Journal of Organometallic Chemistry, 301 (1986) 49–59
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE W(μ-N_2)W SYSTEM

II*. CRYSTAL STRUCTURE OF $[(\eta^5\text{-}C_5Me_5)W(CH_3)_3]_2(\mu\text{-}N_2)$, AN ORGANOTUNGSTEN(VI) COMPLEX CONTAINING A W=N–N=W CORE

MELVYN ROWEN CHURCHILL ** and YONG-JI LI

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214 (U.S.A.)

(Received July 8th, 1985)

Summary

The complex $[(\eta^5\text{-}C_5Me_5)W(CH_3)_3]_2(\mu\text{-}N_2)$ crystallizes in the centrosymmetric orthorhombic space group *Pbca* (No. 61) with a 17.023(6), b 17.651(4), c 18.791(4) Å, V 5646(3) $Å^3$ and D(calcd) 1.78 g cm^{-3} for mol. wt. 756.46 and $Z = 8$. Single-crystal X-ray diffraction data (Mo-K_α, $2\theta = 4.5$–$45.0°$) were collected with a Syntex $P2_1$ automated four-circle diffractometer and the structure was refined to R 7.1% for 2811 reflections with $|F_0| > 3.0\sigma(|F_0|)$. Each tungsten(VI) atom has a coordination environment resembling a "four-legged piano stool". The W=N–N=W core is essentially linear with < W(1)–N(1)–N(2) 167.0(16), N(1)–N(2)–W(2) 170.2(16)°, W(1)–N(1) 1.742(17), W(2)–N(2) 1.763(18) and N(1)–N(2) 1.334(26) Å. The W–C(methyl) linkages *trans* to the μ-N_2 ligand are slightly longer than those *cis* to the μ-N_2 ligand (2.296(33)–2.318(39) vs. 2.223(26)–2.249(25) Å).

Introduction

The first terminal dinitrogen complexes, all salts of the $[Ru(NH_3)_5N_2{}^{2+}]$ cation, were reported by Allen and coworkers some twenty years ago [2–4]. Soon after this, the first bridging dinitrogen complex, $[(NH_3)_5RuN{\equiv}NRu(NH_3)_5{}^{4+}]$ was synthesized [5] and structurally characterized [6]. Progress in this field has been extensively reviewed [7–11]. Until recently, all complexes with a bridging "end-on" dinitrogen ligand contained a μ-N_2 system in which the nitrogen–nitrogen bond length was not substantially longer than that in the dinitrogen molecule (N≡N 1.0976 Å [12]). Such

---

[*] For Part I see Ref. 1.

[**] Address correspondence to this author.

0022-328X/86/$03.50

species are best represented as having the molecular core shown in **1**.

$$\mathrm{M \leftarrow :N{\equiv}N: \rightarrow M}$$

(**1**)

Schrock and coworkers have synthesized μ-N_2 complexes of niobium and tantalum [13,14] in which the nitrogen–nitrogen bond is substantially more activated, as indicated both by chemical reactivity [14] and molecular dimensions. X-ray crystallographic studies show short metal–nitrogen distances and long nitrogen–nitrogen bond lengths. Thus, the complex $[\mathrm{Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2}]_2(\mu\text{-}N_2)$ has Ta(1)–N(1) 1.837(8), N(1)–N(2) 1.298(12) and Ta(2)–N(2) 1.842(8) Å [13,15]; $[\mathrm{TaCl_3(PBz_3)(THF)}]_2(\mu\text{-}N_2)$ has Ta–N 1.796(5) (twice) and N–N′ 1.282(6) Å [16]. Such structures are more accurately described by valence-bond diagram **2**, and are, formally, derivatives of the μ-N_2^{4-} ion.

$$\mathrm{Ta\overset{\leftarrow}{=}\ddot{N}{-}\ddot{N}\overset{\rightarrow}{=}Ta}$$

(**2**)

This work has been extended to tungsten complexes. In particular, hydrazine (N_2H_4) has been deprotonated in reactions leading to the 1,2-hydrazido(2−) complex $[\mathrm{W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))({\equiv}CCMe_3)I}]_2(\mu\text{-}N_2H_2)$ [17] and to the μ-dinitrogen complex $[\mathrm{W(C_6H_5C{\equiv}CC_6H_5)(CH_3OCH_2CH_2OCH_3)Cl_2}]_2(\mu\text{-}N_2)$ [1]; bond lengths within this latter complex (W(1)–N(1) 1.776(11), N(1)–N(2) 1.292(16), W(2)–N(2) 1.735(11) Å) are, again, compatible with its designation as a μ-N_2^{4-} derivative, **3**. The true oxidation state for tungsten in this complex is hard to assess, but probably approximates to +4.

$$\mathrm{W\overset{\leftarrow}{=}\ddot{N}{-}\ddot{N}\overset{\rightarrow}{=}W}$$

(**3**)

Murray and Schrock [18] have recently synthesized a μ-dinitrogen complex that can be regarded as a tungsten(VI) derivative. This species, $[(\eta^5\text{-}C_5Me_5)\mathrm{W(CH_3)_3}]_2(\mu\text{-}N_2)_2$, is accessible by two routes (see Schemes 1 and 2, in which $Cp' = \eta^5\text{-}C_5Me_5$ and $Me = CH_3$).

We now report the crystal structure of $[(\eta^5\text{-}C_5Me_5)\mathrm{W(CH_3)_3}]_2(\mu\text{-}N_2)$. It is only the second high oxidation state μ-dinitrogen complex of tungsten to be isolated; it is the first example of a tungsten(VI)-μ-dinitrogen species.

SCHEME 1

$$[\mathrm{Cp'WMe_4^+}][\mathrm{PF_6^-}] + 2N_2H_4 \rightarrow \mathrm{Cp'WMe_4(NHNH_2)} + [N_2H_5^+][\mathrm{PF_6^-}]$$

$$\mathrm{Cp'WMe_4(NHNH_2)} \rightarrow \mathrm{Cp'WMe_3(NNH_2)} + CH_4$$

$$\mathrm{Cp'WMe_3(NNH_2)} + [\mathrm{Cp'WMe_4^+}][\mathrm{PF_6^-}] \rightarrow \underset{(\sim 50\%)}{[\mathrm{Cp'WMe_3}]_2(\mu\text{-N})_2} + ?$$

SCHEME 2

$$3\mathrm{Cp'WMe_4} + \mathrm{Cp'WCl_4} \rightarrow 4\,\text{“}\mathrm{Cp'WMe_3Cl}\text{”}$$

$$2\,\text{“}\mathrm{Cp'WMe_3Cl}\text{”} \xrightarrow[N_2]{\mathrm{Na/Hg}} \underset{(\sim 5\text{–}20\%)}{[\mathrm{Cp'WMe_3}]_2(\mu\text{-}N_2)}$$

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $[(\eta^5\text{-}C_5Me_5)W(CH_3)_3]_2(\mu\text{-}N_2)$

(A) Crystallographic parameters

Crystal system: orthorhombic
a 17.023(6) Å
b 17.651(4) Å
c 18.791(4) Å
V 5646(3) Å^3
$Z = 8$

Space group: *Pbca* [D_{2h}^{16}; No. 61]
Formula: $C_{26}H_{48}N_2W_2$
Mol. wt: 765.46
D(calcd) 1.78 g cm^{-3}
T 23°C (296 K)

(B) Data collection

Diffractometer: Syntex P2_1
Radiation: Mo-$K_{\bar{\alpha}}$ ($\bar{\lambda}$ 0.710730 Å)
Monochromator: highly oriented graphite, equatorial geometry, $2\theta_m = 12.2°$, assumed 50% perfect
Reflections measured: $+h$, $+k$, $+l$ for $2\theta = 4.0\text{–}45.0°$
Scan type: couple θ(crystal)–2θ(counter)
Scan width: symmetrical, $[1.6 + \Delta(K_{\alpha_2} - K_{\alpha_1})]°$
Scan speed: 2.0 deg min^{-1} (in 2θ)
Background: stationary-crystal, stational-counter at beginning and end of 2θ scan; each for one-half of total scan time
Standards: 3 check reflections remeasured after each 97 reflections; decay was corrected
Reflections collected: 3845 total, merged to 3713 independent reflections [file name: WNFJ]
Absorption coefficient: μ(Mo-K_α) 86.3 cm^{-1}; empirical correction applied

---

Experimental

Data collection

Crystals were kindly provided by Professor R.R. Schrock of the Department of Chemistry, Massachusetts Institute of Technology. The crystal finally selected for data collection (after eliminating several smaller crystals which gave unexpectedly weak diffraction patterns) was an opaque dark-purple parallelepiped of approximate dimensions $0.31 \times 0.39 \times 0.48$ mm^3. This was inserted into a thin-walled glass capillary under an atmosphere of argon in a dry-box. The capillary was temporarily sealed with wax and later flame-sealed. The crystal was aligned on a Syntex P2_1 automated four-circle diffractometer. The determination of unit cell parameters (along with the crystal's orientation matrix) and data collection were carried out as described previously [19]. The final lattice parameters are based on a least-squares analysis of the unresolved Mo-$K_{\bar{\alpha}}$ of 25 reflections, well-separated in reciprocal space and with 2θ-values between 20 and 30°. Details appear in Table 1. The systematic absences ($0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, $hk0$ for $h = 2n + 1$) are consistent only with the centrosymmetric orthorhombic space group *Pbca* (No. 61, D_{2h}^{15}) [20].

All data were corrected for absorption via an empirical method based upon interpolation (in 2θ and ϕ) between a series of transmission curves based on ψ-scans of close-to-axial reflections. Data were further corrected for Lorentz and polarization factors and were converted to unscaled $|F_0|$ values. A Wilson plot was used to place the data on an (approximately) absolute scale.

TABLE 2

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $[(\eta^5\text{-}C_5Me_5)W(CH_3)_3]_2(\mu\text{-}N_2)$

(A) Positional and isotropic thermal parameters

Atom	x	y	z	B_{iso}
W(1)	0.43016(5)	0.43103(5)	0.20411(5)	
W(2)	0.25375(5)	0.34012(5)	0.02288(5)	
N(1)	0.3729(11)	0.3916(10)	0.13684(89)	4.65(40)
N(2)	0.3160(11)	0.3701(11)	0.09242(93)	5.03(42)
C(1)	0.4511(12)	0.5228(12)	0.2992(11)	3.71(41)
C(2)	0.4095(12)	0.4617(13)	0.3265(11)	4.30(48)
C(3)	0.3374(12)	0.4583(12)	0.2928(11)	3.87(43)
C(4)	0.3338(11)	0.5157(11)	0.2406(10)	3.33(40)
C(5)	0.4057(11)	0.5575(11)	0.2442(10)	3.56(40)
C(6)	0.5304(16)	0.5537(16)	0.3249(14)	6.73(66)
C(7)	0.4326(17)	0.4199(16)	0.3896(14)	7.12(66)
C(8)	0.2721(16)	0.4020(15)	0.3092(14)	6.75(66)
C(9)	0.2664(15)	0.5352(14)	0.1904(12)	5.72(56)
C(10)	0.4208(16)	0.6306(15)	0.2068(14)	6.58(62)
C(11)	0.3063(12)	0.2212(12)	0.0009(10)	3.68(44)
C(12)	0.2265(11)	0.2168(11)	−0.0289(10)	3.32(39)
C(13)	0.2229(11)	0.2697(12)	−0.0868(10)	3.70(43)
C(14)	0.2983(13)	0.3070(12)	−0.0937(11)	4.20(47)
C(15)	0.3482(12)	0.2735(11)	−0.0418(10)	3.57(43)
C(16)	0.3409(16)	0.1720(15)	0.0594(14)	6.19(63)
C(17)	0.1632(14)	0.1615(14)	−0.0058(12)	5.20(54)
C(18)	0.1491(15)	0.2802(15)	−0.1317(13)	6.30(62)
C(19)	0.3197(17)	0.3553(16)	−0.1568(14)	7.30(70)
C(20)	0.4374(16)	0.2943(16)	−0.0337(13)	6.32(60)
Cm(1)	0.4844(15)	0.5012(15)	0.1172(13)	6.23(61)
Cm(2)	0.5643(23)	0.4098(22)	0.2112(19)	11.3(11)
Cm(3)	0.4457(17)	0.3164(15)	0.2543(15)	7.15(69)
Cm(4)	0.2698(16)	0.4498(15)	−0.0333(13)	6.47(63)
Cm(5)	0.1801(16)	0.2928(16)	0.1103(14)	6.92(66)
Cm(6)	0.1296(20)	0.3885(18)	0.0082(16)	8.33(81)
H(11)	0.5220	0.5886	0.3626	8.0
H(12)	0.5562	0.5785	0.2867	8.0
H(13)	0.5620	0.5129	0.3414	8.0
H(21)	0.4160	0.4465	0.4308	8.0
H(22)	0.4881	0.4144	0.3903	8.0
H(23)	0.4088	0.3711	0.3889	8.0
H(31)	0.2398	0.4214	0.3461	8.0
H(32)	0.2945	0.3552	0.3239	8.0
H(33)	0.2412	0.3940	0.2676	8.0
H(41)	0.2321	0.5703	0.2128	8.0
H(42)	0.2381	0.4904	0.1788	8.0
H(43)	0.2869	0.5571	0.1480	8.0
H(51)	0.4049	0.6715	0.2363	8.0
H(52)	0.3918	0.6318	0.1636	8.0
H(53)	0.4753	0.6349	0.1967	8.0
H(61)	0.3592	0.1257	0.0395	8.0
H(62)	0.3017	0.1615	0.0940	8.0
H(63)	0.3835	0.1978	0.0812	8.0
H(71)	0.1651	0.1175	−0.0348	8.0
H(72)	0.1131	0.1847	−0.0103	8.0
H(73)	0.1715	0.1476	0.0424	8.0

TABLE 2 (continued)

(A) Positional and isotropic thermal parameters

Atom	x	y	z	B_{iso}
H(81)	0.1507	0.2467	−0.1712	8.0
H(82)	0.1466	0.3310	−0.1482	8.0
H(83)	0.1041	0.2695	−0.1035	8.0
H(91)	0.3352	0.3237	−0.1952	8.0
H(92)	0.3619	0.3879	−0.1443	8.0
H(93)	0.2755	0.3847	−0.1705	8.0
H(101)	0.4679	0.2621	−0.0633	8.0
H(102)	0.4528	0.2876	0.0144	8.0
H(103)	0.4452	0.3455	−0.0472	8.0

(B) Anisotropic thermal parameters [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	2.304(34)	3.507(40)	5.055(44)	0.463(36)	0.219(38)	−0.444(39)
W(2)	2.958(38)	2.711(35)	5.301(44)	−0.303(40)	0.431(43)	−0.675(36)

[a] Anisotropic thermal parameters are in standard Syntex XTL format and enter the expression for the calculated structure factor in the form: $\exp[-0.25(h^2a^{\star 2}B_{11} + \ldots + 2hka^{\star}b^{\star}B_{12} + \ldots)]$.

Solution and refinement of the structure

All calculations were performed using our locally-modified version of the Syntex XTL interactive crystallographic program package [21]. The heavy atoms (two tungsten atoms) were quickly and unambiguously located from a three-dimensional Patterson map. The remaining non-hydrogen atoms were located from difference-Fourier syntheses and the structure was refined to convergence with discrepancy indices [22] of R_F 7.1 and R_{wF} 6.9% for 131 variables refined against 2811 reflections with $|F_0| > 3\sigma(|F_0|)$. Anisotropic thermal parameters were used only for the tungsten atoms. Hydrogen atoms of the η^5-C_5Me_5 ligand were included in the usual positions based upon the assumptions (a) that one hydrogen of each CH_3 group lies vertically above the C_5-ring and points away from the metal atom (cf. refs. 23, 24) and (b) that d(C–H) equals 0.95 Å [25]. Hydrogen atoms of the metal-bonded methyl groups were not located; since their positions are indeterminate, their contributions were not included in the calculations.

Throughout the analysis we used the analytical form of the scattering factors for the neutral atoms [26a]; these were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion [26b]. A correction was made for the effects of secondary extinction, using the approximation to the Zachariasen formula shown in eq. 1.

$$|F_{0,\mathrm{cor}}| = |F_{0,\mathrm{uncor}}|(1.0 + gI_0) \qquad (1)$$

The value determined for g was 0.89×10^{-7}. The function minimized in least-squares refinement processes was $\Sigma w(|F_0| - |F_c|)^2$, where $w^{-1} = [\sigma(|F_0|)]^2 + [0.02|F_0|]^2$.

Final positional and thermal parameters are collected in Table 2.

Discussion

The crystal consists of an ordered arrangement of $[(\eta^5\text{-}C_5Me_5)W(CH_3)_3]_2(\mu\text{-}N_2)$ molecules which are mutually separated by normal Van der Waals' distances; there

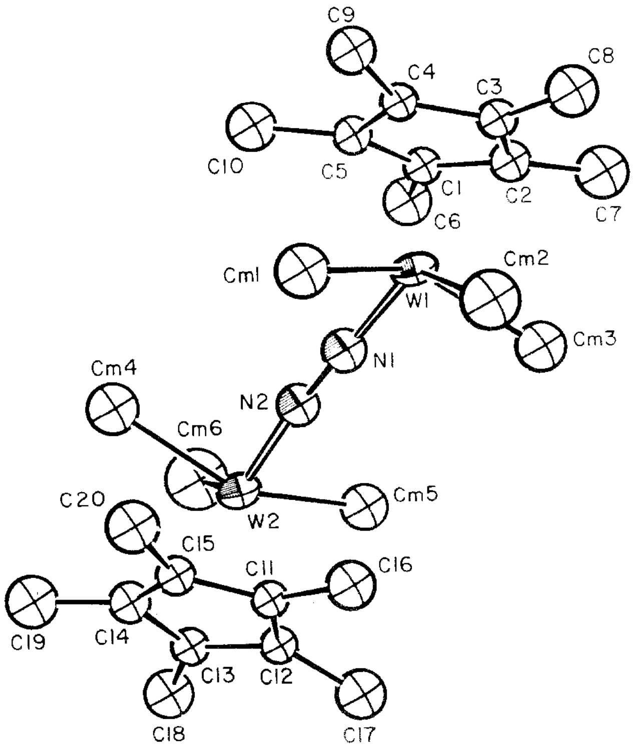


Fig. 1. Stereochemistry and labelling of non-hydrogen atoms in the $[(\eta^5\text{-}C_5Me_5)W(CH_3)_3]_2(\mu\text{-}N_2)$ molecule.

are no unusually short intermolecular contacts. The overall molecular geometry and the atomic numbering scheme are illustrated in Fig. 1. A stereoscopic view of the molecule is provided by Fig. 2. Intramolecular distances and angles are collected in Tables 3 and 4.

No crystallographic symmetry is imposed upon the molecule although it could, in principle, have C_i, C_2 or C_s symmetry. In fact (as can clearly be seen in Fig. 2) the molecule possesses no symmetry other than that of the trivial case, C_1.

The molecule contains two $(\eta^5\text{-}C_5Me_5)W(CH_3)_3$ units which are linked together via a μ-dinitrogen ligand. Each tungsten atom has a coordination environment resembling a "four-legged piano stool", reminiscent of that found in $(\eta^5\text{-}C_5H_5)M(CO)_3X$ (M = Mo, W) complexes [27].

The η^5-C_5Me_5 ligands are symmetrically bound to the tungsten atoms. For W(1), the five independent W–C(η^5-C_5Me_5) distances range from 2.322(19) through 2.437(20) Å, averaging 2.377 ± 0.045 Å. For W(2), the equivalent values are 2.319(21)–2.464(20) and 2.388 ± 0.061 Å. Within the η^5-C_5Me_5 systems, C–C(ring) distances range 1.382(29)–1.473(27) Å (average 1.424 ± 0.026 Å) and C(ring)–C(Me) bond lengths are 1.452(35)–1.569(33) Å (average 1.516 ± 0.030 Å). Thus, despite relatively large esd's on individual bond lengths, the average values are in precise accord with accepted distances. The η^1-ligands are arranged such that one N–W–C(Me) bond angle on each tungsten atom is substantially greater than the other two. The "*pseudo-trans*" angles N(1)–W(1)–Cm(2) 121.9(11) and

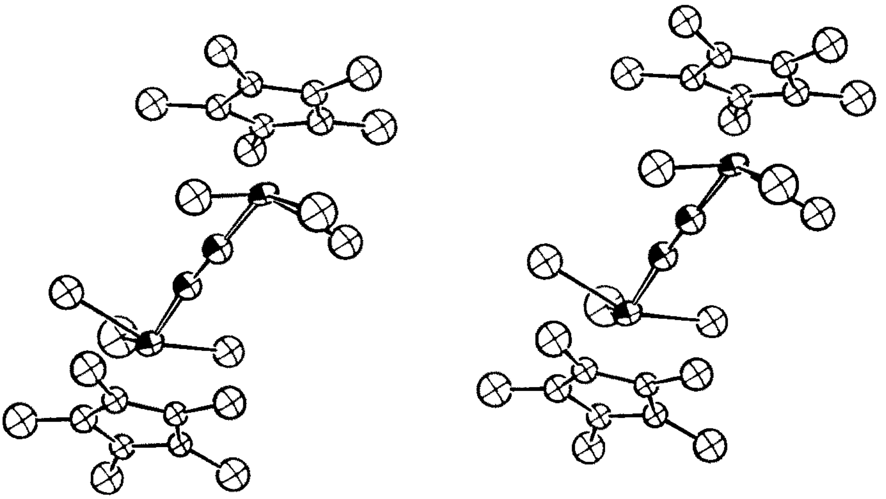


Fig. 2. Stereoview of the $[(\eta^5\text{-}C_5Me_5)W(CH_3)_3]_2(\mu\text{-}N_2)$ molecule.

N(2)–W(2)–Cm(6) 122.0(10)° are some 30–35° more obtuse than the remaining N–W–C(Me) angles (i.e., N(1)–W(1)–Cm(1) 85.6(9), N(1)–W(1)–Cm(3) 90.6(9), N(2)–W(2)–Cm(4) 90.9(9) and N(2)–W(2)–Cm(5) 84.5(9)°). Interestingly, the methyl groups lying "*pseudo-trans*" to the μ-dinitrogen ligand are systematically lengthened

TABLE 3

INTERATOMIC DISTANCES (Å) FOR $[(\eta^5\text{-}C_5Me_5)W(CH_3)_3]_2(\mu\text{-}N_2)$

(A) Distances from the tungsten atom

W(1)–N(1)	1.742(17)	W(2)–N(2)	1.763(18)
W(1)–C(1)	2.437(20)	W(2)–C(11)	2.319(21)
W(1)–C(2)	2.388(21)	W(2)–C(12)	2.430(20)
W(1)–C(3)	2.345(21)	W(2)–C(13)	2.464(20)
W(1)–C(4)	2.322(19)	W(2)–C(14)	2.392(21)
W(1)–C(5)	2.392(20)	W(2)–C(15)	2.333(20)
W(1)–Cm(1)	2.249(25)	W(2)–Cm(4)	2.223(26)
W(1)–Cm(2)	2.318(39)	W(2)–Cm(5)	2.229(27)
W(1)–Cm(3)	2.248(27)	W(2)–Cm(6)	2.296(33)

(B) Distance within the dinitrogen ligand

N(1)–N(2)	1.334(26)

(C) Distances within the C_5Me_5 ligands

C(1)–C(2)	1.388(30)	C(11)–C(12)	1.473(27)
C(2)–C(3)	1.382(29)	C(12)–C(13)	1.435(28)
C(3)–C(4)	1.410(28)	C(13)–C(14)	1.448(30)
C(4)–C(5)	1.431(27)	C(14)–C(15)	1.422(29)
C(5)–C(1)	1.429(28)	C(15)–C(11)	1.417(28)
C(1)–C(6)	1.535(34)	C(11)–C(16)	1.519(33)
C(2)–C(7)	1.452(35)	C(12)–C(17)	1.517(31)
C(3)–C(8)	1.523(34)	C(13)–C(18)	1.524(32)
C(4)–C(9)	1.526(31)	C(14)–C(19)	1.503(35)
C(5)–C(10)	1.491(33)	C(15)–C(20)	1.569(33)

TABLE 4

INTERATOMIC ANGLES (deg.) FOR $[(\eta^5\text{-}C_5Me_5)W(CH_3)_3]_2(\mu\text{-}N_2)$

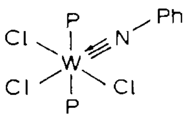
(A) Angles about the tungsten atoms			
N(2)–N(1)–W(1)	167.0(16)	N(1)–N(2)–W(2)	170.2(16)
N(1)–W(1)–Cm(1)	85.6(9)	N(2)–W(2)–Cm(4)	90.9(9)
N(1)–W(1)–Cm(3)	90.6(9)	N(2)–W(2)–Cm(5)	84.5(9)
N(1)–W(1)–Cm(2)	121.9(11)	N(2)–W(2)–Cm(6)	122.0(10)
Cm(1)–W(1)–Cm(2)	74.1(11)	Cm(5)–W(2)–Cm(6)	73.1(11)
Cm(2)–W(1)–Cm(3)	73.4(12)	Cm(6)–W(2)–Cm(4)	74.5(10)
Cm(3)–W(1)–Cm(1)	138.8(10)	Cm(4)–W(2)–Cm(5)	138.3(10)
(B) Angles within the C_5Me_5 groups			
C(2)–C(1)–C(5)	109.0(18)	C(12)–C(11)–C(15)	106.4(17)
C(1)–C(2)–C(3)	108.5(19)	C(11)–C(12)–C(13)	107.1(16)
C(2)–C(3)–C(4)	109.0(18)	C(12)–C(13)–C(14)	109.1(17)
C(3)–C(4)–C(5)	107.5(17)	C(13)–C(14)–C(15)	106.2(18)
C(4)–C(5)–C(1)	105.9(17)	C(14)–C(15)–C(11)	111.1(18)
C(2)–C(1)–C(6)	127.5(20)	C(12)–C(11)–C(16)	127.1(19)
C(5)–C(1)–C(6)	123.5(19)	C(15)–C(11)–C(16)	126.0(19)
C(1)–C(2)–C(7)	123.9(21)	C(11)–C(12)–C(17)	125.4(18)
C(3)–C(2)–C(7)	126.4(21)	C(13)–C(12)–C(17)	127.3(18)
C(2)–C(3)–C(8)	125.7(20)	C(12)–C(13)–C(18)	122.2(18)
C(4)–C(3)–C(8)	125.3(19)	C(14)–C(13)–C(18)	128.7(19)
C(3)–C(4)–C(9)	128.7(18)	C(13)–C(14)–C(19)	122.9(20)
C(5)–C(4)–C(9)	123.7(18)	C(15)–C(14)–C(19)	129.1(20)
C(1)–C(5)–C(10)	128.2(19)	C(11)–C(15)–C(20)	125.7(18)
C(4)–C(5)–C(10)	124.9(19)	C(14)–C(15)–C(20)	123.2(19)

relatively to the other W–CH_3 distances in the molecule. Thus, the *trans* W–C(Me) distances are W(1)–Cm(2) 2.318(39) and W(2)–Cm(6) 2.296(33) Å (average 2.307 ± 0.016 Å), whereas the *cis* W–C(Me) bond lengths are W(1)–Cm(1) 2.249(25), W(1)–Cm(3) 2.248(27), W(2)–Cm(4) 2.223(26) and W(2)–Cm(5) 2.229(27) Å (average 2.237 ± 0.013 Å).

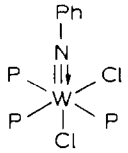
The methyl groups are arranged such that they take up a "*trans*" or "perfectly staggered" arrangement about the W=N–N=W backbone (see Fig. 2). This portion of the molecule thus has C_i ($\bar{1}$) symmetry. The possible full molecular C_i symmetry is broken by the relative rotational orientations (in the crystal) of the pentamethylcyclopentadienyl rings; for C_i symmetry they must be staggered, whereas, in fact, they are eclipsed.

The W=N–N=W system is close to linear, with W(1)–N(1)–N(2) 167.0(16) and W(2)–N(2)–N(1) 170.2(16)°. The tungsten–nitrogen bond lengths are very short (W(1)–N(1) 1.742(17) and W(2)–N(2) 1.763(18) Å; average 1.753 ± 0.015 Å) and in good agreement with values found previously [1] in $[W(C_6H_5C{\equiv}CC_6H_5)(CH_3OCH_2CH_2OCH_3)Cl_2]_2(\mu\text{-}N_2)$ (viz. W–N 1.735(11) and 1.776(11) Å; average 1.756 ± 0.028 Å).

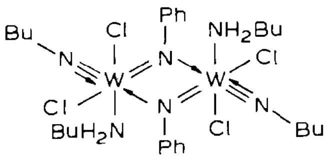
Using the average *cis* W–C(Me) bond length of 2.237 ± 0.013 Å in the present molecule and the Pauling covalent radii of ~ 0.77 Å for C(sp^3) and ~ 0.70 Å for N, we would predict a W–N bond of unit bond order to be associated with a bond length of ~ 2.17 Å, a value some 0.42 Å greater than that observed in the present complex. Comparisons can also be made with data from crystallographic analyses of a variety of complexes also believed to contain tungsten–nitrogen multiple bonds. Thus, the tungsten–imido distance in $W(NPh)Cl_3(PPh_3)_2$ is 1.742(8) Å, while the W–N–C(Ph) angle is 172.3(7)°; in $W(NPh)Cl_2(PMe_3)_3$ the W–NPh distance is 1.755(3) Å and the W–N–C(Ph) angle is 179.5(3)° [28]; these structures may be represented as **4** and **5**. In $[W(N(t\text{-}Bu))Cl_2(NH_2(t\text{-}Bu))]_2(\mu\text{-}NPh)_2$ [29] the terminal



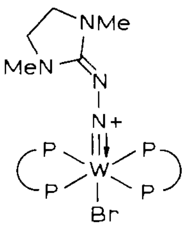
(4)



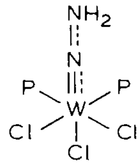
(5)



(6)

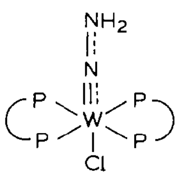


(7)

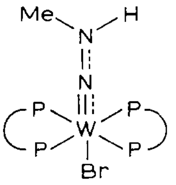


(8)

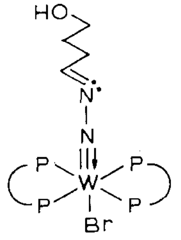
W–N(t-Bu) bond length is 1.729(4) Å, with a W–N–C(t-Bu) angle of 168.3(3)°; in contrast to this, the terminal $W–NH_2(t\text{-}Bu)$ single-bond is increased in length to 2.223(3) Å; this structure is shown as **6**. Other structures clearly containing tungsten–nitrogen multiple bonds include the $[W(NNCNMeCH_2CH_2NMe)Br(diphos)_2]^+$ cation (**7**) in which W–N is 1.776(7), N–N is 1.309(9) Å and W–N–N is 163.0(5)° [30], $W(NNH_2)Cl_3(PMe_2Ph)_2$ (**8**) in which W–N is 1.752(10), N–N is 1.300(17) Å and W–N–N is 178.7(9)° [31], the $[W(NNH_2)Cl(diphos)_2]^+$ cation (**9**) in which W–N is 1.73(1), N–N is 1.37(2) Å and W–N–N is 171(1)° [32], the $[W(NNH_2)Br(PMe_2Ph)_3(MeC_5H_4N)]^+$ cation (W–N 1.75, N–N 1.34 Å, W–N–N 177°) [33], the $[W(NNHMe)Br(diphos)_2]^+$ cation (**10**, wherein W–N 1.768(14), N–N 1.32(2) Å and W–N–N 174(1)°) [34] and the $[W(NNCH(CH_2)_3OH)Br(diphos)_2]^+$ cation (**11**, in which W–N 1.778(14), N–N 1.306(22) Å and W–N–N 172(1)°) [35]. The case for a tungsten–nitrogen bond of multiple bond-order in the present complex, $[(\eta^5\text{-}C_5Me_5)W(CH_3)_3]_2(\mu\text{-}N_2)$, is thus secure.



(9)



(10)



(11)

Finally we come to the observed N(1)–N(2) distance of 1.334(26) Å in the $\mu\text{-}N_2$ ligand of the present complex. While this is numerically the longest N–N distance yet determined in a $\mu\text{-}N_2$ complex of an "early transition metal element", it must be emphasized strongly that it is not statistically distinguishable from previous measurements of 1.298(12) Å in $[Ta(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$ [15], 1.292(16) Å in $[W(C_6H_5C{\equiv}CC_6H_5)(CH_3OCH_2CH_2OCH_3)Cl_2]_2(\mu\text{-}N_2)$ [1] and 1.282(6) Å in $[TaCl_3(PBz_3)(THF)]_2(\mu\text{-}N_2)$ [16]. It is both interesting and significant that these nitrogen–nitrogen bond lengths are all very similar to those observed in a variety of 1,1-hydrazido(2 −) complexes (i.e., $WNNH_2$ and WNNHR complexes): these are listed above along with the appropriate W–N bond lengths.

Finally, we note that the complex $[(\eta^5\text{-}C_5Me_5)W(CH_3)_3]_2(\mu\text{-}N_2)$ is unexpectedly stable both towards hydrolysis (it is not hydrolyzed upon being shaken with 1 *M* NaOH overnight) and towards strong acids (no hydrazine is liberated by gaseous HCl, although a red precipitate is formed) [18].

Additional Material

A table of observed and calculated structure factor amplitudes is available from M.R.C.

Acknowledgments

We thank Professor R.R. Schrock for providing the crystals studied in this analysis.

References

1 M.R. Churchill, Y.J. Li, K.H. Theopold and R.R. Schrock, Inorg. Chem., 23 (1984) 4472. (Crystal Structure of $[W(C_6H_5C{\equiv}CC_6H_5)(CH_3OCH_2CH_2OCH_3)Cl_2]_2(\mu\text{-}N_2)\cdot 0.5CH_3OCH_2CH_2OCH_3$.)
2 A.D. Allen and C.V. Senoff, Chem. Commun., (1965) 621.
3 F. Bottomley and S.C. Nyburg, Chem. Commun., (1966) 897.
4 A.D. Allen and F. Bottomley, Acc. Chem. Res., 1 (1968) 360.
5 D.E. Harrison, E. Weissberger and H. Taube, Science, 159 (1968) 320.
6 I.M. Treitel, M.T. Flood, R.E. Marsh and H.B. Gray, J. Am. Chem. Soc., 91 (1969) 6512.
7 J. Chatt and G.J. Leigh, Chem. Soc. Rev., (1972) 121.
8 A.E. Shilov, Russ. Chem. Rev. (Engl. Transl.), 43 (1974) 378; Usp. Khim., 43 (1974) 863.
9 A.D. Allen, R.O. Harris, B.R. Loescher, J.R. Stevens and R.N. Whiteley, Chem. Rev., 73 (1973) 11.
10 J. Chatt, J.R. Dilworth and R.L. Richards, Chem. Rev., 78 (1978) 589.
11 R.W.F. Hardy, F. Bottomley and R.C. Burns (Eds.), Treatise on Dinitrogen Fixation, Wiley, New York, 1979.
12 P.G. Wilkinson and N.B. Houk, J. Chem. Phys., 24 (1956) 528.
13 H.J. Turner, J.D. Fellman, S.M. Rocklage, R.R. Schrock, M.R. Churchill and H.J. Wasserman, J. Am. Chem. Soc., 102 (1980) 7809.
14 S.M. Rocklage and R.R. Schrock, J. Am. Chem. Soc., 104 (1982) 3077.
15 M.R. Churchill and H.J. Wasserman, Inorg. Chem., 20 (1981) 2899.
16 M.R. Churchill and H.J. Wasserman, Inorg. Chem., 21 (1982) 218.
17 M.R. Churchill, Y.J. Li, L. Blum and R.R. Schrock, Organometallics, 3 (1984) 109.
18 R.C. Murray and R.R. Schrock, J. Am. Chem. Soc., 107 (1985) 4557.
19 M.R. Churchill, R.A. Lashewycz and F.J. Rotella, Inorg. Chem., 16 (1977) 265.
20 International Tables for X-Ray Crystallography, Volume 1, Kynoch Press, Birmingham, 1965, p. 150.
21 Syntex XTL Operations Manual, Syntex Analytical Instruments, Inc., Cupertino, California, U.S.A., 1976.
22 $R_F = 100\Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF} = 100[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.
23 M.R. Churchill and S.W.-Y. Ni, J. Am. Chem. Soc., 95 (1973) 2150.
24 M.R. Churchill and W.J. Youngs, Inorg. Chem., 18 (1979) 1697.
25 M.R. Churchill, Inorg. Chem., 12 (1973) 1213.
26 International Tables for X-Ray Crystallography, Volume 4, Kynoch Press, Birmingham, 1974, (a) pp. 99–101, (b) pp. 149–150.
27 C. Bueno and M.R. Churchill, Inorg. Chem., 20 (1981) 2197.

28 D.C. Bradley, M.B. Hursthouse, K.M.A. Malik, A.J. Nielson and R.L. Short, J. Chem. Soc., Dalton Trans., (1983) 2651.

29 D.C. Bradley, R.J. Errington, M.B. Hursthouse, A.J. Nielson and R.L. Short, Polyhedron, 2 (1983) 843.

30 H.M. Colquhoun and D.J. Williams, J. Chem. Soc., Dalton Trans., (1984) 1675.

31 J. Chatt, M.E. Fakley, P.B. Hitchcock, R.L. Richards and N.T. Luong-Thi, J. Chem. Soc., Dalton Trans., (1982) 345.

32 G.A. Heath, R. Mason and K.M. Thomas, J. Amer. Chem. Soc., 96 (1974) 259.

33 M. Montevalli and M.B. Hursthouse, personal communication reported as ref. 220 in the following review article: J. Chatt, J.R. Dilworth and R.L. Richards, Chem. Rev., 76 (1978) 589–625.

34 F.C. Marsh, R. Mason and K.M. Thomas, J. Organomet. Chem., 96 (1975) C43.

35 P.C. Bevan, J. Chatt, R.A. Head, P.B. Hitchcock and G.J Leigh, J. Chem. Soc., Chem. Commun., (1976) 509.