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The Ta(μ-N_2)Ta System. 2.[1] Crystal Structure of $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)\cdot{\sim}0.7CH_2Cl_2$. A Binuclear Diimido Complex of Octahedral Tantalum(V)

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Crystalline $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)\cdot{\sim}0.7CH_2Cl_2$ (where $P(bz)_3$ is $P(CH_2C_6H_5)_3$) has been studied via a single-crystal X-ray diffraction study. Crystals belong to the centrosymmetric monoclinic space group $P2_1/n$ with a = 10.8138 (25) Å, b = 18.7590 (48) Å, c = 14.6616 (32) Å, β = 106.428 (18)°, V = 2852.8 (12) Å^3, and Z = 2 (dimeric units). Diffraction data were collected with a Syntex P2$_1$ automated four-circle diffractometer, and the structure was solved via Patterson, difference-Fourier, and full-matrix least-squares refinement techniques. The resulting discrepancy indices are R_F = 3.3% and R_{wF} = 3.6% for all 3758 data (R_F = 2.7% and R_{wF} = 3.5% for all those 3403 reflections with $|F_o| > 3.0\sigma(|F_o|)$). The binuclear tantalum(V) complex lies on a crystallographic center of symmetry. Ta–Cl distances range from 2.375 (1) to 2.385 (2) Å, the Ta–$P(bz)_3$ bond length is 2.689 (1) Å, and the Ta–O(THF) distance is 2.308 (4) Å. The tantalum–nitrogen distrances are 1.796 (5) Å while the nitrogen–nitrogen distance is 1.282 (6) Å, suggesting that the complex is best described as a diimido complex, with a Ta=NN=Ta bridge.

Introduction

Recently Schrock and co-workers[2a] showed that the sodium amalgam reduction of the alkylidene complex $Ta(=CHCMe_3)(PMe_3)_2Cl_3$ in the presence of N_2 was a simple and direct method of preparing dinitrogen complexes of a group 5 transition metal. An X-ray crystallographic study of the binuclear species $[Ta(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$ produced by this method indicated that the bridging dinitrogen ligand was "diimido"-like and that the N–N bond was significantly activated relative to bridging dinitrogen complexes of other transition metals.[1,2a]

A second facile synthesis of diimido ditantalum complexes was described involving the reaction of a tantalum alkylidene complex with a diimine reagent PhCH=NN=CHPh. We now report the results of a single-crystal X-ray structural analysis of the species $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)$ (where $P(bz)_3$ is $P(CH_2C_6H_5)_3$) prepared in this manner[2b] (see eq 1).

$$2\,cis,mer\text{-}Ta(=CHCMe_3)(THF)_2Cl_3 \xrightarrow[(-2PhCH=CHCMe_3)]{+PhCH=NN=CHPh} [TaCl_3(THF)_2]_2(\mu\text{-}N_2) \xrightarrow[(-2THF)]{2P(bz)_3} [TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2) \quad (1)$$

Experimental Section

(A) Data Collection. The crystal used in the analysis was taken from a high-quality sample kindly provided by Professor R. R. Schrock of the Massachusetts Institute of Technology. It was a flat trapezoidal plate approximately 0.2 mm thick by 0.3 mm wide by 0.6 mm long. The material was found to be both air and moisture sensitive, and thus all operations were carried out on a crystal which has been carefully sealed in a glass capillary under strictly anaerobic conditions.

The investigation utilized a Syntex P2$_1$ automated diffractometer operated at ambient temperature. Details of the data collection, etc., are given in Table I; a description of the apparatus and experimental techniques has been made available.[3]

Absorption curves obtained for six reflections displayed transmission factor ratios (I_{max}/I_{min}) ranging from 1.20 to 1.47, and all were used to correct the raw intensity data (see Table I).

Table I. Experimental Data for the X-ray Diffraction Study of $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)\cdot 0.7CH_2Cl_2$

(A) Crystal Parameters[a] at 23 (1) °C

a, Å: 10.8138 (25)
b, Å: 18.7590 (48)
c, Å: 14.6616 (32)
β, deg: 106.428 (18)
V, Å^3: 2852.8 (12)

cryst system: monoclinic
space group: $P2_1/n$[b]
Z = 2 (dimeric units)
mol wt: 1415.1[c]
ρ(calcd), g cm^{-3}: 1.65[c]

(B) Data Collection

radiation: Mo K$\bar{\alpha}$ (λ = 0.710 730 Å)
2θ limits, deg: 4.0–45.0
scan type: coupled θ(crystal)–2θ(counter)
scan width, deg: $[1.8 + \Delta(\alpha_2-\alpha_1)]$
scan speed, deg min^{-1}: 2.0
reflctns measd: $+h,+k,\pm l$
reflctns collected: 3989 total, yielding 3758 unique data
abs coeff, cm^{-1}: 44.8
stds: 0,0,10, 0,16,0, and 600 measured after every 97 reflections; no significant changes
abs cor: empirical, employing full ψ scans of the following reflctns: 310 (2θ = 12.0°), 400 (15.7°), 600 (23.7°), $70\bar{1}$ (27.0°), $80\bar{2}$ (30.6°), and $10,0,\bar{2}$ (38.7°)

[a] Unit cell parameters were derived from a least-squares fit to the the setting angles of the unresolved Mo K$\bar{\alpha}$ component of 25 reflections with 2θ between 27 and 33°. [b] Nonstandard setting of space group $P2_1/c$ [C_{2h}^5; No. 14] having the equipoints $\pm(x, y, z)$ and $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$. [c] Based upon the refined partial occupancy (0.7) of the dichloromethane solvent molecule. The binuclear tantalum complex has a formula weight of 1355.6.

(B) Solution and Refinement. The $|F_o|$ values, scaled by means of a Wilson plot ($B_{iso,overall}$ = 3.06 Å^2), were used in the calculation of an unsharpened Patterson map, from which the location of the single crystallographically independent tantalum atom was obtained. A structure factor calculation, followed by a difference-Fourier synthesis, revealed the phosphorus and three chlorine atoms; a second ΔF map located all remaining nonhydrogen atoms in the half-molecule. Full-matrix least-squares refinement (treating the thermal motion of all atoms located thus far anisotropically) led to R_F = 6.4% and R_{wF} = 8.6%.

A difference-Fourier synthesis now revealed two large peaks centered about the crystallographic inversion center at ($^1/_2$, $^1/_2$, 0). This crystallographic evidence, coupled with information on the method of crystallization of the complex, was consistent with a dichloromethane molecule of solvation. Refinement of parameters for the single crystallographically independent chlorine atom led to its occupancy converging with a value of 0.7. The carbon atom of the dichloromethane molecule (which is necessarily disordered about the inversion center) was located from a difference-Fourier map and was input in

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(1) The following reference should be considered as part 1 of this series: Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.*, **1981**, *20*, 2899–2904.

(2) (a) Turner, H. W.; Fellmann, J. D.; Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 7809–7811. (b) At the onset of the crystal structure analysis, the compound under investigation was believed to be $[TaCl_3(P(bz)_3)_2]_2(\mu\text{-}N_2)$ by analogy with the tri*ethyl*phosphine complex **2b** reported in ref 2a.

(3) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

0020-1669/82/1321-0218$01.25/0

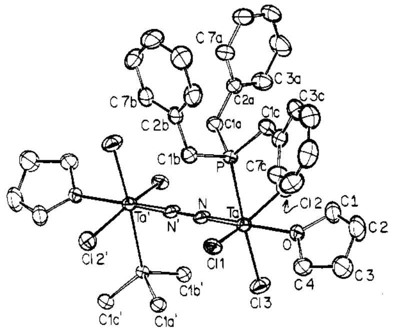

Figure 1. Atomic labeling scheme for the $[\mathrm{TaCl_3(P(bz)_3)(THF)}]_2(\mu\text{-N}_2)$ molecule. All hydrogen atoms are omitted (ORTEP-II diagram, 30% probability ellipsoids).

a fixed position with an occupancy of 0.35.

Hydrogen atoms were included in fixed idealized positions (trigonal or tetrahedral geometry, with d(C–H) = 0.95 Å)[4] and refinement proceeded smoothly to convergence with R_F = 3.3%, R_{wF} = 3.6%, and GOF = 1.31 for all 3758 data (none rejected). The agreement factors for those 3403 reflections with $|F_o| > 3.0\sigma(|F_o|)$ were R_F = 2.7%, R_{wF} = 3.5%, and GOF = 1.33. In the final cycle of refinement the "over-determination" ratio, NO:NV was 11.4:1.

Least-squares refinement minimized the function $\sum w(|F_o| - |F_c|)^2$, where the weight, w, was obtained from standard counting statistics modified by an "ignorance factor" of 0.02. Analytical scattering factors for neutral atoms were used;[5a] both real and imaginary components of anomalous dispersion[5b] were included. All calculations were performed with the Syntex XTL in-house structure-solving package[6] as modified by our research group at SUNY at Buffalo.

Final positional parameters are given in Table II; anisotropic thermal parameters are listed in Table III.

Results and Discussion

Intramolecular distances and their estimated standard deviations (esd's) are presented in Table IV, interatomic angles, with esd's, are given in Table V, and selected least-squares planes (and atomic deviations therefrom) are collected in Table VI. The atomic labeling scheme is illustrated in Figure 1, while Figure 2 provides a stereoscopic image of the molecule. The dimeric molecule lies on a center of symmetry (crystallographically imposed, at 0, 0, 0), which coincides with the center point of the nitrogen–nitrogen linkage. Atoms in the basic crystallographic asymmetric unit (i.e., those defined in Table II) are labeled normally. Those in the "other half" of the dinuclear tantalum complex, which are related to the basic asymmetric unit by the transformation $[x', y', z'] = [-x, -y, -z]$, are labeled with a prime (′).

The two tantalum atoms are therefore chemically and crystallographically equivalent, and each is in a slightly distorted octahedral coordination environment. The three chloride ligands are arranged in a meridional configuration in which Cl(3) is trans to the tribenzylphosphine ligand, while Cl(1) and Cl(2) are mutually trans to each other. Despite the two different chemical environments, the tantalum–chlorine bond lengths are essentially equal, with Ta–Cl(1) = 2.375 (1) Å, Ta–Cl(2) = 2.385 (2) Å, and Ta–Cl(3) = 2.378 (2) Å. The cis angles are Cl(1)–Ta–Cl(3) = 97.73 (5)° and Cl(2)–Ta–Cl(3) = 97.17 (6)°, while the trans angle is Cl(1)–Ta–Cl(2) = 158.45 (5)°. The octahedral coordination geometry about each tantalum atom is completed by a tribenzylphosphine ligand (Ta–P = 2.689 (1) Å and P–Ta–Cl(3) = 176.30 (5)°), a neutral tetrahydrofuran (THF) ligand (Ta–O = 2.308 (4) Å), and one nitrogen atom of the bridging dinitrogen ligand (Ta–N = 1.796 (5) Å and ∠N–Ta–O = 178.00 (17)°).

Table II. Final Positional Parameters for $[\mathrm{TaCl_3(P(bz)_3)(THF)}]_2(\mu\text{-N}_2)\cdot0.7\mathrm{CH_2Cl_2}$

atom	x	y	z
Ta	0.221 90 (2)	0.025 07 (1)	0.090 37 (1)
P	0.136 07 (12)	0.157 21 (7)	0.109 32 (9)
Cl(1)	0.283 15 (14)	0.075 99 (8)	−0.038 69 (10)
Cl(2)	0.194 15 (15)	0.015 16 (8)	0.245 59 (11)
Cl(3)	0.307 52 (15)	−0.090 94 (8)	0.083 48 (13)
O	0.431 10 (32)	0.053 26 (22)	0.173 67 (25)
N	0.058 60 (39)	0.006 15 (23)	0.023 66 (34)
C(1)	0.482 91 (61)	0.070 39 (41)	0.274 89 (44)
C(2)	0.620 60 (68)	0.084 07 (56)	0.292 55 (54)
C(3)	0.654 94 (70)	0.043 94 (62)	0.217 74 (70)
C(4)	0.539 32 (58)	0.038 87 (43)	0.137 76 (51)
C(1A)	−0.022 91 (48)	0.145 58 (29)	0.135 03 (38)
C(2A)	−0.042 60 (47)	0.184 91 (31)	0.218 56 (39)
C(3A)	−0.030 64 (67)	0.149 73 (36)	0.302 55 (48)
C(4A)	−0.048 96 (81)	0.185 68 (49)	0.380 82 (50)
C(5A)	−0.077 84 (69)	0.256 55 (49)	0.375 10 (53)
C(6A)	−0.089 02 (67)	0.293 38 (40)	0.291 82 (57)
C(7A)	−0.071 76 (60)	0.257 69 (35)	0.214 92 (44)
C(1B)	0.098 22 (57)	0.208 90 (31)	−0.002 87 (39)
C(2B)	0.027 04 (58)	0.277 80 (31)	−0.002 54 (37)
C(3B)	0.093 61 (69)	0.339 30 (35)	0.035 01 (48)
C(4B)	0.027 4 (10)	0.400 82 (35)	0.040 46 (56)
C(5B)	−0.105 5 (10)	0.403 62 (44)	0.007 47 (62)
C(6B)	−0.173 48 (72)	0.344 25 (45)	−0.032 15 (51)
C(7B)	−0.107 91 (66)	0.281 24 (35)	−0.036 52 (41)
C(1C)	0.226 20 (51)	0.217 25 (29)	0.202 43 (39)
C(2C)	0.347 44 (49)	0.253 50 (29)	0.192 55 (38)
C(3C)	0.384 70 (57)	0.317 95 (32)	0.239 74 (41)
C(4C)	0.492 57 (71)	0.352 59 (39)	0.238 97 (53)
C(5C)	0.570 23 (67)	0.323 39 (44)	0.189 44 (61)
C(6C)	0.535 88 (65)	0.260 00 (41)	0.139 88 (56)
C(7C)	0.423 78 (57)	0.225 25 (34)	0.141 65 (46)
Cl(S)	0.396 42 (49)	0.477 99 (26)	0.037 67 (37)
C(S)[a]	0.402 9	0.517 6	−0.054 5
H(1)[b]	0.441 3	0.111 5	0.289 9
H(1′)	0.470 0	0.031 4	0.312 5
H(2)	0.636 5	0.133 5	0.287 6
H(2′)	0.667 6	0.067 3	0.353 6
H(3)	0.720 9	0.068 1	0.198 9
H(3′)	0.683 9	−0.002 3	0.240 0
H(4)	0.542 6	0.072 9	0.090 5
H(4′)	0.532 1	−0.007 6	0.111 11
H(1A)	−0.088 2	0.160 7	0.080 3
H(1A′)	−0.033 1	0.096 2	0.145 3
H(3A)	−0.009 6	0.100 4	0.307 4
H(4A)	−0.041 2	0.160 6	0.438 5
H(5A)	−0.090 3	0.280 6	0.428 7
H(6A)	−0.108 4	0.342 8	0.287 8
H(7A)	−0.079 8	0.283 0	0.157 4
H(1B)	0.046 8	0.179 7	−0.052 1
H(1B′)	0.177 2	0.219 7	−0.016 1
H(3B)	0.185 1	0.338 7	0.056 9
H(4B)	0.073 8	0.442 3	0.067 4
H(5B)	−0.149 6	0.446 6	0.012 2
H(6B)	−0.264 7	0.346 1	−0.056 4
H(7B)	−0.155 1	0.239 8	−0.062 9
H(1C)	0.250 6	0.190 3	0.259 6
H(1C′)	0.168 4	0.254 0	0.208 1
H(3C)	0.330 9	0.338 2	0.274 0
H(4C)	0.514 8	0.396 4	0.271 9
H(5C)	0.648 0	0.346 6	0.189 0
H(6C)	0.589 3	0.240 5	0.104 7
H(7C)	0.399 9	0.181 9	0.107 6

[a] B for C(S) is 5.66 (44) A^2. [b] B for all the H atoms is 6.0 A^2.

There is a systematic distortion of the chloride ligands *away from* the bridging dinitrogen ligand. The N–Ta–Cl angles are all obtuse, ranging from 95.65 (15) to 97.74 (15)° and averaging 97.0 [11]°,[7] while the O–Ta–Cl angles are all acute,

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(4) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213–1214.

(5) "International Tables for X-Ray Crystallography"; Kynoch Press: birmingham, England, 1974; Vol. 4: (a) pp 99–101; (b) pp 149–150.

(6) "Syntex XTL Operations Manual", 2nd ed.; Syntex Analytical Instruments (now Nicolet XRD Division): Cupertino, CA 95014, 1976.

(7) Esd's on average distances and angles are calculated by the "scatter" formula given and are enclosed in square brackets: $[\sigma] = [\sum_{i=1}^{i=N}(d_i - \bar{d})^2/(N-1)]^{1/2}$.

Table III. Anisotropic Thermal Parameters (Å^2) for $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)\cdot 0.7CH_2Cl_2$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ta	2.793 (12)	2.807 (12)	3.280 (12)	0.1812 (75)	0.8277 (79)	−0.4584 (79)
P	3.034 (56)	2.905 (58)	2.726 (57)	0.254 (46)	0.910 (45)	−0.350 (46)
Cl(1)	4.658 (67)	4.949 (72)	3.753 (63)	0.668 (57)	2.040 (52)	−0.287 (56)
Cl(2)	5.207 (75)	5.335 (81)	4.091 (69)	0.308 (61)	1.839 (58)	0.860 (59)
Cl(3)	4.917 (76)	3.477 (68)	7.74 (10)	0.964 (58)	1.216 (68)	−0.761 (65)
O	2.87 (16)	5.18 (19)	3.40 (17)	0.31 (14)	0.47 (13)	−0.82 (15)
N	3.23 (18)	2.73 (18)	4.66 (24)	0.34 (16)	1.23 (17)	−0.58 (17)
C(1)	4.74 (32)	7.96 (44)	3.93 (30)	0.32 (31)	0.46 (24)	−0.33 (30)
C(2)	4.51 (35)	13.41 (72)	5.35 (39)	−0.39 (42)	−0.23 (28)	−1.81 (45)
C(3)	3.34 (33)	16.10 (86)	8.79 (56)	0.84 (42)	0.27 (34)	−5.34 (58)
C(4)	3.13 (28)	9.47 (49)	5.95 (37)	0.73 (29)	1.32 (26)	−2.52 (35)
C(1A)	2.89 (22)	4.18 (27)	4.00 (26)	−0.19 (20)	1.19 (20)	−0.79 (21)
C(2A)	2.62 (22)	4.67 (29)	3.82 (27)	0.01 (20)	1.08 (19)	−0.76 (23)
C(3A)	6.38 (37)	5.21 (34)	5.28 (35)	0.30 (28)	3.17 (29)	0.03 (35)
C(4A)	9.35 (52)	8.40 (52)	4.27 (35)	0.18 (43)	3.48 (35)	0.03 (35)
C(5A)	6.16 (39)	8.84 (53)	4.90 (38)	1.23 (36)	2.31 (31)	−2.25 (37)
C(6A)	5.52 (36)	6.22 (40)	6.80 (44)	1.28 (30)	1.95 (31)	−1.88 (35)
C(7A)	5.44 (32)	5.02 (33)	4.50 (31)	1.25 (26)	1.70 (25)	−0.87 (26)
C(1B)	4.96 (29)	4.28 (28)	3.15 (25)	1.00 (23)	1.12 (22)	0.08 (22)
C(2B)	5.61 (33)	4.18 (28)	2.43 (23)	1.36 (25)	0.72 (22)	0.46 (21)
C(38)	6.73 (38)	4.15 (33)	5.01 (34)	0.21 (29)	0.53 (28)	1.18 (27)
C(4B)	11.38 (63)	3.06 (32)	6.21 (42)	0.86 (36)	1.22 (40)	1.09 (28)
C(5B)	11.28 (66)	5.19 (43)	6.65 (46)	4.29 (46)	2.51 (45)	1.38 (35)
C(6B)	6.29 (39)	6.89 (45)	5.23 (37)	3.09 (35)	1.01 (30)	1.30 (33)
C(7B)	6.35 (37)	5.25 (34)	2.96 (27)	1.26 (29)	0.35 (24)	0.11 (24)
C(1C)	4.06 (26)	3.51 (25)	3.66 (25)	−0.26 (21)	1.25 (20)	−0.65 (20)
C(2C)	3.12 (23)	3.84 (26)	3.63 (25)	−0.01 (20)	0.84 (20)	0.48 (21)
C(3C)	4.71 (30)	4.35 (29)	4.05 (28)	−1.11 (24)	1.10 (23)	−0.32 (24)
C(4C)	5.74 (38)	5.45 (37)	6.55 (41)	−1.87 (31)	1.10 (32)	−0.75 (31)
C(5C)	4.56 (35)	6.54 (45)	8.22 (49)	−2.27 (32)	0.51 (33)	1.46 (39)
C(6C)	5.35 (37)	6.43 (42)	7.83 (46)	0.31 (33)	3.35 (34)	1.05 (36)
C(7C)	4.34 (29)	4.58 (30)	5.66 (34)	−0.88 (25)	2.20 (26)	−0.69 (26)
Cl(S)	12.01 (31)	14.20 (38)	11.65 (32)	1.52 (24)	5.22 (26)	−1.12 (25)

[a] The anisotropic thermal parameters enter the expression for the calculated structure factor in the following form: $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

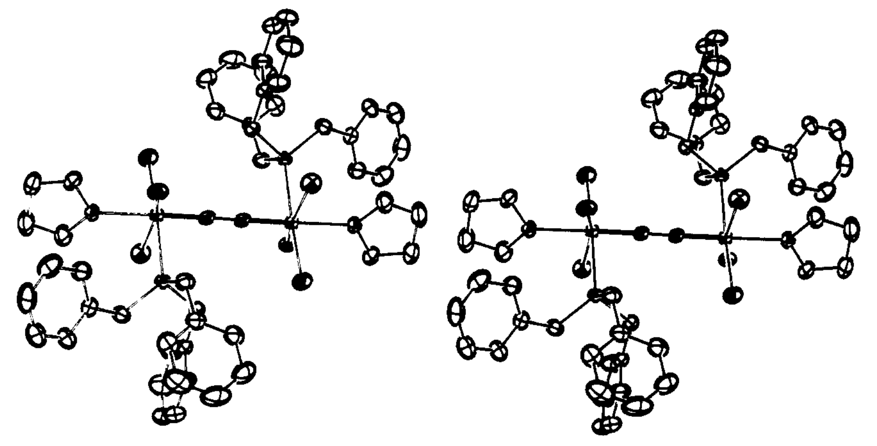

Figure 2. Stereoscopic view of the $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)$ molecule.

ranging from 82.83 (10) to 84.09 (10)°, and averaging 83.4 [7]°. In contrast to this, the phosphine ligand is bent slightly toward the dinitrogen system, with ∠P–Ta–N = 85.61 (15)° and ∠P–Ta–O = 92.83 (10)°. These deviations from idealized octahedral coordination geometry are not unusual in unsymmetrical complexes and arise from a combination a electronic (see below) and steric factors. They are illustrated clearly in Figure 2.

The tantalum–tribenzylphosphine bond length of 2.689 (1) Å is significantly longer than Ta–P distances observed in complexes containing the trimethylphosphine ligand. This results from a combination of (a) the greater basicity of PMe_3, as compared to $P(bz)_3$, and (b) steric influences associated with the larger "cone angle" of space swept out by the $P(bz)_3$ ligand. For comparison, we note that relevant Ta–PMe_3 bond lengths include 2.507 (4) Å in $Ta(\eta^5\text{-}C_5Me_5)({=}CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$,[8] 2.565 (2)–2.567 (2) Å in $Ta(\eta^5\text{-}C_5Me_5)({\equiv}CPh)(PMe_3)_2Cl$,[9] 2.565 (2)–2.569 (2) Å in $Ta({=}CHCMe_3)_2(\eta^1\text{-mesityl})(PMe_3)_2$,[10] 2.585 (3)–2.596 (3) Å in $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$,[1,2a] and 2.602 (2) Å in $[Ta({=}CHCMe_3)(PMe_3)Cl_3]_2$.[8,11]

The THF ligand is bonded to the tantalum(V) center with Ta–O = 2.308 (4) Å, a value close to the Ta—O(THF) distance of 2.356 (6) Å (for the THF trans to the Ta=N linkage)

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(8) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169–176.

(9) (a) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 171–176. (b) McLain, S. J.; Wood, C. D.; Messerle, L. W.; Schrock, R. R.; Hollander, F. J.; Youngs W. J.; Churchill, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5962–5964.

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Table IV. Intramolecular Distances (Å) and Esd's for $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)\cdot 0.7CH_2Cl_2$

(A) Distances from Tantalum Atom			
Ta-N	1.796 (5)	Ta-Cl(1)	2.375 (1)
Ta-O	2.308 (4)	Ta-Cl(2)	2.385 (2)
Ta-P	2.689 (1)	Ta-Cl(3)	2.378 (2)
(B) Nitrogen-Nitrogen Distance			
N-N′	1.282 (6)		
(C) Phosphorus-Carbon Distances			
P-C(1a)	1.874 (6)	P-C(1c)	1.825 (6)
P-C(1b)	1.853 (6)		
(D) Carbon-Carbon Distances within the P(bz)$_3$ Ligand			
C(1a)-C(2a)	1.496 (8)	C(5b)-C(6b)	1.370 (12)
C(2a)-C(3a)	1.371 (9)	C(6b)-C(7b)	1.389 (11)
C(3a)-C(4a)	1.393 (10)	C(7b)-C(2b)	1.404 (10)
C(4a)-C(5a)	1.363 (13)	C(1c)-C(2c)	1.520 (8)
C(5a)-C(6a)	1.378 (11)	C(2c)-C(3c)	1.395 (8)
C(6a)-C(7a)	1.369 (10)	C(3c)-C(4c)	1.338 (10)
C(7a)-C(2a)	1.399 (9)	C(4c)-C(5c)	1.370 (11)
C(1b)-C(2b)	1.505 (8)	C(5c)-C(6c)	1.388 (11)
C(2b)-C(3b)	1.389 (9)	C(6c)-C(7c)	1.383 (10)
C(3b)-C(4b)	1.372 (11)	C(7c)-C(2c)	1.367 (8)
C(4b)-C(5b)	1.382 (15)		
(E) Distances within the THF Ligand			
O-C(1)	1.466 (7)	C(3)-C(4)	1.455 (12)
C(1)-C(2)	1.460 (10)	C(4)-O	1.438 (8)
C(2)-C(3)	1.462 (13)		

in the $[TaCl_3(THF)_2]_2({=}NCMe{=}CMeN{=})$ molecule.[12,13] While the THF ligand in the present molecule is clearly "puckered", its mean plane is oriented so as to approximately bisect the Cl(3)-Ta-Cl(1) angle; this staggered arrangement acts so as to minimize repulsions between the THF ligand and the cis ligands.

The tantalum-nitrogen distances in the binuclear (octahedrally coordinated) $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)$ molecule are each 1.796 (5) Å. This value is far shorter than the predicted Ta-N single-bond length of 2.09 Å (calculated here from the Ta-Cl bond length of 2.38 Å in the present molecule, along with the covalent radii of 0.99 Å for Cl and 0.70 Å for N)[14] and is also substantially less than the Ta^V-N single-bond lengths found in the pentagonal-bipyramidal complex $Ta(NMe_2)(O_2CNMe_2)_3$ (Ta-N = 1.964 (8) and 1.977 (9) Å; average = 1.971 [9] Å).[15] The observed Ta-N distance in the complex under investigation is, however, completely consistent with Ta(V) species that have formal Ta=N *double* bonds. Among these are Ta=N = 1.840 [4] Å in the binuclear (trigonal bipyramidally coordinated) tantalum(V) complex $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$[1,2a] and 1.747 (7) Å in the binuclear (octahedrally coordinated) tantalum(V) complex $[TaCl_3(THF)_2]_2({=}NCMe{=}CMeN{=})$.[12]

The nitrogen-nitrogen distance of 1.282 (6) Å in the present molecule is quite similar to the value of 1.298 (12) Å found in our previous study of $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$.[1,2a] These values each represent a substantial reduction in bond order from that in free dinitrogen (N≡N = 1.0976 Å)[16] and from the range of distances found previously in simple mononuclear or dinuclear complexes with terminal or linear-bridging dinitrogen ligands.[17] In particular, comparison may be made with two bridging dinitrogen complexes of the earlier transition metals: in $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2(\mu\text{-}N_2)$,[18] the N-N(bridging) bond length is 1.182 (5) Å while the N-N(terminal) bond lengths are 1.114 (7)-1.116

Table V. Intermolecular Angles (Deg) with Esd's for $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)\cdot 0.7CH_2Cl_2$

(A) Angles about Tantalum Atom			
N-Ta-O	178.00 (17)	O-Ta-Cl(3)	84.09 (10)
N-Ta-P	85.61 (15)	P-Ta-Cl(1)	83.89 (5)
N-Ta-Cl(1)	95.65 (15)	P-Ta-Cl(2)	80.39 (5)
N-Ta-Cl(2)	97.74 (15)	P-Ta-Cl(3)	176.30 (5)
N-Ta-Cl(3)	97.51 (15)	Cl(1)-Ta-Cl(2)	158.45 (5)
O-Ta-P	92.83 (10)	Cl(1)-Ta-Cl(3)	97.73 (5)
O-Ta-Cl(1)	82.93 (10)	Cl(2)-Ta-Cl(3)	97.17 (6)
O-Ta-Cl(2)	83.22 (10)		
(B) Angle about Nitrogen			
Ta-N-N′	178.91 (40)		
(C) Tantalum-Phosphorus-Carbon Angles			
Ta-P-C(1a)	106.06 (17)	Ta-P-C(1c)	121.30 (19)
Ta-P-C(1b)	112.76 (19)		
(D) Other Angles Involving Phosphorus			
P-C(1a)-C(2a)	117.3 (4)	C(1a)-P-C(1b)	104.75 (25)
P-C(1b)-C(2b)	115.5 (4)	C(1b)-P-C(1c)	106.16 (26)
P-C(1c)-C(2c)	119.8 (4)	C(1c)-P-C(1a)	104.33 (25)
(E) C(sp^3)-C(sp^2)-C(sp^2) Angles			
C(1a)-C(2a)-C(3a)	119.9 (5)	C(1b)-C(2b)-C(7b)	121.3 (5)
C(1a)-C(2a)-C(7a)	122.2 (5)	C(1c)-C(2c)-C(3c)	118.5 (5)
C(1b)-C(2b)-C(3b)	120.4 (5)	C(1c)-C(2c)-C(7c)	123.1 (5)
(F) Internal Angles of Phenyl Rings			
C(7a)-C(2a)-C(3a)	117.8 (6)	C(7b)-C(2b)-C(3b)	118.2 (6)
C(2a)-C(3a)-C(4a)	120.5 (7)	C(2b)-C(3b)-C(4b)	120.1 (7)
C(3a)-C(4a)-C(5a)	120.4 (8)	C(3b)-C(4b)-C(5b)	121.3 (8)
C(4a)-C(5a)-C(6a)	120.3 (8)	C(4b)-C(5b)-C(6b)	119.8 (8)
C(5a)-C(6a)-C(7a)	119.1 (7)	C(5b)-C(6b)-C(7b)	119.4 (8)
C(6a)-C(7a)-C(2a)	121.9 (6)	C(6b)-C(7b)-C(2b)	121.0 (6)
C(7c)-C(2c)-C(3c)	118.2 (5)	C(4c)-C(5c)-C(6c)	120.4 (7)
C(2c)-C(3c)-C(4c)	123.2 (6)	C(5c)-C(6c)-C(7c)	120.0 (7)
C(3c)-C(4c)-C(5c)	118.5 (7)	C(6c)-C(7c)-C(2c)	119.7 (6)
(G) Angles Involving the THF Ligand			
Ta-O-C(1)	128.5 (4)	C(1)-C(2)-C(33)	103.8 (7)
Ta-O-C(4)	122.7 (4)	C(2)-C(3)-C(4)	107.2 (8)
C(1)-O-C(4)	107.1 (5)	C(3)-C(4)-O	107.2 (6)
O-C(1)-C(2)	107.3 (6)		

Table VI. Important Least-Squares Planes[a] for $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)\cdot 0.7CH_2Cl_2$

atom	dev (esd), Å	atom	dev (esd), Å
(A) Equatorial Coordination Plane about Ta			
$-0.8053X - 0.2926Y - 0.5156Z = -2.5741$			
Ta*[b]	0.1506 (2)	P*	0.098 (1)
Cl(1)*	−0.157 (2)	N	1.937 (4)
Cl(2)*	−0.161 (2)	O	−2.152 (4)
Cl(3)*	0.069 (2)		
(B) Phenyl Ring "a"			
$-0.9281X - 0.2185Y - 0.3015Z = -0.4201$			
C(2a)*	0.004 (5)	C(5a*)	0.003 (8)
C(3a)*	−0.005 (7)	C(6a)*	−0.003 (8)
C(4a)*	0.001 (9)	C(7a)*	−0.001 (7)
(C) Phenyl Ring "b"			
$0.3366X + 0.2643Y - 0.9038Z = 1.5193$			
C(2b)*	−0.007 (5)	C(5b)*	−0.007 (9)
C(3b)*	0.010 (7)	C(6b)*	0.010 (7)
C(4b)*	−0.003 (8)	C(7b)*	−0.002 (6)
(D) Phenyl Ring "c"			
$-0.2886X + 0.5064Y - 0.8126Z = -0.6372$			
C(2c)*	−0.009 (5)	C(5c)*	−0.008 (8)
C(3c)*	0.004 (6)	C(6c)*	0.004 (8)
C(4c)*	0.005 (7)	C(7c)*	0.005 (6)
(E) THF Plane			
$0.0868X + 0.9397Y - 0.3308Z = 0.4378$			
O*	0.036 (4)	C(3)*	−0.139 (11)
C(1)*	−0.121 (8)	C(4)*	0.064 (8)
C(2)*	0.161 (10)		
(F) Dihedral Angles (Deg)			
A–B	14.81	B–C	95.61
A–C	83.25	B–D	66.28
A–D	59.79	C–D	39.55
A–E	110.04	D–E	43.98

[a] Equations of planes are expressed in orthonormal (Å) coordinates. [b] Atoms marked with an asterisk (*) received unit weighting in the calculations; all others were given zero weight.

(8) Å; in $[(\eta^5\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$,[19] the N–N(bridging) bond lengths for the two crystallographically distinct molecules are 1.155 (14) and 1.165 (14) Å.

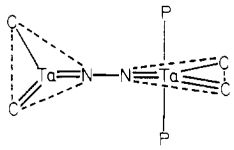
The dinitrogen ligand in the present complex bridges the two tantalum(V) centers in a close-to-linear arrangement in which ∠Ta–N–N′ = ∠N–N′–Ta′ = 178.9 (4) Å. The available evidence thus suggests that the overall bonding in the Ta(μ-N_2)Ta system is better represented by the valence bond structure I (with formal Ta═N double bonds and a N—N single bond) than by the alternative structure II (with Ta—N single bonds and a N≡N triple bond). A structure such as III is also possible, but further discussion is better continued within the framework of molecular orbital theory.

Ta═NN═Ta	TaN≡NTa	$\overset{-}{Ta}=\overset{+}{N}=\overset{+}{N}=\overset{-}{Ta}$
I	II	III

With the complex viewed as a tantalum(V) derivative, the bridging ligand must be regarded, *formally* at least, as a N_2^{4-} ligand; otherwise the assignment of formal charges is not balanced.[20] The electronic configuration for the homonuclear diatomic tetraanion N_2^{4-} is as follows:[21] $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2$-$(\sigma^*_{2s})^2(\sigma_{2p_z})^2(\pi_{2p_{x,y}})^4(\pi^*_{2p_{x,y}})^4$. There is a net bond order of one for the N–N linkage in the free N_2^{4-} ion. The observed N–N bond lengths of 1.282 (6) Å in the present molecule, $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)$, and 1.298 (12) Å in $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$ are intermediate between the accepted N═N double-bond length (~1.24–1.25 Å) and the N—N single-bond length (~1.40–1.45 Å). Our explanation for this discrepancy is that it derives from the mode of bonding of the N_2^{4-} ion to the two tantalum(V) ions. There are two components to this bonding: (a) σ donation from the ligand to the metal atoms and (b) π donation, again *from the ligand to the metal atoms.*

If we consider the z axis for each tantalum atom to be coincident with the Ta–N–N–Ta group, the x axis to be Cl(1)–Ta–Cl(2) and the y axis to be Cl(3)–Ta–P, one can see (Figure 1) that two Ta d_{xz} orbitals (one from each tantalum) interact with the $\pi^*_{2p_x}$ orbital of the N_2^{4-} system and that two Ta d_{yz} orbitals (one from each tantalum) interact with the $\pi^*_{2p_y}$ orbital of the N_2^{4-} system. The net result is two mutually perpendicular two-electron four-center molecular orbitals over the Ta–N–N–Ta system. This causes the Ta–N–N–Ta system to be linear and also explains why the equatorial ligands on tantalum in the $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)$ molecule (i.e., the two $TaCl_3P$ fragments) are in a mutually eclipsed conformation, rather than the more sterically favored staggered conformation.

The $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$ molecule[1,2] takes up a conformation in which the two trigonal-bipyramidal arrangements of ligands around the tantalum(V) atoms are linked by an equatorial–equatorial Ta═NN═Ta bridge in such a way that the equatorial triangular planes are perpendicular to one another (see IV; the phosphine ligands on the left-hand tantalum(V) ion lie above and below the plane of projection and are omitted for clarity).



IV

Finally, we note that the N–N bond order in the coordinated N_2^{4-} ligand increases from unity as a result of donation of $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ electron density from the ligand to the two d^0 Ta(V) ions.

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Registry No. $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)\cdot 0.7CH_2Cl_2$, 79499-30-2.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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(20) The conventional assignment of oxidation states requires that shared electrons are assigned formally to the more electronegative of the two atoms sharing them. The molecule may then be written formally as $(P(bz)_3)(THF)(Cl^-)_3Ta^V(N_2^{4-})Ta^V(Cl^-)_3(THF)(P(bz)_3)$.

(21) The ordering of the (σ_{2p_z}) and $(\pi_{2p_{x,y}})$ orbitals may be reversed.