2352 *Inorg. Chem.* **1980**, *19*, 2352-2354

Contribution from Department of Chemistry,
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Reactions of Niobium(III) and Tantalum(III) Compounds with Acetylenes. 1. Preparation and Structure of Pyridinium Tetrachloro(pyridine)(tolane)tantalate, $[pyH][TaCl_4(py)(PhC\equiv CPh)]$

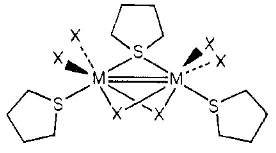
F. ALBERT COTTON* and WILLIAM T. HALL

Received December 28, 1979

The reaction of $Ta_2Cl_6(SC_4H_8)_3$ with diphenylacetylene (tolane) in toluene gives a yellow solid which is converted by recrystallization from pyridine/CH_2Cl_2, 1:9, into orange crystals of the title compound. These crystals are triclinic with a = 11.345 (8) Å, b = 12.335 (4) Å, c = 9.352 (4) Å, α = 101.12 (3)°, β = 106.82 (4)°, γ = 87.07 (4)°, and V = 1232.5 (1.0) $Å^3$. With Z = 2 and a formula weight of 585.28 the calculated density is 1.58. The structure was solved and refined in space group $P\bar{1}$ to R_1 = 0.031 and R_2 = 0.051 with hydrogen atoms omitted and all others treated anisotropically. The Ta atom is seven-coordinate with a pyridine nitrogen atom on one side and the PhCCPh ligand on the other side of a Cl_4 plane, from which the Ta atom is displaced 0.38 Å toward PhCCPh. The binding of the PhCCPh is very strong, with a mean Ta–C distance of 2.07 (1) Å. It is proposed that this implies that there is an approximately four-electron interaction with the Ta atom and that the latter is effectively in an oxidation state of V.

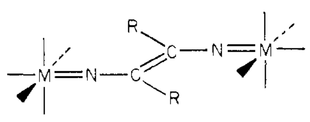
Introduction

We have recently reported[1] that the niobium(III) and tantalum(III) compounds,[2-4] **1a** and **1b** serve as useful starting



1a: M = Nb; X = Cl
b: M = Ta; X = Cl

materials for the preparation of other Nb^{III} and Ta^{III} compounds, as well as the unusual M^V species of type **2** that arise



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when RCN molecules are dimerized to give ligands capable of forming two nitrene linkages.

Among the reactions in which the oxidation state of III is maintained, at least formally, in the products, there are several with acetylenes, RC≡CR′. We have examined a number of these reactions and found that the product of the reaction varies considerably with the identity of R and R′. One of the first of these varied reaction products that we characterized in detail is the one obtained by using tolane, diphenylacetylene, and **1b**. The reaction takes place readily in toluene, but it was found convenient to recrystallize the product from CH_2Cl_2 containing pyridine whereby an ionic product containing the pyridinium ion is obtained. This substance has been briefly described in a preliminary communication,[1] but we present here a full report on its isolation, structure, and bonding.

Experimental Section

Synthesis and Crystal Preparation. $Ta_2Cl_6(SC_4H_8)_3$ (500 mg) was dissolved in toluene, and 2 equiv of tolane was added. Over a period of several hours, a yellow-orange precipitate collected in the bottom of the flask; this solid was isolated and dried. The product was then dissolved in a 10% pyridine/dichloromethane solution, and after 1 day, well-formed orange, rhombohedral crystals (ca. 100 mg; 30% yield on the basis of $Ta_2Cl_6(SC_4H_8)_3$) precipitated from the solution.

Table I. Atomic Positional Parameters

atom	x	y	z
Ta(1)	0.31514 (3)	0.26535 (3)	0.07696 (4)
Cl(1)	0.1685 (2)	0.3731 (2)	−0.0819 (3)
Cl(2)	0.1919 (2)	0.1046 (2)	−0.0722 (3)
Cl(3)	0.4644 (2)	0.4180 (2)	0.1532 (3)
Cl(4)	0.4909 (2)	0.1546 (2)	0.1823 (3)
N(10)	0.3980 (6)	0.2326 (6)	−0.1390 (8)
N(40)	0.7074 (9)	0.2790 (9)	0.0622 (13)
C(11)	0.4074 (9)	0.3132 (9)	−0.2122 (10)
C(12)	0.4526 (10)	0.2964 (9)	−0.3360 (11)
C(13)	0.4930 (9)	0.1905 (9)	−0.3884 (11)
C(14)	0.4816 (9)	0.1072 (9)	−0.3129 (10)
C(15)	0.4341 (9)	0.1278 (8)	−0.1910 (11)
C(20)	0.2457 (7)	0.2385 (7)	0.2483 (9)
C(21)	0.2100 (8)	0.1642 (8)	0.3296 (10)
C(22)	0.1604 (9)	0.2052 (9)	0.4512 (10)
C(23)	0.1346 (10)	0.1328 (10)	0.5351 (11)
C(24)	0.1532 (9)	0.0218 (9)	0.5000 (13)
C(25)	0.2008 (11)	−0.0218 (9)	0.3766 (13)
C(26)	0.2288 (9)	0.0491 (8)	0.2924 (11)
C(30)	0.2479 (8)	0.3463 (7)	0.2521 (9)
C(31)	0.2158 (9)	0.4527 (7)	0.3361 (9)
C(32)	0.3085 (10)	0.5290 (9)	0.4242 (12)
C(36)	0.0920 (9)	0.4786 (9)	0.3191 (12)
C(33)	0.2777 (11)	0.6296 (10)	0.5002 (13)
C(34)	0.1554 (12)	0.6562 (9)	0.4871 (13)
C(35)	0.0632 (11)	0.5815 (10)	0.3974 (13)
C(41)	0.7359 (11)	0.3529 (9)	−0.0147 (15)
C(42)	0.8417 (13)	0.3355 (11)	−0.0623 (16)
C(43)	0.9134 (10)	0.2452 (9)	−0.0324 (15)
C(44)	0.8810 (12)	0.1746 (10)	0.0419 (17)
C(45)	0.7774 (12)	0.1878 (12)	0.0892 (16)

Table II. Bond Lengths (Å)

Ta(1)–Cl(2)	2.420 (2)	C(20)–C(30)	1.825 (12)
–Cl(2)	2.436 (2)	C(30)–C(31)	1.481 (11)
–Cl(3)	2.459 (2)	C(31)–C(32)	1.406 (13)
–Cl(4)	2.436 (2)	C(32)–C(33)	1.389 (14)
–N(10)	2.425 (7)	C(33)–C(34)	1.388 (16)
–C(20)	2.066 (8)	C(34)–C(35)	1.394 (17)
–C(30)	2.069 (8)	C(35)–C(36)	1.412 (14)
N(10)–C(11)	1.335 (11)	N(40)–C(41)	1.368 (17)
N(10)–C(15)	1.376 (11)	C(41)–C(42)	1.393 (19)
C(11)–C(12)	1.375 (13)	C(42)–C(43)	1.371 (18)
C(12)–C(13)	1.408 (14)	C(43)–C(44)	1.338 (19)
C(13)–C(14)	1.384 (14)	C(44)–C(45)	1.366 (16)
C(14)–C(15)	1.374 (13)	C(45)–N(40)	1.366 (18)
C(20)–C(21)	1.437 (12)	C(23)–C(24)	1.366 (15)
C(21)–C(22)	1.410 (12)	C(24)–C(25)	1.416 (15)
C(22)–C(23)	1.390 (14)	C(25)–C(26)	1.387 (14)

One of these crystals was sealed in a capillary, in mineral oil, and used for data collection. All manipulations were performed under

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(1) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094.
(2) Mass, E. T., Jr.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1096.
(3) Templeton, J. L.; Dorman, W. C.; Clardy, J. C.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1263.
(4) Templeton, J. L.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 2293.

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Table III. Bond Angles (Deg)

Cl(1)–Ta(1)–Cl(2)	86.46 (8)
–Cl(3)	90.04 (8)
–Cl(4)	164.14 (8)
–N(10)	81.94 (17)
–C(20)	108.67 (22)
–C(30)	85.87 (23)
Cl(2)–Ta(1)–Cl(3)	161.04 (8)
–Cl(4)	93.45 (8)
–N(10)	81.12 (17)
–C(20)	84.43 (23)
–C(30)	112.59 (25)
Cl(3)–Ta(1)–Cl(4)	84.91 (8)
–N(10)	79.94 (17)
–C(20)	114.28 (23)
–C(30)	85.68 (25)
Cl(4)–Ta(1)–N(10)	82.38 (17)
–C(20)	87.07 (22)
–C(30)	108.65 (23)
N(10)–Ta(1)–C(20)	161.52 (27)
–C(30)	161.08 (29)
C(20)–Ta(1)–C(30)	37.38 (32)
C(11)–N(10)–C(15)	118.47 (75)
N(10)–C(11)–C(12)	122.97 (83)
C(11)–C(12)–C(13)	119.42 (87)
C(12)–C(13)–C(14)	117.16 (84)
C(13)–C(14)–C(15)	121.21 (85)
C(14)–C(15)–N(10)	120.73 (85)
C(21)–C(20)–C(30)	138.24 (80)
C(20)–C(21)–C(22)	120.53 (80)
C(20)–C(21)–C(26)	120.36 (80)
C(22)–C(21)–C(26)	119.07 (87)
C(21)–C(22)–C(23)	119.61 (91)
C(22)–C(23)–C(24)	121.45 (94)
C(23)–C(24)–C(25)	120.01 (98)
C(24)–C(25)–C(26)	119.60 (98)
C(21)–C(26)–C(25)	120.24 (92)
C(20)–C(30)–C(31)	141.16 (82)
C(30)–C(31)–C(32)	120.16 (83)
C(30)–C(31)–C(36)	119.02 (84)
C(32)–C(31)–C(36)	120.71 (83)
C(31)–C(32)–C(33)	119.9 (1.0)
C(32)–C(33)–C(34)	120.3 (1.0)
C(33)–C(34)–C(35)	119.9 (1.0)
C(34)–C(35)–C(36)	121.0 (1.0)
C(35)–C(36)–C(31)	118.2 (1.0)
C(41)–N(40)–C(45)	122.0 (1.1)
N(40)–C(41)–C(42)	118.4 (1.1)
C(41)–C(42)–C(43)	119.6 (1.2)
C(42)–C(43)–C(44)	119.8 (1.2)
C(43)–C(44)–C(45)	122.6 (1.2)
N(40)–C(45)–C(44)	117.6 (1.3)

an inert atmosphere, and all solvents were dried and degassed by standard methods.

Crystallographic investigation has revealed the formula of the compound to be [pyH][$TaCl_4$(py)(PhC≡CPh)], where py = pyridine. Apparently there were adventitious traces of water in the pyridine/dichlormethane which hydrolyzed some of the Ta compound, producing the pyridinium chloride which was incorporated in the crystallized species. We infer that the initial yellow-orange product which precipitated on addition of diphenylacetylene is a seven-coordinate compound, $TaCl_3(THT)_2$(PhC≡CPh).

When $TaCl_3(THT)_2$(PhC≡CPh) is treated with aqueous acetone, *cis*-stilbene is isolated by filtering and evaporating the acetone solution. Complete hydrolysis takes about 15 min at room temperature.

X-ray Data Collection. Preliminary examination indicated that the crystals are triclinic, and ω scans of several reflections showed the crystal used in data collection to be of good quality. The following cell constants were obtained by centering on 15 intense reflections in the range $15° < 2\theta < 25°$: $a = 11.345$ (8) Å, $b = 12.335$ (4) Å, $c = 9.352$ (4) Å, $\alpha = 101.12$ (3)°, $\beta = 106.82$ (4)°, $\gamma = 87.07$ (4)°, and $V = 1232.5$ (1.0) Å^3. For $Z = 2$ and a formula weight of 585.28 the calculated density is 1.578.

Data were collected at 21 ± 2 °C on a Syntex P$\bar{1}$ diffractometer using Mo Kα radiaton. The θ–2θ scan technique was employed by using a variable scan rate of 4.0–24.0°/min with a scan range of 0.9° below Kα_1 to 0.9° above Kα_2. Reflections were collected in the range $0.0° < 2\theta < 45.0°$, and a total of 3238 reflections, 2756 with intensity greater than 3σ, were obtained. The intensities of three standard reflections, measured every 97 reflections, showed no change with time. Lorentz and polarization corrections were applied to the data as was an empirical absorption correction based on Ψ scans at $\chi = 90°$ of five reflections.

Structure Solution. The Ta position was determined from the three-dimensional Patterson function and refined by least-squares methods, on the assumption of the space group being $P\bar{1}$. Subsequent difference maps revealed the rest of the structure. In this way it was found that the molecular formula of the compound is [pyH]-[$TaCl_4$(py)(PhC≡CPh)].

The structure was then refined by the full-matrix least-squares method, with hydrogen atoms omitted and all other atoms treated anisotropically. The final discrepancy indices were $R_1 = 0.031$ and $R_2 = 0.051$, and the error in an observation of unit weight was 1.125. Anomalous dispersion effects were included in the calculated structure factors for all atoms. A table of structure factors is available as supplementary material.

Computer programs used in the structure solution and refinement were those of the Enraf-Nonius structure determination package on a PDP 11/45 computer. All procedures, definitions, and sources of data required in the structure solution and refinement have been discussed and referenced elsewhere.[5]

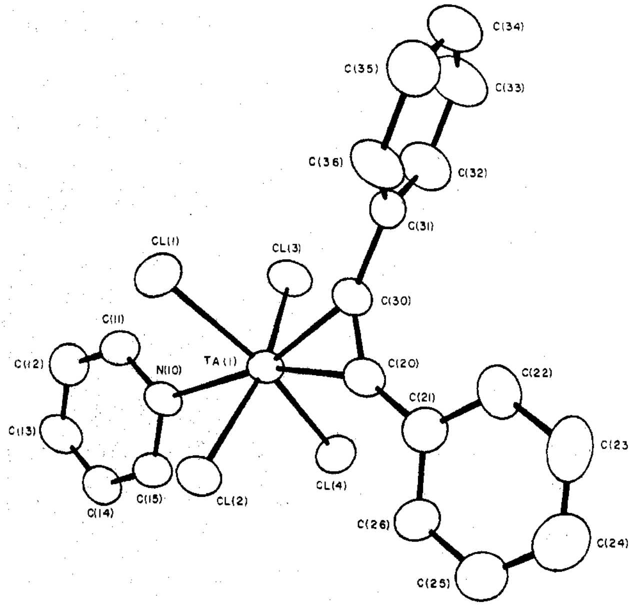

Figure 1. Structure of the anion [$TaCl_4$(py)(PhCCPh)]$^-$. The numbering scheme used in the tables is shown.

Results

The positional parameters of all atoms are listed in Table I. A list of thermal vibration parameters is available as supplementary material. Figure 1 shows the anion portion of the structure and defines the numbering scheme. Atoms N(40) and C(41)–C(45) belong to the pyridinium counterion. The bond distances and angles are listed Tables II and III.

The entire formula unit is the crystallographic asymmetric unit, and no crystallographic symmetry is imposed. The coordination about the Ta atom may be described as distorted octahedral, if the tolane is considered as a unit, or the coordination number may be taken as 7, with a 2, 4, 1 arrangement of two carbon atoms, four Cl atoms, and a pyridine nitrogen atom. The Ta atom is displaced 0.38 Å out of the plane of

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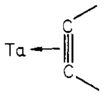
(5) Cotton, F. A.; Frenz, B. A.; Stultz, B. R.; Webb, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 2768.

the chlorine atoms toward the tolane, and the coordinated pyridine molecule is 9.3° from coplanarity with the acetylenic unit, Ta(1)-C(20)-C(30). The pyridinium nitrogen atom, N(40), is 3.41 Å from Cl(3) and 3.51 Å from Cl(4). It is possible that the proton may be hydrogen bonded to these chlorine atoms.

Discussion

The most remarkable feature of this structure is the binding of the tolane to the tantalum atom, which is very strong and symmetrical. The Ta-C distances are 2.066 (8) and 2.079 (8) Å; the C-C distance is 1.325 (12) Å, and the two C(phenyl)-C-C angles are 138.24 (80) and 141.16 (82)°. The benzyne complex[6] ($(\eta^5\text{-}C_5Me_5)Ta(C_6H_4)(CH_3)_2$ is the only prior example of such a strongly bonded Ta(η-C≡C) moiety. The Ta-C distances are also very similar to that in the Ta=C bond found in the Ta-benzylidene complex $(C_5H_5)_2Ta(CHPh)(CH_2Ph)$,[7] where the bond length is 2.07(1) Å and the Ta-C_α-C_β angle is 135.2 (7)°. Thus a simple μ-bond representation, **3**, or one with two single bonds, **4**, does not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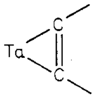
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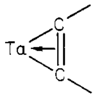
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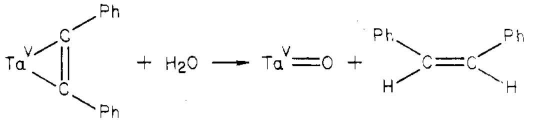
seem to account adequately for the structure. We may, therefore, in a purely formal way, consider an arrangement[8] in which even more electrons become involved in the bonding, namely, **5**. The actual electron distribution may, perhaps, be best represented by a combination of **4** and **5**.

The electronic structures implied by **4** and/or **5** are consistent with the hydrolysis of the compound to yield *trans*-stilbene and a whitish precipitate that appears to contain Ta^V:



To the extent that the tantalum bonding involves, at least in part, four-electron donation, it is pertinent to compare this case to the structure of $W(CO)(S_2CNEt_2)_2(C_2H_2)$ reported by Ricard et al.[9] They find a W(HCCH) unit with W-C distances of 2.03 Å and a C-C distance of 1.29 Å and on the basis of these facts and other reasoning propose that the acetylene is acting as a four-electron donor. In their case this allows the metal to achieve an 18-electron configuration whereas for our compound Ta reaches only a 16-electron configuration.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. [pyH][$TaCl_4$(py)(PhC≡CPh)], 71763-72-9; $Ta_2Cl_6(SC_4H_8)_3$, 66758-43-8.

Supplementary Material Available: A table of thermal vibration parameters and a table of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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[6] McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263.

[7] Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793.

[8] We now suggest **5** rather than the structure **7** given in ref 1 since the latter implies too high a formal oxidation state, viz., VII, if taken as implying a four-covalent tolane ligand. Structure **5** would be consistent with a valence state of V for tantalum.

[9] Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318.

Contribution from Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Reactions of Niobium(III) and Tantalum(III) Compounds with Acetylenes. 2. Preparation and Structure of $Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}Me_3CC{\equiv}CCMe_3)(THF)_2$. The Shortest Known Ta-Ta Bond

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Received December 28, 1979

The reaction of $Ta_2Cl_6(SC_4H_8)_3$ with $(CH_3)_3CC{\equiv}CC(CH_3)_3$ (di-*tert*-butylacetylene, DTBA) in toluene gives a dark red solution after 2 days. Solvent was removed, and the solid residue recrystallized from THF to give orange crystals of the title compound, $Ta_2Cl_6(DTBA)(THF)_2$. These air-sensitive crystals belong to the monoclinic system with a = 15.181 (9) Å, b = 10.185 (8) Å, c = 17.301 (2) Å, β = 101.48 (6)°, and V = 2628.4 (4) Å^3. With a formula weight of 836.08, d(calcd) is 2.19 g cm^{-3} for Z = 4. The structure was solved and refined in space group $C2/c$ to R_1 = 0.031 and R_2 = 0.044, with hydrogen atoms omitted and all others treated anisotropically. The molecule lies on a crystallographic C_2 axis and has a structure similar to that of $Ta_2Cl_6(SC_4H_8)_3$, with the bridging SC_4H_8 replaced by the DTBA, which is oriented across but not exactly perpendicular to the Ta-Ta axis, and the terminal SC_4H_8 ligands replaced by THF molecules. The Ta-Ta distance, 2.677 (1) Å, is the shortest one known and is consistent with the postulated double bond. The tantalum atoms are seven-coordinate with the THF oxygen atom on one side and the acetylenic carbon atoms on the other side of a median $TaCl_4$ plane. The acetylene can be considered as a two-π-electron donor to each of the Ta atoms.

Introduction

The niobium(III) and tantalum(III) compounds $M_2X_6(SC_4H_8)_3$[1-3] are among the few readily available, well-defined substances with which to investigate the chemistry of Nb^{III} and Ta^{III}. We have already shown that interesting and novel products can be obtained by reacting them with alkyl cyanides[4a] and acetylenes.[4a,b] Their reactions with acetylenes, RC≡CR′, follow quite different courses depending on the identities of R and R′. In part 1 of this series[4b] we have

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[1] Maas, E. T., Jr.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1096.

[2] Templeton, J. L.; Dorman, W. C.; Clardy, J. C.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1263.

[3] Templeton, J. L., McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 2293.

[4] (a) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094; (b) *Inorg. Chem.*, preceding paper in this issue.

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