infrared spectrum is as follows: 3395 (ms), 1345 (vs), 1303 (ms), 1242 (s), 1195 (vs), 1152 (m), 1058 (m), 992 (vs), 955 (ms), 895 (w), 845 (w), 612 (w), 548 (m), 500 (ms) cm^{-1}.

Anal. Calcd for C_4F_8SNHO: C, 18.25; N, 5.32; H, 0.38. Found: C, 18.20; N, 5.51; H, 0.40.

Preparation of $\overline{CF_2CF_2CF_2CF_2S}(O){=}NCH_3$. Similarly, in a 100-mL reaction vessel which contained 0.88 g of MCPBA, 2.18 mmol of $\overline{CF_2CF_2CF_2CF_2S}{=}NCH_3$ was condensed at −196 °C. The reaction vessel was held at −78 °C for 19 h, at 0 °C for 12 h, and at 25 °C for 10 h. The product was purified by trap-to-trap distillation through a trap at −64 °C. $\overline{CF_2CF_2CF_2CF_2S}(O){=}NCH_3$ was obtained in a yield of 79.4%. This is a transparent liquid with a boiling point of 57.0 °C from the equation $\log P_{\text{torr}} = 2.27 - 1779.4/T$. The molar heat of vaporization is 8.1 kcal, and the Trouton constant is 24.7 eu.

The ^{19}F and ^{1}H NMR spectral data are found in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum is as follows: 2867–3012 (w), 1447 (w), 1316 (vs), 1340 (s), 1303 (s), 1247 (s), 1190 (vs), 1061 (w), 992 (vs), 972 (s), 884 (w), 841 (m), 664 (w), 614 (w), 580 (w), 548 (w), 520 (m), 492 (m) cm^{-1}.

Anal. Calcd for $C_5F_8SNH_3O$: C, 21.66; N, 5.05; H, 1.08. Found: C, 21.20; N, 4.97; H, 1.21.

Preparation of $\overline{CF_2CF_2CF_2CF_2S}(O){=}NC_2H_5$. In a 100-mL reaction vessel which contained 0.43 g of MCPBA, 1.07 mmol of $\overline{CF_2CF_2CF_2CF_2S}{=}NC_2H_5$ was condensed at −196 °C. Then, the reaction vessel was kept at −78 °C for 16 h, at 0 °C for 10 h, and at 25 °C for 8 h. The volatile product was found to be pure $\overline{CF_2CF_2CF_2CF_2S}(O){=}NC_2H_5$ (0.90 mmol). Its yield was 83.6%. This is a transparent liquid with a boiling point of 60.2 °C from the equation $\log P_{\text{torr}} = 7.80 - 1640.0/T$. The molar heat of vaporization is 7.5 kcal, and the Trouton constant is 22.5 eu.

The ^{19}F and ^{1}H NMR spectral data are recorded in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum is as follows: 2893–2993 (w), 1386 (m s), 1337 (v s), 1303 (s), 1248 (s), 1192 (v s), 1063 (w), 994 (s), 954 (m s), 888 (w), 793 (w), 665 (w), 615 (w), 583 (w), 552 (w), 528 (m), 493 (w) cm^{-1}.

Anal. Calcd for $C_6F_8SNH_5O$: C, 24.74; N, 4.81; H, 1.72. Found: C, 24.54; N, 4.80; H, 1.70.

Acknowledgment is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grant CHE-7727395) for support of this research. We thank Charles Barinaga and Dennis Gage for mass and ^{19}F NMR spectral data.

Registry No. $\overline{CF_2CF_2CF_2CF_2S}{=}NH$, 77110-87-3; $\overline{CF_2CF_2CF_2CF_2S}{=}NCH_3$, 77984-24-8; $\overline{CF_2CF_2CF_2CF_2S}{=}NC_2H_5$, 77984-25-9; $\overline{CF_2CF_2CF_2CF_2S}{=}NCF(CF_3)_2$, 77984-26-0; $\overline{CF_2CF_2CF_2CF_2S}{=}NC(CF_3)_2N{=}C(CF_3)_2$, 77984-27-1; $\overline{CF_2CF_2CF_2CF_2S}{=}NCl$, 77984-28-2; $\overline{CF_2CF_2CF_2CF_2S}{=}NBr$, 77984-29-3; $\overline{CF_2CF_2CF_2CF_2S}(O){=}NH$, 77589-47-0; $\overline{CF_2CF_2CF_2CF_2S}(O){=}NCH_3$, 77589-48-1; $\overline{CF_2CF_2CF_2CF_2S}(O){=}NC_2H_5$, 77984-30-6; $\overline{CF_2CF_2CF_2CF_2S}F_2$, 42060-60-6; $(CF_3)_2S{=}NH$, 60646-40-4; $\overline{CF_2CF_2CF_2CF_2S}$, 706-76-3; $LiNH_2$, 7782-89-0; $(CF_3)_2SF_2$, 30341-38-9; CH_3NH_2, 74-89-5; $C_2H_5NH_2$, 75-04-7; $LiN{=}C(CF_3)_2$, 31340-36-0.

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Crystal and Molecular Structure of $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$, a Molecule with a Dinitrogen Ligand Behaving as a Diimido Group in a Ta=NN=Ta Bridge

MELVYN ROWEN CHURCHILL* and HARVEY J. WASSERMAN

Received November 20, 1980

The complex $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$ has been studied by means of a single-crystal X-ray diffraction study. The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 9.712$ (2) Å, $b = 14.845$ (3) Å, $c = 18.448$ (4) Å, $\alpha = 67.278$ (14)°, $\beta = 84.812$ (15)°, $\gamma = 71.743$ (12)°, $V = 2328.5$ (7) Å^3, and $Z = 2$. Diffraction data were collected on 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 $R_F = 4.5\%$ and $R_{wF} = 3.1\%$ for all 4308 data (*none* rejected) and $R_F = 3.1\%$ and $R_{wF} = 3.0\%$ for those 3626 data with $|F_o| > 3\sigma(|F_o|)$. The binuclear complex contains two tantalum(V) atoms in trigonal-bipyramidal coordination environments. Each tantalum atom has two axial PMe_3 ligands; the equatorial sites are occupied by neopentylidene ligands [Ta(1)–C(1) = 1.932 (9) Å, Ta(2)–C(17) = 1.937 (9) Å], neopentyl ligands [Ta(1)–C(6) = 2.285 (10) Å, Ta(2)–C(22) = 2.299 (10) Å], and the bridging dinitrogen ligand. Bond lengths within the Ta–(μ-N_2)–Ta fragment [Ta(1)–N(1) = 1.837 (8) Å, Ta(2)–N(2) = 1.842 (8) Å, N(1)–N(2) = 1.298 (12) Å] indicate that it is best described as a Ta=NN=Ta system. The N(1)–N(2) distance of 1.298 (12) Å shows this molecule (with a pair of "14-electron" transition metal atoms) to have a far more activated μ-N_2 system that is observed in such other μ-N_2 derivatives of the early transition metals as $[(\eta^5\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$ (a "16-electron" complex) or $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2(\mu\text{-}N_2)$ (an "18-electron" complex).

Introduction

The preparation of the first terminal dinitrogen complexes, $[Ru(NH_3)_5N_2]X_2$ (X = Br^-, I^-, BF_4^-, PF_6^-), was reported in 1965.[1] This was followed, in 1968, by the synthesis[2] and crystallographic characterization[3] of a closely related species containing a bridging dinitrogen group, $[(NH_3)_5RuN{\equiv}NRu(NH_3)_5]^{4+}$.

Since this time a variety of other dinitrogen complexes has been synthesized, and their chemistry (including efforts to reduce the coordinated N_2 to NH_3 etc.) has been reviewed.[4-8]

---

(1) Allen, A. D.; Senoff, C. V. *Chem. Commun.* **1965**, 621–622. Bottomley, F.; Nyburg, S. C. *Ibid.* **1966**, 897–898. Allen, A. D.; Bottomly, F. *Acc. Chem. Res.* **1968**, *1*, 360–365.

(2) Harrison, D. E.; Weissberger, E.; Taube, H. *Science (Washington, D.C.)* **1968**, *159*, 320–322.

(3) Treitel, I. M.; Flood, M. T.; Marsh, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1969**, *91*, 6512–6513.

(4) Chatt, J.; Leigh, G. J. *Chem. Soc. Rev.* **1972**, 121–144.

0020-1669/81/1320-2899$01.25/0

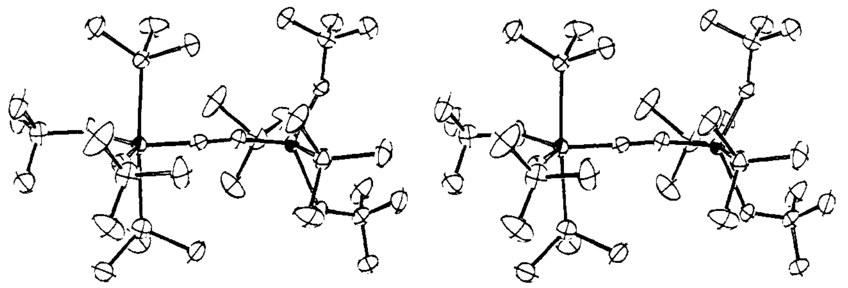

Figure 1. Stereoscopic view of the $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$ molecule (ORTEP-II diagram, 30% ellipsoids).

In general (as observed by Chatt et al.[7]) the nitrogen–nitrogen distances in systems with terminal "end-on" (I) or

$$\underset{\text{I}}{M{-}N{\equiv}N} \qquad \underset{\text{II}}{M{-}N{\equiv}N{-}M}$$

bridging "end-on" (II) dinitrogen ligands are only slightly longer than, and often within experimental error of, that of free dinitrogen (N≡N = 1.0976 Å).[9] There are only two exceptions to this generalization. (1) The unusual species $[(PhLi)_6Ni_2(N_2)(Et_2O)_2]_2$ has N–N = 1.35 Å, but the nitrogen atoms here each interact with both nickel and lithium atoms.[10] (2) The species $(MeO)Cl_4Mo(N_2)ReCl(PMe_2Ph)_4$ has N–N = 1.28 (5) Å.[11]

We now report the results of a single-crystal X-ray structural analysis on the species $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$, prepared as in eq 1. This complex contains

$$Ta({=}CHCMe_3)(PMe_3)_2Cl_3 \xrightarrow{2Na/Hg,\ PMe_3,\ N_2} [Ta({=}CHCMe_3)(PMe_3)_2Cl]_2N_2 \xrightarrow{LiCH_2CMe_3} [Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)]_2(\mu\text{-}N_2)$$

an activated bridging dinitrogen ligand. A preliminary account of this work has been reported.[12]

Experimental Section

A. Diffraction Data Collection. Red-brown crystals of $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$ were provided by Professor R. R. Schrock of MIT. The material was found to decompose in air within a period of several minutes, forming an amorphous white powder.

All data were obtained with use of a rather irregular fragment of approximate dimensions 0.33 × 0.17 × 0.23 mm, which was sealed into a glass capillary under inert-atmospheric conditions. All orientation and indexing operations as well as room-temperature data collection were carried out on a Syntex P2$_1$ diffractometer using the standard techniques of this laboratory.[13] Final cell parameters are based on a least-squares analysis of 25 reflections in well-separated regions of reciprocal space, all having 25° < 2θ < 30°. See Table I for details and results.

A careful survey of the data set revealed no systematic extinctions and no diffraction symmetry higher than $C_i(\bar{1})$. Successful solution of the structure proved the space group to be $P\bar{1}$ (C_i^1, No. 2).

Table I. Experimental Data for the X-ray Diffraction Study of $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$

(A) Crystal Data

cryst system: triclinic	space group: $P\bar{1}$
a = 9.712 (2) Å	α = 67.278 (14)°
b = 14.845 (3) Å	β = 84.812 (15)°
c = 18.448 (4) Å	γ = 71.743 (12)°
V = 2328.5 (7) Å^3	Z = 2
ρ(calcd) = 1.39 g cm^{-3}	mol wt 976.9
temp = 23 °C	

(B) Data Collection

radiation: Mo K$\bar{\alpha}$ (λ = 0.710 730 Å)
2θ limits: 4.0–45.0°
scan width: $[2.0 + \Delta(\alpha_2 - \alpha_1)]°$
scan speed: 2.50 deg min^{-1}
scan type: θ–2θ
reflctns measd: $+h, \pm k, \pm l$
reflctns collected: 4655 total yielding 4308 unique data
abs coeff: 51.1 cm^{-1}

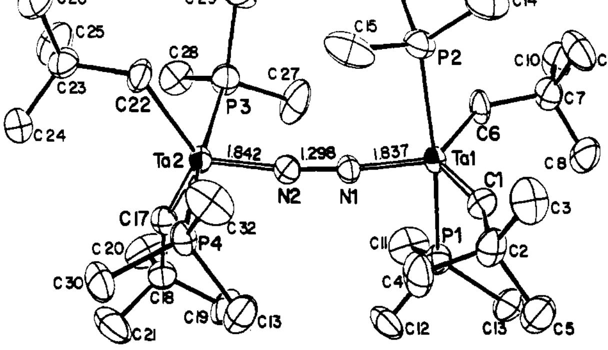

Figure 2. Labeling of atoms in the $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$ molecule.

Following the data collection, a series of ψ scans about the diffraction vector of five close to axial reflections were collected and used for the empirical absorption correction (μ = 51.1 cm^{-1}) calculated in the program TAPER.[14] The 2θ values of the reflections ranged from 8.83 to 32.37°, and transmission factor ratios ranged from 0.72 to 0.78.

Symmetry-equivalent data were then averaged, yielding an internal agreement factor of $R(I)$ = 1.62%. All 4308 unique reflections were converted to unscaled $|F_o|$ values following correction for Lorentz and polarization effects, and a Wilson plot was used to place the data on an approximate absolute scale.

B. Solution and Refinement of the Structure. The two tantalum atoms were readily located from a Patterson map. All other nonhydrogen atoms were then located with use of difference-Fourier maps and full-matrix least-squares refinement routines. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $1/w = [\sigma(|F_o|)]^2 + [0.01|F_o|]^2$. All hydrogen atoms were included in fixed calculated positions on the assumption that d(C–H) = 0.95 Å.[15] With use of anisotropic

---

(5) Shilov, A. E. *Russ. Chem. Rev.* (*Engl. Transl.*) **1974**, *43(5)*, 378–398; *Usp. Khim.* **1974**, *43*, 863–902.

(6) Allen, A. D.; Harris, R. O.; Loescher, B. R.; Stevens, J. R.; Whiteley, R. N. *Chem. Rev.* **1973**, *73*, 11–20.

(7) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625.

(8) Bottomley, F., Burns, R. C., Eds. "Treatise on Dinitrogen Fixation"; Wiley: New York, 1979.

(9) Wilkinson, P. G.; Houk, N. B. *J. Chem. Phys.* **1956**, *24*, 528.

(10) Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 998–999.

(11) Cradwick, P. D.; Chatt, J.; Crabtree, R. H.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1965**, 351.

(12) Turner, H. J.; Fellmann, J. D.; Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 7809–7811.

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

(14) "Syntex XTL Operations Manual", 2nd ed.; Syntex Analytical Instruments: Cupertino, CA, 1976.

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

Table II. Final Positional Parameters for $[Ta(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$[a]

atom	x	y	z	atom	x	y	z
Ta(1)	0.26108 (4)	0.30015 (3)	0.30280 (2)	H(6A)	0.0443	0.2604	0.2524
Ta(2)	0.16699 (4)	0.67632 (3)	0.18760 (2)	H(6B)	0.1634	0.2603	0.1904
N(1)	0.22895 (69)	0.43873 (56)	0.27113 (40)	H(8A)	0.1450	−0.0036	0.3550
N(2)	0.19487 (71)	0.53793 (57)	0.24009 (38)	H(8B)	0.0373	0.0976	0.3568
P(1)	0.04288 (27)	0.31829 (19)	0.39294 (15)	H(8C)	0.2003	0.0689	0.3786
P(2)	0.45539 (30)	0.30208 (21)	0.19631 (16)	H(9A)	0.3270	−0.0027	0.2590
P(3)	0.03098 (30)	0.66798 (21)	0.07627 (16)	H(9B)	0.3799	0.0702	0.2833
P(4)	0.33165 (27)	0.66328 (18)	0.29581 (15)	H(9C)	0.3407	0.0993	0.1958
C(1)	0.40140 (90)	0.22087 (63)	0.38944 (51)	H(10A)	0.0768	0.0364	0.2226
C(2)	0.5091 (11)	0.19899 (69)	0.45237 (56)	H(10B)	0.0803	0.1389	0.1560
C(3)	0.6589 (12)	0.13592 (83)	0.43853 (67)	H(10C)	−0.0369	0.1384	0.2191
C(4)	0.5183 (12)	0.29936 (85)	0.45086 (64)	H(14A)	0.6651	0.2058	0.1601
C(5)	0.4634 (12)	0.13878 (82)	0.53368 (66)	H(14B)	0.5710	0.1362	0.2067
C(6)	0.1442 (10)	0.23233 (66)	0.24472 (53)	H(14C)	0.6624	0.1691	0.2510
C(7)	0.1619 (12)	0.12088 (75)	0.26110 (59)	H(15A)	0.6176	0.3932	0.1521
C(8)	0.1336 (14)	0.06590 (87)	0.34567 (73)	H(15B)	0.5916	0.3723	0.2406
C(9)	0.3168 (15)	0.06691 (89)	0.24869 (80)	H(15C)	0.4779	0.4582	0.1774
C(10)	0.0610 (13)	0.10740 (82)	0.20992 (64)	H(16A)	0.4755	0.3425	0.0644
C(11)	−0.1375 (10)	0.38268 (95)	0.34277 (68)	H(16B)	0.3328	0.4142	0.0813
C(12)	0.0535 (12)	0.40200 (78)	0.44300 (61)	H(16C)	0.3423	0.3031	0.0930
C(13)	0.0128 (11)	0.20842 (77)	0.47679 (59)	H(17)	−0.0057	0.8270	0.1798
C(14)	0.6064 (11)	0.19010 (91)	0.20456 (64)	H(19A)	−0.2484	0.7143	0.3524
C(15)	0.5463 (15)	0.3920 (11)	0.19101 (84)	H(19B)	−0.0820	0.6618	0.3603
C(16)	0.3944 (13)	0.34555 (93)	0.09726 (64)	H(19C)	−0.1747	0.6515	0.3013
C(17)	−0.00589 (92)	0.76155 (62)	0.21709 (49)	H(20A)	−0.3563	0.8654	0.2364
C(18)	−0.1414 (10)	0.79250 (71)	0.26059 (59)	H(20B)	−0.2883	0.0039	0.1837
C(19)	−0.1638 (11)	0.69589 (89)	0.32477 (65)	H(20C)	−0.2617	0.9078	0.1669
C(20)	−0.2741 (12)	0.8475 (10)	0.20701 (69)	H(21A)	−0.2153	0.8815	0.3252
C(21)	−0.1290 (14)	0.8637 (11)	0.29861 (84)	H(21B)	−0.1150	0.9239	0.2592
C(22)	0.3242 (10)	0.74089 (69)	0.09644 (54)	H(21C)	−0.0487	0.8302	0.3351
C(23)	0.3105 (10)	0.85432 (70)	0.04753 (58)	H(22A)	0.4147	0.7142	0.1244
C(24)	0.2954 (14)	0.91523 (82)	0.09801 (70)	H(22B)	0.3296	0.7110	0.0586
C(25)	0.1778 (13)	0.90193 (88)	−0.00637 (70)	H(24A)	0.2873	0.9844	0.0655
C(26)	0.4427 (12)	0.86452 (84)	−0.00248 (68)	H(24B)	0.3784	0.8872	0.1323
C(27)	−0.0524 (16)	0.5683 (10)	0.11617 (72)	H(24C)	0.2110	0.9126	0.1281
C(28)	−0.1178 (11)	0.77593 (87)	0.02245 (59)	H(25A)	0.1692	0.9718	−0.0365
C(29)	0.1289 (14)	0.63691 (89)	−0.00501 (67)	H(25B)	0.0940	0.8974	0.0240
C(30)	0.3422 (13)	0.77609 (76)	0.31143 (62)	H(25C)	0.1862	0.8665	−0.0406
C(31)	0.2772 (11)	0.58918 (79)	0.39325 (55)	H(26A)	0.4318	0.9349	−0.0320
C(32)	0.5251 (10)	0.59196 (88)	0.29636 (68)	H(26B)	0.4512	0.8298	−0.0372
H(1)	0.4040	0.1532	0.3970	H(26C)	0.5274	0.8351	0.0307
H(3A)	0.7251	0.1229	0.4788	H(27A)	−0.1018	0.5657	0.0752
H(3B)	0.6909	0.1727	0.3889	H(27B)	−0.1196	0.5816	0.1542
H(3C)	0.6539	0.0727	0.4392	H(27C)	0.0199	0.5045	0.1402
H(4A)	0.5861	0.2863	0.4904	H(28A)	−0.1558	0.7611	−0.0158
H(4B)	0.4256	0.3386	0.4603	H(28B)	−0.0849	0.8341	−0.0029
H(4C)	0.5489	0.3362	0.4008	H(28C)	−0.1915	0.7896	0.0576
H(5A)	0.5328	0.1259	0.5723	H(29A)	0.0620	0.6373	−0.0398
H(5B)	0.4575	0.0755	0.5348	H(29B)	0.1980	0.5708	0.0153
H(5C)	0.3712	0.1775	0.5443	H(29C)	0.1771	0.6863	−0.0326

[a] Each hydrogen atom is in its idealized calculated position and was assigned an isotropic thermal parameter of $B = 6.0$ Å^2.

thermal parameters for all nonhydrogen atoms (361 parameters) the model converged with $R_F = 4.5\%$, $R_{wF} = 3.1\%$, and GOF = 1.53 for all 4308 data. The residuals using only those 3626 data with $|F_o| > 3\sigma(|F_o|)$ were $R_F = 3.1\%$ and $R_{wF} = 3.0\%$.

An analysis of the function $\sum w(|F_o| - F_c|)^2$ showed no unusual trends as a function of Miller indices, $|F_o|$, $(\sin\theta)/\lambda$ or sequence number and also indicated that the effects of secondary extinction were minimal. A final difference-Fourier synthesis was featureless.

Final positional and thermal parameters are collected in Tables II and III.

Discussion

The crystal consists of discrete molecular units of $[Ta(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$, separated by normal van der Waals distances. There are no abnormally short contacts. Figure 1 shows a stereoscopic view of the molecule, while Figure 2 gives the atomic numbering scheme. Interatomic distances and angles are collected in Tables IV and V, while significant molecular planes are listed in Table VI. The binuclear molecule possesses no crystallographically imposed symmetry. Each of the tantalum atoms has a trigonal-bipyramidal coordination geometry. Two trimethylphosphine ligands occupy the axial sites [Ta(1)–P(1) = 2.585 (3) Å, Ta(1)–P(2) = 2.596 (3) Å, Ta(2)–P(3) = 2.601 (3) Å, Ta(2)–P(4) = 2.582 (3) Å]. The equatorial positions of each tantalum atom are occupied by a neopentylidene ligand, a neopentyl ligand, and a single nitrogen atom of a μ-N_2 ligand. Angles between axial and equatorial ligands are all close to 90°. Thus, P–Ta–equatorial atom angles range from 87.36 (24) to 93.93 (28)° about Ta(1) and from 86.98 (24) to 94.56 (27)° about Ta(2).

Some rather larger deviations from the ideal value of 120° occur for the diequatorial interligand angles. The C(alkylidene)–Ta–C(alkyl) angles are the greatest [C(1)–Ta(1)–C(6) = 124.75 (37)°, C(17)–Ta(2)–C(22) = 123.46 (36)°], the N–Ta–C(alkyl) angles have intermediate values [N(1)–Ta(1)–C(6) = 122.54 (34)°, N(2)–Ta(2)–C(22) = 122.89 (34)°], and the N–Ta–C(alkylidene) angles have the smallest values [N(1)–Ta(1)–C(1) = 112.68 (36)°, N(2)–Ta(2)–C(17) = 113.65 (35)°]. These differences are probably the net result of the differing intramolecular ligand···ligand repulsions.

The overall geometry about each tantalum atom is thus similar to that found in the complex Ta(=CHCMe₃)₂(mes-

Table III. Anisotropic Thermal Parameters (in Å^2)^a

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ta(1)	3.773 (22)	3.029 (20)	3.986 (22)	−1.176 (16)	−0.043 (16)	−1.345 (16)
Ta(2)	3.913 (22)	3.059 (20)	4.086 (22)	−1.280 (16)	0.236 (16)	−1.223 (16)
N(1)	3.91 (38)	3.80 (39)	4.47 (37)	−1.60 (30)	0.47 (29)	−1.52 (31)
N(2)	4.36 (39)	4.41 (41)	4.12 (37)	−1.94 (31)	−0.27 (29)	−1.92 (33)
P(1)	4.45 (14)	4.82 (14)	5.39 (14)	−1.89 (11)	0.80 (11)	−1.68 (11)
P(2)	5.57 (15)	5.85 (15)	5.94 (16)	−1.85 (12)	1.53 (12)	−3.11 (13)
P(3)	6.58 (16)	5.29 (15)	5.04 (14)	−2.04 (13)	−0.84 (12)	−1.56 (12)
P(4)	4.77 (14)	3.82 (12)	5.64 (14)	−1.47 (10)	−0.72 (11)	−1.80 (11)
C(1)	4.22 (48)	4.34 (48)	5.17 (52)	−2.24 (39)	−0.37 (41)	−1.48 (40)
C(2)	5.64 (60)	3.29 (49)	5.60 (60)	−1.53 (45)	−0.92 (47)	−0.71 (44)
C(3)	6.25 (66)	6.60 (66)	9.13 (76)	−1.57 (55)	−1.88 (56)	−1.78 (58)
C(4)	9.11 (77)	6.83 (71)	7.51 (69)	−3.28 (59)	−1.99 (58)	−1.48 (56)
C(5)	8.51 (74)	6.67 (66)	7.25 (71)	−2.88 (57)	−1.40 (57)	−1.77 (57)
C(6)	7.05 (60)	3.46 (49)	5.37 (54)	−1.28 (43)	−1.48 (44)	−1.01 (41)
C(7)	6.65 (65)	4.93 (58)	5.54 (59)	−2.39 (49)	−0.24 (49)	−2.11 (48)
C(8)	12.4 (10)	6.94 (70)	8.74 (81)	−5.89 (68)	−0.05 (69)	−2.57 (63)
C(9)	11.5 (10)	6.27 (70)	13.4 (10)	−3.56 (69)	1.92 (79)	−6.13 (73)
C(10)	11.41 (87)	6.50 (66)	7.51 (69)	−4.42 (62)	−1.89 (62)	−2.34 (55)
C(11)	2.71 (50)	11.44 (88)	9.86 (80)	−0.62 (52)	−0.15 (49)	−3.57 (69)
C(12)	9.13 (72)	6.86 (63)	7.94 (67)	−4.02 (56)	3.11 (55)	−5.30 (55)
C(13)	8.21 (68)	6.21 (60)	6.25 (58)	−4.51 (53)	2.59 (50)	−1.57 (48)
C(14)	5.52 (60)	10.39 (85)	7.82 (71)	−1.11 (57)	1.04 (51)	−4.39 (64)
C(15)	11.9 (10)	13.1 (10)	14.9 (11)	−8.90 (86)	8.38 (86)	−9.47 (92)
C(16)	10.20 (85)	9.31 (81)	6.07 (67)	−1.22 (67)	1.88 (59)	−2.33 (60)
C(17)	4.76 (51)	4.01 (46)	4.37 (47)	−1.87 (39)	0.07 (39)	−1.13 (38)
C(18)	4.74 (56)	4.38 (52)	6.30 (58)	−1.79 (44)	1.85 (48)	−2.03 (48)
C(19)	6.27 (64)	8.57 (76)	7.75 (70)	−2.51 (56)	2.64 (53)	−2.45 (61)
C(20)	5.37 (66)	10.99 (91)	7.70 (74)	0.17 (61)	1.61 (56)	−1.44 (66)
C(21)	9.48 (87)	12.1 (10)	14.2 (11)	−5.29 (77)	5.76 (77)	−9.54 (92)
C(22)	5.52 (55)	4.47 (53)	6.06 (56)	−1.57 (43)	1.52 (43)	−1.70 (45)
C(23)	4.82 (56)	4.21 (53)	5.78 (56)	−1.25 (43)	1.43 (47)	−1.67 (47)
C(24)	11.87 (91)	5.84 (64)	8.91 (78)	−5.00 (64)	3.18 (67)	−2.86 (61)
C(25)	8.28 (78)	7.31 (72)	8.18 (76)	−2.83 (62)	0.48 (63)	−0.26 (60)
C(26)	7.82 (72)	7.70 (71)	9.32 (76)	−4.18 (59)	3.43 (61)	−3.22 (61)
C(27)	16.7 (12)	11.4 (10)	8.02 (79)	−9.73 (92)	−3.67 (79)	−0.09 (70)
C(28)	6.66 (65)	9.15 (77)	6.03 (62)	−1.63 (57)	−1.77 (51)	−2.02 (57)
C(29)	12.31 (93)	8.17 (76)	7.61 (72)	−0.81 (67)	−0.21 (65)	−5.08 (63)
C(30)	10.92 (81)	5.11 (57)	7.85 (69)	−3.56 (55)	−1.23 (59)	−2.98 (52)
C(31)	8.14 (68)	7.35 (66)	4.86 (55)	−3.87 (55)	−0.61 (48)	−0.48 (48)
C(32)	3.79 (54)	9.37 (76)	10.58 (81)	−0.04 (50)	−1.63 (51)	−5.02 (66)

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

Table IV. Interatomic Distances (Å) and Esd's for $[Ta(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$

atoms	dist	atoms	dist
(A) Distances from the Tantalum Atoms			
Ta(1)–N(1)	1.837 (8)	Ta(2)–N(2)	1.842 (8)
Ta(1)–C(1)	1.932 (9)	Ta(2)–C(17)	1.937 (9)
Ta(1)–C(6)	2.285 (10)	Ta(2)–C(22)	2.299 (10)
Ta(1)–P(1)	2.585 (3)	Ta(2)–P(3)	2.601 (3)
Ta(1)–P(2)	2.596 (3)	Ta(2)–P(4)	2.582 (3)
(B) Nitrogen-Nitrogen Distance			
N(1)–N(2)	1.298 (12)		
(C) Distances within the Neopentylidene Ligands			
C(1)–C(2)	1.504 (14)	C(17)–C(18)	1.517 (14)
C(2)–C(3)	1.524 (16)	C(18)–C(19)	1.531 (16)
C(2)–C(4)	1.510 (17)	C(18)–C(20)	1.501 (16)
C(2)–C(5)	1.529 (15)	C(18)–C(21)	1.514 (19)
(D) Distances within the Neopentyl Ligands			
C(6)–C(7)	1.518 (15)	C(22)–C(23)	1.541 (15)
C(7)–C(8)	1.502 (16)	C(23)–C(24)	1.500 (16)
C(7)–C(9)	1.510 (19)	C(23)–C(25)	1.506 (16)
C(7)–C(10)	1.526 (17)	C(23)–C(26)	1.524 (16)
(E) Phosphorus–Carbon Distances			
P(1)–C(11)	1.844 (12)	P(3)–C(27)	1.786 (16)
P(1)–C(12)	1.842 (12)	P(3)–C(28)	1.795 (12)
P(1)–C(13)	1.845 (11)	P(3)–C(29)	1.835 (13)
P(2)–C(14)	1.804 (13)	P(4)–C(30)	1.839 (12)
P(2)–C(15)	1.787 (16)	P(4)–C(31)	1.840 (10)
P(2)–C(16)	1.775 (12)	P(4)–C(32)	1.844 (12)

ityl)$(PMe_3)_2$[16] save for the replacement of a neopentylidene ligand by a μ-N_2 ligand and the mesityl ligand by a neopentyl ligand. There is, however, significantly less distortion of the axial phosphine ligands in the present dimeric molecule, with P(1)–Ta(1)–P(2) = 171.92 (9)° and P(3)–Ta(2)–P(4) = 171.81 (9)° as opposed to P–Ta–P = 166.34 (7)° in $Ta(=CHCMe_3)_2(mesityl)(PMe_3)_2$.

In the $[Ta(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$ molecule, the alkylidene ligands are linked to the metal atoms via the bonds Ta(1)–C(1) = 1.932 (9) Å and Ta(2)–C(17) = 1.937 (9) Å. These values are very close to those observed in our study of $Ta(=CHCMe_3)_2(mesityl)(PMe_3)_2$ for which $Ta=CHCMe_3$ distances are 1.932 (7) and 1.955 (7) Å.

The Ta–C(α)–C(β) angles for the neopentylidene systems are very obtuse, with Ta(1)–C(1)–C(2) = 158.5 (7)° and Ta(2)–C(17)–C(18) = 160.3 (7)°. They are, however, consistent with previous measurements of neopentylidene complexes of tantalum[16–19] and tungsten[20–22] (see Table VII).

---

(16) (a) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1930–1935. (b) Churchill, M. R.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1978**, 1048–1049.

(17) Schultz, A. J.; Williams, J. M.; Brown, R. K.; Schrock, R. R. "Abstracts of Papers", 2nd Chemical Congress of the North American Continent, San Francisco, CA, August 25–29, 1980; Paper INOR-133.

(18) Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, G. A.; Fellman, J. D. *J. Am. Chem. Soc.* **1979**, *101*, 1593–1595.

(19) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957–1962.

(20) Churchill, M. R.; Youngs W. J. *Inorg. Chem.* **1979**, *18*, 2454–2458.

Table V. Interatomic Angles (Deg) with Esd's for $[Ta({=}CHMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$

atoms	angle	atoms	angle
(A) Angles about the Tantalum Atoms			
N(1)-Ta(1)-C(1)	112.68 (36)	N(2)-Ta(2)-C(17)	113.65 (35)
N(1)-Ta(1)-C(6)	122.54 (34)	N(2)-Ta(2)-C(22)	122.89 (34)
C(1)-Ta(1)-C(6)	124.75 (37)	C(17)-Ta(2)-C(22)	123.46 (36)
P(1)-Ta(1)-P(2)	171.92 (9)	P(3)-Ta(2)-P(4)	171.81 (9)
P(1)-Ta(1)-N(1)	87.86 (24)	P(3)-Ta(2)-N(2)	88.03 (24)
P(2)-Ta(1)-N(1)	87.36 (24)	P(4)-Ta(2)-N(2)	86.98 (24)
P(1)-Ta(1)-C(1)	93.93 (28)	P(3)-Ta(2)-C(17)	93.38 (28)
P(2)-Ta(1)-C(1)	93.93 (28)	P(4)-Ta(2)-C(17)	94.56 (27)
P(1)-Ta(1)-C(6)	88.04 (26)	P(3)-Ta(2)-C(22)	89.05 (26)
P(2)-Ta(1)-C(6)	89.04 (26)	P(4)-Ta(2)-C(22)	88.21 (26)
(B) Angles about the Nitrogen Atoms			
Ta(1)-N(1)-N(2)	171.43 (65)	Ta(2)-N(2)-N(1)	172.42 (65)
(C) Angles within the Neopentylidene Ligands			
Ta(1)-C(1)-C(2)	158.5 (7)	Ta(2)-C(17)-C(18)	160.3 (7)
C(1)-C(2)-C(3)	110.8 (9)	C(17)-C(18)-C(19)	108.7 (9)
C(1)-C(2)-C(4)	108.9 (9)	C(17)-C(18)-C(20)	112.1 (9)
C(1)-C(2)-C(5)	111.1 (9)	C(17)-C(18)-C(21)	111.7 (9)
C(3)-C(2)-C(4)	108.9 (9)	C(19)-C(18)-C(20)	108.7 (9)
C(3)-C(2)-C(5)	107.9 (9)	C(19)-C(18)-C(21)	108.7 (10)
C(4)-C(2)-C(5)	109.2 (9)	C(20)-C(18)-C(21)	106.8 (10)
(D) Angles within the Neopentyl Ligands			
Ta(1)-C(6)-C(7)	129.4 (7)	Ta(2)-C(22)-C(23)	127.6 (7)
C(6)-C(7)-C(8)	110.5 (9)	C(22)-C(23)-C(24)	112.3 (9)
C(6)-C(7)-C(9)	110.0 (9)	C(22)-C(23)-C(25)	109.5 (9)
C(6)-C(7)-C(10)	113.2 (9)	C(22)-C(23)-C(26)	111.0 (9)
C(8)-C(7)-C(9)	106.0 (10)	C(24)-C(23)-C(25)	107.7 (9)
C(8)-C(7)-C(10)	108.0 (10)	C(24)-C(23)-C(26)	107.8 (9)
C(9)-C(7)-C(10)	108.9 (10)	C(25)-C(23)-C(26)	108.4 (9)
(E) Angles within the PMe_3 Ligands			
Ta(1)-P(1)-C(11)	115.9 (4)	Ta(2)-P(3)-C(27)	110.0 (5)
Ta(1)-P(1)-C(12)	109.2 (4)	Ta(2)-P(3)-C(28)	119.6 (4)
Ta(1)-P(1)-C(13)	122.8 (4)	Ta(2)-P(3)-C(29)	121.2 (4)
C(11)-P(1)-C(12)	102.9 (5)	C(27)-P(3)-C(28)	102.0 (6)
C(11)-P(1)-C(13)	102.5 (5)	C(27)-P(3)-C(29)	100.8 (6)
C(12)-P(1)-C(13)	100.9 (5)	C(28)-P(3)-C(29)	100.1 (6)
Ta(1)-P(2)-C(14)	122.0 (4)	Ta(2)-P(4)-C(30)	122.9 (4)
Ta(1)-P(2)-C(15)	109.0 (5)	Ta(2)-P(4)-C(31)	109.9 (4)
Ta(1)-P(2)-C(16)	117.8 (4)	Ta(2)-P(4)-C(32)	116.3 (4)
C(14)-P(2)-C(15)	101.6 (6)	C(30)-P(4)-C(31)	101.0 (5)
C(14)-P(2)-C(16)	101.8 (6)	C(30)-P(4)-C(32)	101.7 (5)
C(15)-P(2)-C(16)	102.0 (7)	C(31)-P(4)-C(32)	102.2 (5)

As expected, the tantalum–neopentyl (single) bond lengths are substantially longer than tantalum–neopentylidene distances. Relevant data are Ta(1)–C(6) = 2.285 (10) Å and Ta(2)–C(22) = 2.299 (10) Å. The Ta–C(α)–C(β) angles within the neopentyl ligands are increased substantially from the ideal (sp^3) tetrahedral angle of 109.5°, with Ta(1)–C(6)–C(7) = 129.4 (7)° and Ta(2)–C(22)–C(23) = 127.6 (7)°. A similar value was found for the tungsten–neopentyl bond length in $W({\equiv}CCMe_3)({=}CHCMe_3)(CH_2CMe_3)(dmpe)$, where W–C(α)–C(β) = 124.5 (7)°.[20] This phenomenon is probably general in transition-metal alkyls.[23]

The most exciting and salient feature of this structural study is the nature of the μ-N_2 ligand which acts as the sole bridge between the two tantalum atoms. The tantalum–nitrogen distances, Ta(1)–N(1) = 1.837 (8) Å and Ta(2)–N(2) = 1.842 (8) Å (average 1.840 [4] Å)[24] are substantially shorter than the average tantalum–neopentylidene distances in this structure (Ta═C(av) = 1.935 [4] Å) and are close to the Ta═N distance of 1.747 (7) Å found in the rather dissimilar octahedral tantalum(V) complex $[(THF)_2Cl_3Ta{=}NCMe{=}CMeN{=}TaCl_3(THF)_2$.[25] In contrast to this, the Ta(V)–N *single* bond lengths in $Ta(NMe_2)_2(O_2CNMe_2)_3$, which has a tantalum(V) atom in a distorted pentagonal-bipyramidal (7-coordinate) environment, are 1.964 (8) and 1.977 (9) Å (average 1.971 [9] Å).[26] All of this information supports the designation of the tantalum–nitrogen linkages in $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$ as Ta═N *double* bonds.

Table VI. Least-Squares Planes and Atom Deviations (Å) Therefrom and Dihedral Angles (Deg) for $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$[a, b]

atom	dev	atom	dev
A. Equatorial Coordination Planes			
Ia: $0.6931x - 0.3153y - 0.6483z = -2.2633$			
Ta(1)*	0.0026 (4)	P(1)	−2.576 (3)
C(1)*	−0.001 (9)	P(2)	+2.592 (3)
C(6)*	−0.001 (10)	N(2)	0.023 (7)
N(1)*	−0.001 (7)	Ta(2)	0.2992 (4)
Ib: $-0.6244x - 0.2925y - 0.7243z = -8.6562$			
Ta(2)*	0.0033 (4)	P(3)	2.600 (3)
C(17)*	−0.001 (9)	P(4)	−2.569 (3)
C(22)*	−0.001 (10)	N(1)	0.012 (7)
N(2)*	−0.001 (7)	Ta(1)	0.3030 (4)
B. Axial Coordination Planes			
IIa: $-0.5351x - 0.8247y - 0.1830z = -8.5426$			
Ta(1)*	0.000	C(1)	−0.454 (9)
P(1)*	0.000	C(6)	2.130 (10)
P(2)*	0.000	N(1)	−1.481 (7)
IIb: $0.5900x + 0.4294y - 0.6838z = 5.4694$			
Ta(2)*	0.000	C(17)	−0.467 (9)
P(3)*	0.000	C(22)	2.167 (10)
P(4)*	0.000	N(2)	−1.459 (7)
C. Dihedral Angles			
Ia-Ib	82.59	IIa-IIb	57.00
Ia-IIa	89.55	Ib-IIb	89.93

[a] Cartesian (orthonormalized, Å) coordinates. [b] Atoms marked with an asterisk were used in calculating the plane.

Table VII. M=C(α)–C(β) Angles in Neopentylidene Complexes

complex	M=C(α)-C(β), deg	ref
$Ta({=}CHCMe_3)(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_2H_4)(PMe_3)$	170.2 (2)	17
$Ta({=}CHCMe_3)_2(\eta^1\text{-mesityl})(PMe_3)_2$	168.9 (6), 150.0 (6)	16
$[Ta({=}CHCMe_3)(PMe_3)Cl_3]_2$	161.2 (1)	18
$[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$	160.3 (7), 158.5 (7)	this work
$Ta({=}CHCMe_3)(\eta^5\text{-}C_5H_5)_2Cl$	150.4 (5)	19
$W({\equiv}CCMe_3)({=}CHCMe_3)(CH_2CMe_3)(dmpe)$	150.4 (8)	20
$W({=}O)({=}CHCMe_3)(PMe_3)_2Cl_2$	141.1 (16)	21
$W({=}O)({=}CHCMe_3)(PEt_3)Cl_2$	140.6 (11)	22

The N(1)–N(2) bond length of 1.298 (12) Å represents a significant *activation* of this linkage relative to its value in free dinitrogen (N≡N = 1.0976 Å).[9]

Our present study contrasts sharply with previous structural studies of bridging dinitrogen complexes of the early transition metals, where the nitrogen–nitrogen linkages are far less activated. Thus, in $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2(\mu\text{-}N_2)$[27] the nitrogen–nitrogen distance in the Zr–N–N–Zr bridge is short

---

(21) Churchill, M. R.; Rheingold, A. L.; Youngs, W. J.; Schrock, R. R.; Wengrovius, J. H. *J. Organomet. Chem.* **1981**, *204*, C17–C20.

(22) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515–4516.

(23) Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1967**, *6*, 1213–1220. (See, especially, Table VIII on p 1220).

(24) Esd's on average values are shown in square brackets. They are calculated with use of the "scatter" formula $[\sigma] = [\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$, where d_i is the *i*th and $\bar{d}$ is the mean of *N* "equivalent" measurements.

(25) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1978**, *17*, 3525–3528.

(26) Chisholm, M. H.; Cotton, F. A.; Extine, M. W. *Inorg. Chem.* **1978**, *17*, 2000–2003.

(27) Sanner, R. D.; Manriquez, J. M.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8351–8357.

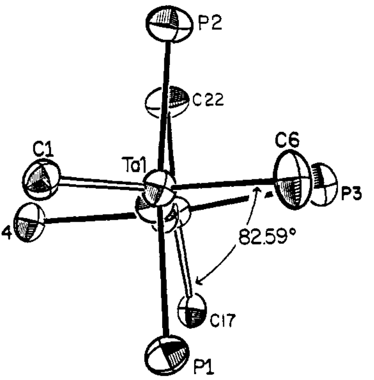

Figure 3. Relative conformation of the trigonal equatorial coordination planes about Ta(1) and Ta(2), as viewed approximately down the N(1)–N(2) bond.

[1.182 (5) Å] and the zirconium–nitrogen distances are relatively long [Zr–N(bridging) = 2.087 (3) and 2.075 (3) Å], although not as long as the Zr–N_2 (terminal) bond lengths [2.188 (4) and 2.188 (4) Å]. A similar pattern emerges for $[(\eta^5\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$.[28] There are two independent molecules in the crystal; bridging nitrogen–nitrogen distances are relatively short [1.165 (4) and 1.155 (14) Å], and titanium–nitrogen distances are not unusually short (Ti–N = 2.005 (10)–2.033 (10) Å).

We now return to a consideration of the bonding within the Ta(μ-N_2)Ta system. There are two closely interrelated problems. First, what is the formal oxidation state of the tantalum atoms? Second, what is the nature of the N_2 ligand and of the tantalum–nitrogen bonding?

To a first approximation we regard the complex as a tantalum(V) derivative. We base this assignment on the classical definition of oxidation state—i.e., the net electronic charge associated with the metal ion when each electron shared between metal and ligand is assigned completely to the more electronegative of the atoms sharing it. The Allred–Rochow electronegativity values for the atoms under consideration are as follows:[29] 1.33 for Ta, 2.06 for P, 2.50 for C, and 3.07 for N. As a tantalum(V) complex, the central metal atoms each have d^0 electronic configurations;[30] i.e., within the framework of this approach, the Ta═N double bonds do not arise via metal-to-ligand back-donation, but, rather, they result from a combination of ligand-to-metal σ donation and ligand-to-metal π donation.

We now come to a consideration of the nature of the bridging N_2 ligand. In order to be consistent with our terming the complex a derivative of Ta(V), we should view the ligand formally as a N_2^{4-} ligand. Thus eq 1 (see Introduction) shows the net reduction of dinitrogen, rather than of tantalum(V). The electronic configuration of N_2^{4-} is $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2$-$(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$; the bond order in the N–N linkage is thus 1.

Established nitrogen–nitrogen bond lengths include 1.0976 Å for the N≡N bond in dinitrogen,[9] about 1.24 Å for N═N,[31] and about 1.45 Å for the N–N single bond.[32] The observed value of 1.298 (12) Å for the N–N linkage in the present complex suggests a bond order somewhere between 1 and 2. This is precisely what one would predict as a result of donation of electrons from the π^*_{2p} orbitals of N_2^{4-} into the empty d orbitals of Ta(V).

The entire Ta(μ-N_2)Ta unit is close to linear with Ta(1)–N(1)–N(2) = 171.4 (7)° and Ta(2)–N(2)–N(1) = 172.4 (7)°. Figure 3 shows a skeletal view of the $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$ molecule viewed almost directly along its nitrogen–nitrogen vector. As is clearly shown, the equatorial coordination planes about the two tantalum atoms are oriented almost perpendicular to one another. The dihedral angle is 82.59° (see Table VI). This can be explained by the N_2^{4-} ligand's donating electron density from the $\pi^*_{2p_x}$ orbital to one tantalum and from the degenerate orthogonal $\pi^*_{2p_y}$ orbital to the other tantalum atom, in the subsidiary ligand-to-metal π donation. (Here, we assign the z direction to the N–N axis.)

Finally, we note that the complex under study is formally a 14-electron Ta(V) derivative. In contrast to this, the species $[(\eta^5\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$[28] is a 16-electron Ti(II) derivative and $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2(\mu\text{-}N_2)$ is an 18-electron Zr(II) derivative. These latter two species are significantly more "electron-rich" than our Ta(V) complex.

Further studies of bridging dinitrogen complexes of Ta(V) are under way and will be reported at a later date. Related studies of imido complexes containing the Ta═NR fragment are also in progress.

Acknowledgment. We thank Professor R. R. Schrock for providing the sample studied. This work was supported by the National Science Foundation (Grant CHE79-24560, to M.R.C.).

Registry No. $[Ta({=}CHCMe_3)(OH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$, 75737-70-1.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

---

(28) Sanner, R. D.; Duggan, D. M.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358–8365.

(29) Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.

(30) The assignment of oxidation state is rendered rather more difficult by the propensity of alkylidene ligands to engage in α-hydride interaction with the transition-metal atom. See the following reports: Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104. Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169–176.

(31) Churchill, M. R.; Lin, K.-K. G. *Inorg. Chem.* **1975**, *14*, 1133–1138.

(32) *Chem. Soc., Spec. Publ.* **1965**, *No. 18*, S7s.