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Synthesis and Crystallographic Characterization of a Dinuclear 1,2-Hydrazido(2–) Complex of Tungsten(VI), $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)\cdot CH_2Cl_2$

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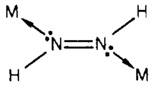
The dinuclear hydrazido(2–) complexes $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)X]_2(\mu\text{-}N_2H_2)$ (X = Cl, I) have been synthesized by the elimination of HX from a 2:1 mixture of $W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)X_2$ and hydrazine carried out in the presence of excess base (NEt_3) and have been characterized spectroscopically (NMR, IR). The iodo derivative crystallizes from dichloromethane as the 1:1 solvate, of stoichiometry $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)\cdot CH_2Cl_2$, in the centrosymmetric monoclinic space group $C2/c$ (No. 15) with a = 17.831 (4) Å, b = 14.588 (4) Å, c = 17.169 (5) Å, β = 99.95 (2)°, and Z = 4. The structure was refined to R_F = 3.7% for all 3896 reflections with 2θ = 3.5–50.0° (Mo Kα radiation). The dinuclear tungsten(VI) complex has crystallographically imposed C_2 symmetry with a symmetrical trans geometry for the W–NH–NH–W skeleton. Distances within this system (W–N = 1.932 (7) Å, N–N = 1.410 (9) Å) are consistent with those of the symmetrical hydrazido(2–) structure, rather than those of the neutral diimine structure.

Introduction

We have recently reported the synthesis of some dinuclear complexes of tantalum that contain a bridging dinitrogen ligand.[2,3] The results of crystallographic studies on $[Ta(CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$[3,4] and $[TaCl_3(PBz_3)(THF)]_2(\mu\text{-}N_2)$,[5] which yielded the bond lengths Ta–N ≈ 1.8 Å and N–N ≈ 1.3 Å, strongly indicate that the $Ta(\mu\text{-}N_2)Ta$ core of these molecules may best be represented formally as a Ta═NN═Ta system, rather than as a $Ta\leftarrow:N\equiv N:\rightarrow Ta$ system. All previously reported "end-on" bridging dinitrogen complexes[6] had been represented as complexes of the neutral dinitrogen ligand. Thus, the $[(NH_3)_5Ru\leftarrow:N\equiv N:\rightarrow Ru(NH_3)_5{}^{4+}]$ ion is considered to be an octahedral ruthenium(II) complex of neutral dinitrogen; the N≡N bond length is "short" (1.124 (15) Å) while the $Ru\leftarrow:N_2$ distance is 1.928 (6) Å.[7] In contrast to this, the species $[TaCl_3(PBz_3)(THF)]_2(\mu\text{-}N_2)$[5] has a "long" N–N bond (1.282 (6) Å) and "short" Ta–N bonds (1.796 (5) Å); this latter distance is similar to the Ta═N distance found in $TaCl_3(PEt_3)(THF)(NPh)$.[8] The $\mu\text{-}N_2$ ligand in the $Ta(\mu\text{-}N_2)Ta$ complexes may thus be viewed *formally* as an $N_2{}^{4-}$ ligand and the complexes as typical Ta(V) derivatives.

Similar variations are possible for a bridging ligand of identity $\mu\text{-}N_2H_2$. (Note: we are considering specifically a symmetrical ligand with the connectivity HNNH; we are not considering NH_2 derivatives.) Such a ligand could behave as a neutral diimine ligand (see I), and such behavior has been observed in the dinuclear chromium(0) complex $[Cr(CO)_5]_2(\mu\text{-}N_2H_2)$ in which Cr–N = 2.076 (1) Å and N═N = 1.25 Å.[9] A second possibility is that the $\mu\text{-}N_2H_2$ ligand may behave as a hydrazido(2–) ligand (see II). This latter behavior has not, to the best of our knowledge, been reported previously. It is now reported for the tungsten(VI) species $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)X]_2(\mu\text{-}N_2H_2)$ (X = Cl, I).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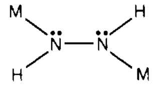
II

Experimental Section

Preparation of $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)Cl]_2(\mu\text{-}N_2H_2)$. A mixture of $W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)Cl_2$ (1.06 g, 2.1 mmol)[10] dissolved in 15 mL of ether and 4 equiv of NEt_3 (1.18 mL, 8.5 mmol) were added over a 20 min period to ether (15 mL) containing hydrazine (34 μL, 1.1 mmol) maintained at –78 °C. The purple mixture was warmed to room temperature over a 2-h period. It turned red at 0 °C. After 12 h the mixture was filtered, and the $Et_3NH^+Cl^-$ was washed with ether. The ether was removed from the filtrate in vacuo and the resulting red oil triturated with pentane. The pentane was decanted away from the resulting orange-red solid (which was saved), concentrated in vacuo, and cooled to –30 °C to give after 1 day a second quantity of orange solid (overall 0.46 g, 45%). The compound can be recrystallized from dichloromethane: ^1H NMR ($CDCl_3$) δ 10.7 (s, 1, NH), 2.56, 2.18, 1.99, and 1.94 (each a s, 3, $C_5Me_4(t\text{-}Bu)$), 1.37 (s, 9, CMe_3), 1.11 (s, 9, CMe_3); ^{13}C NMR ($CDCl_3$) δ 298.7 (s, $CCMe_3$), 120.0, 118.2, 117.3, 113.0, and 112.6 (each a s, $C_5Me_4(t\text{-}Bu)$), 50.3 (s, CMe_3), 34.7 (s, CMe_3), 32.6 (q, J_{CH} = 125 Hz, CMe_3), 32.1 (q, J_{CH} = 125 Hz, CMe_3), 16.8, 14.8, 12.1, and 10.9 (each a q, J_{CH} = 128 Hz, $C_5Me_4(t\text{-}Bu)$); IR (Nujol) 3260 cm^{-1} (NH). Anal. Calcd for $W_2C_{36}H_{62}Cl_2N_2$: C, 44.97; H, 6.50. Found: C, 45.00; H, 7.14.

Preparation of $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I_2$. $W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)Cl_2$ (0.82 g, 1.6 mmol) was dissolved in 10 mL of toluene and 2.2 equiv of $(CH_3)_3SiI$ (0.72 g, 3.6 mmol) were added. The solution turned emerald green after 10 min. After 1 h the toluene was removed in vacuo and the green residue was dissolved in pentane. The solution was filtered, and the pentane was removed in vacuo to give a flocculent green solid (yield 1.01 g, 90%): ^1H NMR (C_6D_6) δ 2.42 (s, 6, $C_5Me_4(t\text{-}Bu)$), 1.86 (s, 6, $C_5Me_4(t\text{-}Bu)$), 1.41 (s, 9, CMe_3), 1.30 (s, 9, CMe_3); ^{13}C NMR (C_6D_6) δ 335.6 (s, $CCMe_3$), 134.0, 122.3, and 112.0 (each a s, $C_5Me_4(t\text{-}Bu)$), 47.9 (s, CMe_3), 35.2 (s, CMe_3), 34.0 (q, J_{CH} = 131 Hz, CMe_3), 33.5 (q, J_{CH} = 131 Hz, CMe_3), 17.8 (q, J_{CH} = 128 Hz, $C_5Me_4(t\text{-}Bu)$), 15.3 (q, J_{CH} = 128 Hz, $C_5Me_4(t\text{-}Bu)$).

Preparation of $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)$. NEt_3 (0.61 mL, 4.4 mmol) and N_2H_4 (12 μL, 0.4 mmol) were

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Table I. Experimental Data for the X-ray Diffraction Study of $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)\cdot CH_2Cl_2$

(A) Crystal Data

cryst system: monoclinic	space group: $C2/c$ [C^6_{2h}; No. 15]
a = 17.8313 (38) Å	V = 4398.7 (19) Å^3
b = 14.5879 (38) Å	Z = 4 (dimeric units)
c = 17.1685 (47) Å	mol wt = 1227.4 amu
β = 99.947 (20)°	ρ(calcd) = 1.85 g cm^{-3}
	μ(Mo Kα) = 71.0 cm^{-1}

(B) Data Collection

radiation:	Mo K$\bar{\alpha}$ ($\bar{\lambda}$ = 0.710 730 Å)
2θ limits:	3.5–50.0°
scan width:	[2θ(Kα_1) – 1.0]–[2θ(Kα_2) + 1.0]°
scan speed:	2.50 deg min^{-1}
scan type:	θ(crystal)–2θ(counter)
monochromator:	highly oriented graphite, equatorial mode (2θ_{mono} = 12.2°)
bkgd meast:	stationary crystal and counter at beginning and end of 2θ scan, each for half of the scan time
reflctns measd:	$+h,+k,\pm l$
reflctns collected:	4345 total, 3869 unique data
standard reflctns:	three remeasured after each 97 reflctns (12,2,3; 2,10,3; 2,4,9), a slight decay was observed, and a correction was made based on the intensities of the standard reflctns

dissolved in 30 mL of diethyl ether and cooled to −78 °C. An ether solution of $W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I_2$ (0.5 g, 0.7 mmol) was added over a 40-min period. The solution turned orange at first and then green-brown once all of the tungsten was added. The solution was warmed to room temperature over a 2-h period and stirred overnight. The resulting pink solution was filtered, and the precipitate was washed with ether. This precipitate is a mixture of product and $Et_3NH^+I^-$. The $Et_3NH^+I^-$ was removed by washing with 10 mL of cold acetonitrile to give 0.070 g of pink product. The ether was removed in vacuo from the initial filtrate, and the resulting red oil was triturated with pentane to give more pink solid. The pentane supernatant was concentrated in vacuo and stored at −30 °C. After 1 day, a third crop of pink solid was collected (total crude yield 0.25 g, 31%). The product can be recrystallized from dichloromethane to give magenta crystals: ^{1}H NMR ($CDCl_3$) δ 10.95 (s, 1, NH), 2.53, 2.17, 2.13, and 2.06 (each a s, 3, $C_5Me_4(t\text{-}Bu)$), 1.39 (s, 9, CMe_3), 1.14 (s, 9, CMe_3); IR (Nujol) 3260 cm^{-1} (NH). The compound was too insoluble for a high quality ^{13}C NMR spectrum to be obtained easily.

Collection of X-ray Diffraction Data for $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)\cdot CH_2Cl_2$. A well-formed single-crystal of approximate dimensions 0.44 × 0.32 × 0.22 mm was placed into a thin-walled glass capillary tube while in an inert atmosphere (Ar) drybox. The capillary was temporarily sealed with wax and later flame-sealed. [Note that crystals are air sensitive and form an amorphous white powder within a few hours of exposure to air.] The capillary was mounted on a eucentric goniometer on the Syntex P2$_1$ automated four-circle diffractometer at SUNY—Buffalo. Crystal alignment and determination of the orientation matrix and unit-cell parameters were carried out as described previously.[11] Final lattice parameters are based on a least-squares analysis of the unresolved Mo K$\bar{\alpha}$ peaks of 25 reflections with 2θ values between 25° and 35° and in well-separated regions of reciprocal space. Information on data collection etc. appears in Table I. Symmetry-equivalent data were averaged, yielding internal discrepancy indices $R(I)$ = 1.1% and $R_w(I)$ = 0.5%. All 3869 unique reflections were converted to unscaled $|F_o|$ values following correction for absorption and for Lorentz and polarization effects. A Wilson plot was used to place the data on an approximate absolute scale.

Solution and Refinement of the Structure. The systematic absences of hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$ ($h = 2n + 1$) are consistent with Cc (No. 9) or $C2/c$ (No. 15) as possible space groups.

The heavy atoms were located from a Patterson map, which strongly indicated that the true space group was the centrosymmetric $C2/c$, with the dimeric molecule lying about a crystallographic twofold axis.

The remaining non-hydrogen atoms were located from difference Fourier syntheses and the structure converged with R_F = 3.7%, R_{wF} = 5.2%, and GOF = 3.13 for 204 variables refined against all 3896 reflections (none rejected). Hydrogen atoms of the $\eta^5\text{-}C_5Me_4(t\text{-}Bu)$ and $CCMe_3$ ligands were included in idealized calculated positions with d(C–H) = 0.95 Å.[12] A dichloromethane solvent molecule was found, lying on a twofold axis. The crystal composition is thus $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)\cdot CH_2Cl_2$.

All calculations were performed with the Syntex XTL interactive structure-solving package[13] as modified by our research group at SUNY—Buffalo. Analytical scattering factors for neutral atoms[14a] were corrected for both the $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion.[14b] The function minimized during full-matrix least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$.

Final positional parameters are collected in Table II; anisotropic thermal parameters are deposited as Table II-S (supplementary material).

Results and Discussion

Molecular Geometry of $(W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)$. Intramolecular distances and angles are collected in Tables III and IV. The overall molecular geometry and the scheme used in labeling atoms are illustrated in Figure 1. The dinuclear tungsten complex is bisected by a crystallographic twofold axis at $x = 0$ and $z = {}^1/_4$ which passes through the midpoint of the N–N′ bond. The crystallographic asymmetric unit thus contains only half of the $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)$ molecule. Atoms in the basic asymmetric unit (as defined by the coordinates in Table II) are labeled normally; those in the other half of the molecule are labeled with a prime and are related to atoms in the basic unit by the transformation $x', y', z' = -x, y, {}^1/_2 - z$. (It should be noted here that the dichloromethane ligand also lies on a two fold axis at $x = {}^1/_2$ and $z = {}^1/_4$; the atom Cl″ is related to the Cl in Table II by the transformation $x'', y'', z'' = 1 - x, y, {}^1/_2 - z$.)

Geometry about the Tungsten(VI) Center. Each tungsten(VI) atom is in a chiral environment, being surrounded tetrahedrally by four different ligand—an $\eta^5\text{-}C_5Me_4(t\text{-}Bu)$ ligand, a neopentylidyne fragment, an iodide ion, and one end of the $\mu\text{-}N_2H_2$ ligand. (The two halves of the dinuclear molecule, being related by a C_2 axis, have the same chirality. Nevertheless, the crystal as a whole is centrosymmetric, being composed of equal numbers of *R,R* and *S,S* molecules which are related to one another by crystallographic inversion centers.)

The tungsten(VI) atoms have a coordination geometry that is easily described as "resembling a three-legged piano stool". Angles between the monodentate ligands are fairly regular, with I–W–N = 101.56 (20)°, I–W–C(1) = 93.98 (26)°, and N–W–C(1) = 99.91 (33)°.

The $\mu\text{-}N_2H_2$ Ligand. The complexes $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)X]_2(\mu\text{-}N_2H_2)$ (X = Cl, I) are prepared from the appropriate halide as shown in eq 1. For each complex

$$2W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)X_2 + N_2H_4 + 2NEt_3 \rightarrow [W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)X]_2(\mu\text{-}N_2H_2) + 2Et_3NH^+X^- \quad (1)$$

the $\mu\text{-}N_2H_2$ fragment was characterized spectroscopically

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Table II. Atomic Positional Parameters for $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)\cdot CH_2Cl_2$ [a]

atom	x	y	z	B_{iso}, Å^2
W	0.10857 (2)	0.15747 (2)	0.17949 (2)	
I	0.13001 (4)	−0.02672 (5)	0.17888 (4)	
N	0.01047 (38)	0.16603 (46)	0.21224 (37)	
C(1)	0.16889 (44)	0.17343 (55)	0.27172 (49)	
C(2)	0.22886 (49)	0.18235 (63)	0.34398 (52)	
C(3)	0.30773 (59)	0.16712 (88)	0.32149 (72)	
C(4)	0.22537 (62)	0.27592 (80)	0.38311 (60)	
C(5)	0.21288 (61)	0.10402 (83)	0.40161 (61)	
C(11)	0.17915 (45)	0.25884 (61)	0.11187 (51)	
C(12)	0.18313 (50)	0.17616 (63)	0.07348 (54)	
C(13)	0.10861 (51)	0.15264 (67)	0.03251 (52)	
C(14)	0.05804 (47)	0.22189 (65)	0.04766 (51)	
C(15)	0.10074 (49)	0.28858 (61)	0.09896 (49)	
C(21)	0.24931 (53)	0.31198 (68)	0.14829 (60)	
C(22)	0.25326 (58)	0.12380 (79)	0.06990 (68)	
C(23)	0.09082 (62)	0.07422 (77)	−0.02181 (62)	
C(24)	−0.02467 (56)	0.21962 (83)	0.01002 (62)	
C(25)	0.07303 (56)	0.38435 (67)	0.12054 (58)	
C(26)	0.11291 (75)	0.41918 (78)	0.20163 (71)	
C(27)	−0.01159 (70)	0.39198 (82)	0.12067 (78)	
C(28)	0.09205 (64)	0.44973 (72)	0.05614 (69)	
C	0.50000 (0)	0.2564 (14)	0.25000 (0)	
Cl	0.46026 (29)	0.19523 (50)	0.17072 (30)	
HN	−0.0277	0.1707	0.1733	3.5
H(31)	0.3458	0.1727	0.3673	3.5
H(32)	0.3161	0.2116	0.2835	3.5
H(33)	0.3099	0.1075	0.2997	3.5
H(41)	0.2639	0.2796	0.4286	3.5
H(42)	0.1769	0.2836	0.3981	3.5
H(43)	0.2330	0.3227	0.3468	3.5
H(51)	0.2496	0.1066	0.4487	3.5
H(52)	0.2159	0.0462	0.3768	3.5
H(53)	0.1634	0.1117	0.4141	3.5
H(211)	0.2667	0.3475	0.1086	3.5
H(212)	0.2881	0.2704	0.1707	3.5
H(213)	0.2371	0.3513	0.1884	3.5
H(221)	0.2731	0.1414	0.0242	3.5
H(222)	0.2419	0.0601	0.0673	3.5
H(223)	0.2898	0.1361	0.1158	3.5
H(231)	0.0954	0.0924	−0.0738	3.5
H(232)	0.0402	0.0541	−0.0212	3.5
H(233)	0.1253	0.0255	−0.0052	3.5
H(241)	−0.0309	0.2482	−0.0404	3.5
H(242)	−0.0539	0.2514	0.0426	3.5
H(243)	−0.0413	0.1577	0.0040	3.5
H(261)	0.0935	0.4779	0.2114	3.5
H(262)	0.1661	0.4234	0.2020	3.5
H(263)	0.1036	0.3777	0.2415	3.5
H(271)	−0.0234	0.4526	0.1344	3.5
H(272)	−0.0256	0.3502	0.1581	3.5
H(273)	−0.0388	0.3778	0.0695	3.5
H(281)	0.0762	0.5101	0.0662	3.5
H(282)	0.0662	0.4301	0.0058	3.5
H(283)	0.1454	0.4492	0.0566	3.5
HC	0.4615	0.2939	0.2652	3.5

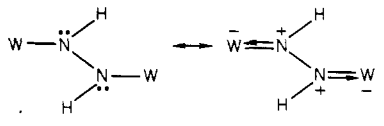
[a] Atoms C, Cl, and HC define the CH_2Cl_2 molecule, which lies about the C_2 axis at $x = 1/2$ and $z = 1/4$.

by ^{1}H NMR (NH at δ 10.7 for X = Cl and δ 10.95 for X = I) and IR ($\nu_{N\text{-}H}$ 3260 cm^{-1} for X = Cl and 3260 cm^{-1} for X = I).

The X-ray structural analysis of the iodo complex defines the μ-N_2H_2 fragment as a symmetrical hydrazido(2–) ligand, rather than as a diimine, by virtue of the following properties.

(1) The N–N′ bond length of 1.410 (9) Å is much closer to the accepted N–N single-bond length of ~1.45 Å[15] than to the N=N double-bond length of ~1.25 Å.[15]

(2) The tungsten–nitrogen bond lengths (W—N = W′—N′ = 1.932 (7) Å) are rather short and indicative, possibly, of some partial double-bond character. One may postulate contributions to the overall structure that involve donation of the lone pairs of electrons on N and N′ to the metal atoms W and W′, respectively (III ↔ IV). In this regard it should be noted that the hydrogen atom on N (and, by symmetry, that on N′) *was* located directly by difference Fourier methods (coordinates for H_{obsd}, x = −0.0433, y = +0.1779, z = +0.1681) in a position *strictly coplanar* with the W–N–N′ system; geometric parameters within this system are $d(N\text{–}H_{obsd})$ = 1.13 Å, <W–N–H_{obsd} = 121.5°, and ∠N′–N–H_{obsd} = 106.8°. However, this hy-



III IV

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(15) (a) Spec. Pub.—*Chem. Soc.* **1965**, *No. 18* p S-7s. (b) Pauling, L. "Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Table 7-2 (p 224) and Table 7-5 (p 228).

Table III. Interatomic Distances (Å) and Esd's for $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)\cdot CH_2Cl_2$

(A) Distances from the Tungsten Atom			
W-I	2.714 (1)	W-C(12)	2.447 (9)
W-N	1.932 (7)	W-C(13)	2.525 (9)
W-C(1)	1.769 (8)	W-C(14)	2.473 (9)
W-C(11)	2.371 (9)	W-C(15)	2.350 (9)
(B) Distances within the Bridging NH-NH Group			
N-N′	1.410 (9)		
(C) Distances within the Neopentylidyne Ligand			
C(1)-C(2)	1.497 (12)	C(2)-C(3)	1.538 (14)
C(2)-C(4)	1.527 (15)	C(2)-C(5)	1.569 (14)
(D) Distances within the η^5-C_5Me_4(*t*-Bu) Ligand			
C(11)-C(12)	1.382 (13)	C(13)-C(23)	1.476 (14)
C(12)-C(13)	1.434 (13)	C(14)-C(24)	1.505 (13)
C(13)-C(14)	1.408 (13)	C(15)-C(25)	1.548 (13)
C(14)-C(15)	1.439 (13)	C(25)-C(26)	1.536 (16)
C(15)-C(11)	1.444 (12)	C(25)-C(27)	1.513 (16)
C(11)-C(21)	1.512 (13)	C(25)-C(28)	1.542 (15)
C(12)-C(22)	1.476 (14)		
(E) Distance within CH_2Cl_2 Molecule			
C-Cl	1.679 (12)		

drogen atom was not well-behaved under least-squares refinement and was eventually replaced by an atom in a fixed, idealized, coplanar location (with d(N–H) = 0.87 Å)[12] noted as HN in Table II. While it is difficult to know that weight to give to the difference Fourier observations, they are, at least, consistent with some contribution from structure IV. The angles W-N-N′ and N-N′-W′ are each 131.7 (5)°—suggestive more of sp^2 than sp^3 hybridization of the nitrogen atoms. However, it is also possible that these large M-N-N angles result, in part, from steric interaction between the M-NH-NH-M fragment and neighboring ligands.

If we assume that the W–I bond length of 2.714 (1) Å represents a normal covalent bond, we can estimate the covalent radius of tungsten as ~1.38 Å in this complex [d(W–I) – r(I) = 2.71–1.33 Å[15b] = 1.38 Å]. The predicted W–N single bond length is then (1.38 + 0.72) 2.10 Å; the observed W–N distance in some 0.16 Å shorter than this value.

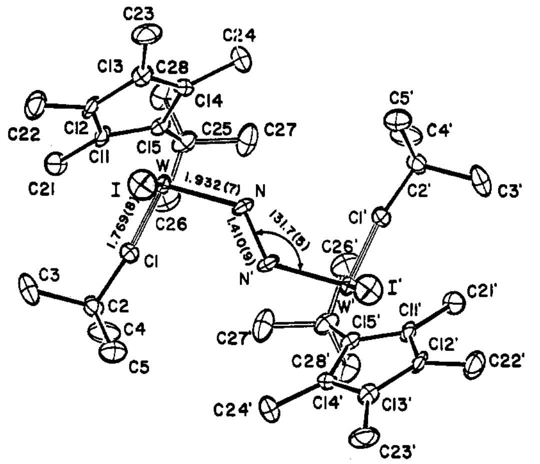
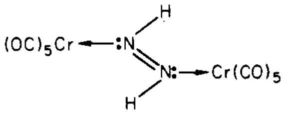


Figure 1. Geometry of the $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)$ molecule [ORTEP-II diagram]. The crystallographic C_2 axis is perpendicular to the plane of the paper and passes through the midpoint of the N–N′ bond. The hydrogen atoms of the μ-N_2H_2 ligand *probably* lie in the W–N–N′–W′ plane (see text).

Finally, in this regard, we observe that the *W*–N distances of 1.935 (8) Å in the present complex are substantially shorter than the *Cr*–N distances of 2.076 (1) Å found in the diimine complex $[Cr(CO)_5]_2(\mu\text{-}N_2H_2)$,[9] which has structure V, with d(N=N) = 1.25 Å and <N-N-Cr = 130.5°.



The Neopentylidyne Ligand. The neopentylidyne ligands are essentially linearly coordinated to tungsten, with a formal tungsten–carbon triple bond. The W≡C(1)—C(2) angle is 171.9 (7)°, and (as can clearly be seen in Figure 1) the slight deviation from linearity appears to result from intramolecular repulsions. The W≡C(1) dis-

Table IV. Interatomic Angles (deg) with Esd's for $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)\cdot CH_2Cl_2$

(A) Angles about the Tungsten Atom			
I-W-N	101.56 (20)	I-W-C(1)	93.98 (26)
N-W-C(1)	99.91 (33)		
(B) Angles within the Bridging NH-NH Group			
W-N-N′	131.66 (50)	N-N′-W′	131.66 (50)
(C) Angles within the Neopentylidyne Ligand			
W-C(1)-C(2)	171.87 (67)	C(1)-C(2)-C(4)	111.39 (76)
C(1)-C(2)-C(3)	109.43 (77)	C(1)-C(2)-C(5)	106.12 (74)
(D) Internal Angles of the η^5-C_5Me_4(*t*-Bu) Ligand			
C(15)-C(11)-C(12)	108.5 (8)	W-C(11)-C(21)	126.0 (6)
C(11)-C(12)-C(13)	108.9 (8)	W-C(12)-C(22)	123.1 (7)
C(12)-C(13)-C(14)	107.9 (8)	W-C(13)-C(23)	128.1 (7)
C(13)-C(14)-C(15)	108.1 (8)	W-C(14)-C(24)	124.1 (7)
C(14)-C(15)-C(11)	106.7 (7)	W-C(15)-C(25)	125.6 (6)
(E) External Angles of the η^5-C_5Me_4(*t*-Bu) Ligand			
C(21)-C(11)-C(15)	128.3 (8)	C(25)-C(15)-C(14)	126.9 (8)
C(21)-C(11)-C(12)	122.5 (8)	C(25)-C(15)-C(11)	125.1 (8)
C(22)-C(12)-C(11)	125.8 (9)	C(26)-C(25)-C(15)	113.5 (8)
C(22)-C(12)-C(13)	125.2 (9)	C(27)-C(25)-C(15)	115.2 (9)
C(23)-C(13)-C(12)	125.1 (9)	C(28)-C(25)-C(15)	105.5 (8)
C(23)-C(13)-C(14)	126.8 (9)	C(26)-C(25)-C(27)	106.3 (9)
C(24)-C(14)-C(13)	121.1 (8)	C(26)-C(25)-C(28)	108.7 (9)
C(24)-C(14)-C(15)	130.8 (3)	C(27)-C(25)-C(28)	107.4 (9)
(F) Angle in CH_2Cl_2 Molecule			
Cl-C-Cl″	115.8 (8)		

tance of 1.769 (8) Å is comparable to the previously measured tungsten–neopentylidyne distance (viz., W≡C = 1.785 (8) Å in $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe))$[16] and to related tungsten–alkylidyne bond lengths—1.807 (6) Å in $W(\mathit{CH}\cdot AlMe_{2-x}Cl_{1+x})(Cl)(PMe_3)_3$,[17] 1.813 (5) Å in $W(CAl_2Me_4Cl)(CH_3)(PMe_3)_2(\eta^2\text{-}C_2H_4)$,[18] 1.82 (2) Å in $W[\mathit{C}(p\text{-tol})](\eta^5\text{-}C_5H_5)(CO)_2$,[19] and 1.83 (3) Å in $[W_2(\mathit{C}PMe_3)_2(PMe_3)_4Cl_4](AlCl_4)_2$.[20]

It is of interest to note that the hydrogen atoms of the $\mu\text{-}N_2H_2$ ligand are *not* transferred to the neopentylidyne ligand under reaction conditions—i.e., the reaction shown in eq 2 has not taken place. This is in sharp contrast to

$$[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)X]_2(\mu\text{-}N_2\mathit{H}_2) \rightarrow [W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(C\mathit{H}CMe_3)X]_2(\mu\text{-}N_2) \quad (2)$$

the known reaction of complexes such as $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$ which are converted from alkylidyne amido complexes to alkylidene imido complexes upon heating (eq 3).[21]

$$W(CCMe_3)(NHPh)(PEt_3)_2Cl_2 \xrightarrow[70\ ^\circ C]{toluene} W(CHCMe_3)(NPh)(PEt_3)_2Cl_2 \quad (3)$$

Conclusion

The first formal derivatives of the $\mu\text{-}N_2H_2{}^{2-}$ dianion have been synthesized by deprotonation of hydrazine by the high oxidation state organometallic complexes $W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)X_2$ (X = Cl, I). The resulting dinuclear species $[W(\eta^5\text{-}C_5Me_4(t\text{-}Bu))(CCMe_3)X]_2(\mu\text{-}N_2H_2)$ contain trans W–NH–NH–W systems. The iodo complex is shown to have a formal N–N single bond (1.410 (9) Å)[22] along with rather short W–N distances (1.932 (7) Å). These results are in strict contrast to the diimine (i.e., neutral HN=NH) complex of chromium $[Cr(CO)_5]_2(\mu\text{-}N_2H_2)$ previously reported[9] and to the terminal unsymmetrical $=NNH_2$ system found in $[W(=NNH_2)Cl(diphos)_2{}^+][BPh_4{}^-]$ (W=N = 1.73 (1) Å, N–N = 1.37 (2) Å, ∠W=N—N = 171 (1)°).[23]

The present molecule, with its central W–NH–NH–W core, provides a further potential model for an intermediate stage in the process of the reduction of dinitrogen to ammonia.

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Registry No. $[W(\eta_5\text{-}C_5Me_4\text{-}(t\text{-}Bu))(CCMe_3)Cl]_2(\mu\text{-}N_2H_2)$, 87556-57-8; $W(\eta^5\text{-}C_5Me_4\text{-}(t\text{-}Bu))(CCMe_3)I_2$, 87556-58-9; $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu))(CCMe_3)I]_2(\mu\text{-}N_2H_2)\cdot CH_2Cl_2$, 87556-60-3.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes and Table II-S, anisotropic thermal parameters (21 pages). Ordering information is given on any current masthead page.

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