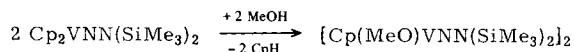


The action of methanol on the reddish brown compound does not lead to liberation of trimethylsilyl groups but instead, according to



to loss of cyclopentadienyl groups with formation of a brown diamagnetic complex of unknown structure which can be vacuum sublimed at 110°C. Its <sup>1</sup>H-NMR spectrum contains only one signal for the trimethylsilyl protons and one for the methoxy protons at δ = -22 and -128 Hz (TMS internal standard, C<sub>6</sub>H<sub>6</sub>) respectively. The course of reaction can be interpreted by assuming that the vanadium central atom, which formally possesses an "excess" electron (*i.e.* 19 valence electrons)<sup>[10]</sup> in the complex Cp<sub>2</sub>VNN(SiMe<sub>3</sub>)<sub>2</sub>, confers negative partial charges upon the two Cp ligands, thus facilitating attack of the cyclopentadienyl ring by a proton.

#### Procedure:

A mixture of CuCl (10.1 mmol) and (Me<sub>3</sub>Si)<sub>2</sub>N<sub>2</sub><sup>[3]</sup> in diethyl ether (50 ml) is stirred with exclusion of oxygen and moisture at -50°C until all the CuCl has dissolved (*ca.* 3 h). During this process, the initially yellow, then reddish brown, and finally colorless solution precipitates reddish brown fine crystals of [(2a)·2 CuCl], which is purified by repeated washing with ether.

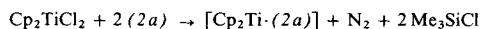
Combination of Cp<sub>2</sub>V (5.0 mmol) in diethyl ether (25 ml) at -78°C with (Me<sub>3</sub>Si)<sub>2</sub>N<sub>2</sub><sup>[3]</sup> in ether (10 ml) under similar conditions immediately yields a dark green solution which deposits blackish green crystals on concentration. Above -20°C they transform into the dark brown isomeric product Cp<sub>2</sub>V=NN(SiMe<sub>3</sub>)<sub>2</sub>, m. p. 76–78°C, which can be recrystallized from ether.

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German version: Angew. Chem. 88, 383 (1976)

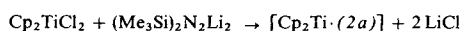
#### CAS Registry numbers:

[(2a)·2 CuCl], 59301-73-4; Cp<sub>2</sub>V·{Me<sub>3</sub>SiNNSiMe<sub>3</sub>}, 59301-74-5;  
Cp<sub>2</sub>V=NN(SiMe<sub>3</sub>)<sub>2</sub>, 59301-87-0; Cp<sub>2</sub>V, 1277-47-0; Cp<sub>2</sub>TiCl<sub>2</sub>, 1271-19-8;  
[Cp(MeO)VNN(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, 59361-81-6

- [1] Part 20 of Diimine and Its Derivatives. Also Part 38 of Compounds of Silicon and Its Group Homologs. This work was supported by the Deutsche Forschungsgemeinschaft.—Parts 19 and 37, respectively: N. Wiberg, S. K. Vasisht, and G. Fischer, *Angew. Chem.* 88, 257 (1976); *Angew. Chem. Int. Ed. Engl.* 15, 236 (1976).
- [2] Cf., *e.g.*, M. Herberhold, W. Golla, and K. Leonhard, *Chem. Ber.* 107, 3209 (1974); references cited therein.
- [3] N. Wiberg, W.-Ch. Joo, and W. Uhlenbrock, *Angew. Chem.* 80, 661 (1968); *Angew. Chem. Int. Ed. Engl.* 7, 640 (1968); N. Wiberg, *ibid.* 83, 379 (1971) and 10, 374 (1971), respectively.
- [4] Complexes of isodiazenes N=NH<sub>2</sub> and diazenes HN=NH are already known: a) J. Chatt, *J. Organomet. Chem.* 100, 17 (1975); b) D. Sellmann, A. Brandl, and R. Endell, *ibid.* 90, 309 (1975).
- [5] Corresponding compounds showing somewhat greater thermal stability are obtained with CuBr and CuI.
- [6] I. D. Brown and J. D. Dunitz, *Acta Crystallogr.* 13, 28 (1960).
- [7] G. Fachinetti, G. Fochi, and C. Floriani, *J. Organomet. Chem.* 57, C 51 (1973).
- [8] According to



and



a dark violet diamagnetic titanium complex, which is sublimable at 60°C, is also accessible. Its <sup>1</sup>H-NMR spectrum contains only a single trimethylsilyl proton signal at δ = -17.5 Hz (TMS int. std., Et<sub>2</sub>O). It probably has the structure Cp<sub>2</sub>TiNN(SiMe<sub>3</sub>)<sub>2</sub> analogous to Cp<sub>2</sub>VNN(SiMe<sub>3</sub>)<sub>2</sub>.

[9] M. Veith, *Angew. Chem.* 88, 384 (1976); *Angew. Chem. Int. Ed. Engl.* 15, 387 (1976).

[10] (Me<sub>3</sub>Si)<sub>2</sub>N=N can act as a four-electron donor.

## Structure of an "Isodiimine" Complex: Bis-(trimethylsilyl)isodiazenebis(cyclopentadienyl)vanadium

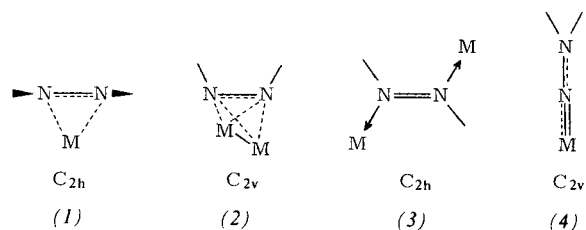
By Michael Veith<sup>[\*]</sup>

Complexes of diazene (diimine) derivatives with transition metals can be distinguished according to structural criteria:

1) The azo group forms a π bond to the metal, the substituents on the NN unit being *trans* configured (type (1)). In the case of dinuclear complexes the diazene group spans the coordination centers in such a way that the two metal atoms and the two nitrogen atoms approximately form a tetrahedron (type (2)). In both structural types the N—N bond length is considerably greater than in the free molecule and almost reaches the value for a single bond (137–139 pm)<sup>[1]</sup>.

2) The azo group is coordinated to the metal *via* a σ bond (type (3)). The N—N bond length is hardly affected (125–126 pm). In this way diazenes usually act as bridging ligands between two metal atoms<sup>[2]</sup>.

3) The substituents on the azo group migrate during complex formation and the resulting 1,2-disubstituted diazene ligand coordinates *via* a multiple bond between the terminal nitrogen and the metal atom (type (4)).



The last-named structural type is assumed for the N<sub>2</sub>H<sub>2</sub> ligand in the cation of [W(N<sub>2</sub>H<sub>2</sub>)Cl(diphos)<sub>2</sub>]BPh<sub>4</sub>. Although the positions of the hydrogen atoms could unfortunately not be established on X-ray structure analysis, the N—N bond length of 137 pm, the WNN angle of 171°, and the short W—N distance of 173 pm do evidence a structure of type (4).

In this communication we wish to report the results of a structure determination<sup>[4]</sup> performed on a complex formed

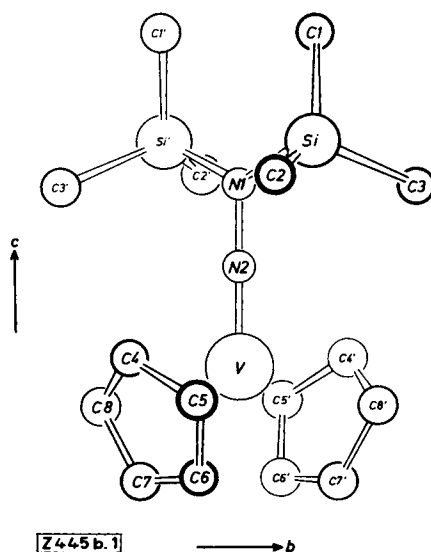


Fig. 1. Molecular structure of bis(trimethylsilyl)isodiazenebis(cyclopentadienyl)vanadium

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Selected bond lengths [pm] and angles [°]:

V—N(2)	166.6(6)	Si—C	184(1) (average value)
N(1)—N(2)	136.9(9)	V—C	240(13) (average value)
Si—N(1)	175.6(3)		
∠ VN(1)N(2)	180	∠ SiN(1)Si'	136.7(4)

by reaction of bis(trimethylsilyl)diazene with bis(cyclopentadienyl)vanadium<sup>[5]</sup>. The structure of this complex (Fig. 1) provides the first insight into the geometry of a monohapto-coordinated isodiazene.

In the crystal the molecule strictly possesses C<sub>2</sub> symmetry, although deviations from C<sub>2v</sub> symmetry are only minimal. The V, N(1), and N(2) atoms are located on the twofold axis, *i. e.* in a linear arrangement. The entire isodiazene ligand is strictly planar, a feature which should facilitate delocalization of π electrons from vanadium across to silicon. Other features of the molecular structure are:

1) The V—N bond length is exceptionally short. A metal-nitrogen multiple bond is present, as is also encountered in Cl<sub>3</sub>VNCl (V—N, 164.2 pm<sup>[6]</sup>).

2) The N—N bond length is considerably greater than in free bis(trimethylsilyl)diazene (117.1(7) pm) and thus almost lies in the range of the N—N single bond<sup>[7]</sup>.

3) The mutual eclipsed arrangement of the trimethylsilyl groups is associated with a significant opening of the SiN(1)Si' angle. The SiNSi angle in bis(dioxane)potassium bis(trimethylsilyl)amide<sup>[8]</sup>—a compound which also has an eclipsed conformation of the Me<sub>3</sub>Si groups—amounts to 136.2°.

4) The cyclopentadienyl ligands display a distinct tendency to engage in trihapto rather than the usual pentahapto coord-

ination. Thus the vanadium-carbon distances for C(4), C(5), and C(8) are 20 pm shorter than those for C(6) and C(7). For the same reason the cyclopentadienyl ring is not strictly planar, but is made up of a triangle [C(4), C(5), C(8)] and a planar rectangle [C(5), C(6), C(7), C(8)] whose normals enclose an angle of 6.2°. The deviation from planarity of the five-membered ring is thus directed away from the metal atom.

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CAS Registry number:

Bis(trimethylsilyl)isodiazenebis(cyclopentadienyl)vanadium, 59301-87-0

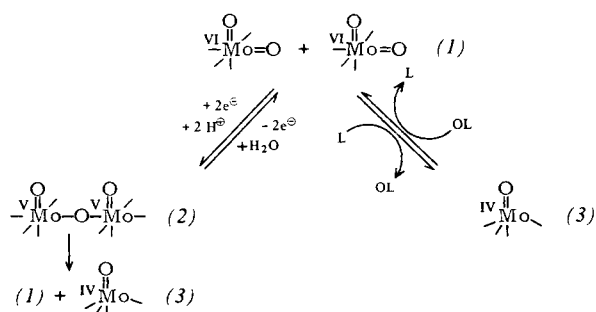
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- [2] K. K. Kakati and B. Chaudhuri, *Acta Crystallogr. B* 24, 1645 (1968); G. Huttner, W. Gartzke, and K. Allinger, *J. Organomet. Chem.* 91, 47 (1975).
- [3] G. A. Heath, R. Mason, and K. M. Thomas, *J. Am. Chem. Soc.* 96, 259 (1974).
- [4] X-Ray diffraction, single crystal (Picker four-circle diffractometer). Space group Fdd<sub>2</sub>; cell constants *a*=1692(1), *b*=2140(1), *c*=1105.3(7) pm; *Z*=8. 1056 reflections, *R* value = 4.6%.
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- [6] J. Strähle and H. Bärnighausen, *Z. Anorg. Allg. Chem.* 357, 325 (1968).
- [7] M. Veith and H. Bärnighausen, *Acta Crystallogr. B* 30, 1806 (1974); M. Veith, *ibid.* B 31, 678 (1975).
- [8] A. M. Domingos and G. M. Sheldrick, *Acta Crystallogr. B* 30, 517 (1974).

## ABSTRACTS

### Reviews

Abstracts of selected progress reports and review articles

**The reaction mechanism of enzymes containing molybdenum** is reviewed by R. A. D. Wentworth. The most important enzymes containing Mo catalyze reductions of dinitrogen to ammonia, nitrate to nitrite, and oxidations of sulfite to sulfate, xanthine to uric acid, and aldehydes to carboxylic acids. A discussion of the chemistry of inorganic oxo complexes of Mo<sup>VI</sup>, Mo<sup>V</sup>, and Mo<sup>IV</sup> leads to a new suggestion for the mechanism of oxidase and reductase action:



In its resting state, the enzyme contains two hexacoordinate Mo<sup>VI</sup> atoms carrying at least two oxo ligands (1). Under physiological conditions these can be reduced to a dinuclear Mo<sup>V</sup> species (2); (2) can disproportionate to a pentacoordinate Mo<sup>IV</sup> species (3) and (1). Species (3) is the active entity effecting reduction by taking over an oxo ligand from OL, the oxidized form of the substrate (reductase action). Acting as oxidase, (1) loses an oxo ligand to L, the reduced substrate, and forms (3). This mechanism is also able to explain the inhibition of xanthine oxidase by allopurinol. [Mechanisms for the Reactions of Molybdenum in Enzymes. *Coord. Chem. Rev.* 18, 1—27 (1976); 136 references]

[Rd 849 IE—H]

**The evolution of bacterial energy metabolism** is discussed by R. E. Dickerson, R. Timkovich, and R. J. Almassy on the basis of the folding of the evolutionarily homologous cytochromes of type c. Oxygen respiration of bacteria and eukaryotes is considered to have developed from a double purpose (photosynthesis and respiration) electron transport chain, as found in the purple non-sulfur bacteria, with loss of photosynthetic capability. An elaborate scheme is drawn up for the development of photosynthesis and respiration in bacteria, beginning with a symbiotic sulfur cycle, followed by development of the Krebs cycle, and culminating in the present symbiotic oxygen cycle between plants and animals. [The Cytochrome Fold and the Evolution of Bacterial Energy Metabolism. *J. Mol. Biol.* 100, 173—491 (1976); 42 references]

[Rd 852 IE—R]