(1)–N(1) = 2.320 (11) and W(2)–N(2) = 2.353 (11) Å, all as one would expect for a bridging hydrazine ligand. Some other distances can be found in the figure, and a complete table of bond lengths and angles can be found in the supplementary material.

To our knowledge only one other type of related μ-η^2,η^2-N_2R_2 complex, $Fe_2(CO)_6(N_2R_2)$,[11] has been structurally elucidated. In $Fe_2(CO)_6(N_2Me_2)$ and $Fe_2(CO)_6(N_2C_{12}H_8)$ an Fe–Fe bond is present, the N–N bond lengths are 1.366 (8) and 1.399 (8) Å, respectively, and the dihedral angles between the FeN_2 planes are 91.1° and 89.5°, respectively.

Upon addition of 2 equiv of gaseous HCl to **1** in ether at −78 °C a pale yellow precipitate of $[W(NPh)Me_2Cl]_2(\mu$-$NH_2NH_2)(\mu$-$NHNH)$ (**2**) forms in ~80% yield.[12] In the ^1H NMR spectrum of **2**[13] the methyl groups are inequivalent, the NHNH protons are equivalent, and there are two types of coupled NH_2NH_2 protons present (Figure 1c), all consistent with a chloride having replaced one of the exterior methyl groups on each metal to yield a molecule containing a C_2 axis that passes through the midpoint of the NHNH and NH_2NH_2 ligands. We suspect that neither the NHNH nor NH_2NH_2 ligand is protonated first, as an analogous reaction between **1** and DCl yields a product identical by ^1H NMR with that formed in the reaction between **1** and HCl.

$[W(NPh)Me_3]_2(\mu$-$NH_2NH_2)(\mu$-$NHNH)$ can be dissolved in methanol and recovered unchanged upon removing the methanol in vacuo. Upon recovery of **1** from methanol-d_4, >90% of the protons in the NHNH ligand have been replaced by deuterium; virtually no deuterium is incorporated into the hydrazine ligand. When NEt_3 is added to a solution of **1** in methanol-d_4 no obvious change occurs and **1** can be recovered quantitatively by removing the methanol and triethylamine in vacuo. In this case, however, the recovered product is largely $[W(NPh)Me_3]_2(\mu$-$ND_2ND_2)(\mu$-$NDND)$. It is also important to note that addition of excess NEt_3 to an ^1H NMR sample of **1** in acetone-d_6 causes the signal at 5.70 ppm to virtually disappear into the base line. Only small amounts of unidentifiable solids have been observed to precipitate from larger scale reaction mixtures under a variety of conditions, and removing all the solvent in vacuo yields **1** quantitatively. Among other things, we suspect that NEt_3 is deprotonating the NHNH ligand and are in the process of eludicating this and other reactions involving bases.

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Supplementary Material Available: Tables of final atomic coordinates and thermal parameters and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

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[6] Hydrazine-$^{15}N_2$ was prepared from hydrazine sulfate (99% ^{15}N) by a published method starting with 1.9 mmol (0.250 g) of $^{15}N_2H_4 \cdot H_2SO_4$.[7]

[7] Audrieth, L. F.; Ogg, B. A. "The Chemistry of Hydrazine"; Wiley: New York, 1956; Chapter 3.

[8] ^1H NMR (CD_2Cl_2) δ 7.40–7.05 (m, 5, NC_6H_5), 4.12 (s, 1, NH), 3.63 (s, 2, NH_2), 0.72 (s, 6, CH_3), 0.57 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$) δ 155 (s, C_{ipso}), 129, 125.6, 125.4 (d, $J_{CH} = 180$ Hz, C_o, C_m, C_p) 34.0 (q, $J_{CH} = 122$, $J_{CW} = 60$ Hz, CH_3), 18.5 (q, $J_{CH} = 122$, $J_{CW} = 60$ Hz, CH_3).

[9] The ^{15}N NMR spectrum was obtained at 9.04 MHz in CH_2Cl_2. The ^{15}N shift is relative to NH_3 (liquid). Aniline-^{15}N was employed as the external reference.

[10] **1**–0.5 toluene[5] crystallizes in the orthorhombic space group *Pbca* (No. 62) with $a = 23.957$ (3) Å, $b = 15.329$ (4) Å, $c = 14.051$ (2) Å, $V = 5160.4$ Å^3, and $\rho_{calcd} = 1.95$ g cm^{-3} for $Z = 8$. 2500 unique observed reflections ($I \geq 2\sigma(I)$) collected at 250 K on an Enraf-Nonius CAD4 diffractometer with Mo Kα ($\lambda = 0.7107$ Å) radiation to $2\theta = 45°$ were used in the solution and refinement of the structure by conventional methods to a value of the discrepancy index $R_1 = 0.043$. No absorption correction applied. The disordered toluene molecule was found sandwiched between the phenyl ring of the two phenylimido ligands. The hydrogen atoms on the HNNH and H_2NNH_2 ligands were placed in positions in which interactions with other substituents were calculated to be minimized (assuming $d_{NH} = 0.95$ Å and N–N–H = 109.5°).

[11] (a) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2709. (b) Doedens, R. J. *Inorg. Chem.* **1970**, *9*, 429.

[12] Anal. Calcd for $WC_8H_{14}N_3Cl$: C, 25.86; H, 3.80; N, 11.31; Cl, 9.54. Found: C, 25.52; H, 5.54; N, 11.98; Cl, 10.25.

[13] ^1H NMR of $W_2(NPh)_2Me_4Cl_2(\mu$-η^2,η^2-$N_2H_2)(\mu$-η^1,η^1-$N_2H_4)$-(CD_3CN) δ 7.41–7.17 (m, 5, C_6H_5), 5.95 (s, 1 NH), 4.96 (d, $J_{H_AH_B} = 8$ Hz, 1, NH_2), 4.56 (d, $J_{H_AH_B} = 8$ Hz, 1, NH_2), 1.00 (s, 3, CH_3), 0.88 (s, 3, CH_3).

Cobalt–Carbon Bond Dissociation Energy of Coenzyme B_{12}

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According to the widely accepted mechanism of coenzyme B_{12} dependent rearrangements a principal role of the coenzyme is to undergo enzyme-induced cobalt–carbon bond homolysis, thereby generating a 5′-deoxyadenosyl radical (Ado·) which triggers the rearrangement of the substrate by abstracting a H atom from the latter.[1] Accordingly, a knowledge of the cobalt–carbon bond dissociation energy of coenzyme B_{12} (adenosylcobalamin, abbreviated Ado-B_{12}) and an understanding of the factors that may contribute to the weakening of this bond and to the enzyme-induced bond dissociation are central to a full appreciation of this distinctive coenzyme's role. Following our earlier development of procedures for the determination of transition metal–alkyl bond dissociation energies and their application to various coenzyme B_{12} model compounds,[2-4] we now report the determination of the cobalt–carbon bond dissociation energy of the coenzyme itself.

Our procedure is an adaptation of the kinetic approach that we developed and applied previously to determine the cobalt–carbon bond dissociation energies of various alkyl cobalt Schiff

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[1] (a) Abeles, R. H. *Vitam. B_{12}, Proc. Eur.* Symp., *3rd* **1979**, 373. (b) Babior, B. M. *Vitam. B_{12}, Proc. Eur. Symp., 3rd* **1979**, 461. (c) Halpern, J. In "B_{12}"; Dolphin, D., Ed.; Wiley: New York, 1982; p 502 and references therein. (d) Halpern, J. *Pure Appl. Chem.* **1983**, *55*, 1059.

[2] (a) Halpern, J.; Ng, F. T. T.; Rempel, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 7124. (b) Ng, F. T. T.; Rempel, G. L.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 621. (c) Ng, F. T. T.; Rempel, G. L.; Halpern, J. *Inorg. Chim. Acta* **1983**, *77*, L65.

[3] Tsou, T. T.; Loots, M.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 623.

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