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Two Reactions of Bis(diphenylphosphino)acetylene with $Ta_2Cl_6(SMe_2)_3$. Dinuclear Products with Coupled Acetylenes and $\overline{\mathrm{P{-}Ta{-}C}}$ or $\overline{\mathrm{P{-}Ta{=}C}}$ Rings[†]

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The tantalum compound $Ta_2Cl_6(SMe_2)_3$ reacts with $Ph_2PC{\equiv}CPPh_2$ to give either of two products, 1 or 2, depending on the mole ratio of reactants used. If a 1:1 ratio is used, 1, with a molecular formula $Cl_4Ta{-}CH(PPh_2)C(PPh_2){=}C(PPh_2)CH(PPh_2){-}TaCl_4{\cdot}2CH_2Cl_2$, is obtained. When a mole ratio of 1:2 is used, the related compound 2, having two fewer hydrogen atoms and two Ta=C double bonds, $(Me_2S)Cl_3Ta{=}C(PPh_2)C(PPh_2){=}C(PPh_2)C(PPh_2){=}TaCl_3(SMe_2)$, is obtained. Both compounds have been identified and structurally characterized by X-ray crystallography. 1 forms monoclinic crystals in space group $P2_1/n$ with unit-cell dimensions $a = 11.884$ (2) Å, $b = 14.143$ (4) Å, $c = 17.681$ (5) Å, $\beta = 94.26$ (1)°, $V = 2963$ (2) Å^3, and $Z = 2$. Compound 2 also forms monoclinic crystals in space group $P2_1/n$ with $a = 14.851$ (4) Å, $b = 12.245$ (6) Å, $c = 15.848$ (4) Å, $\beta = 97.32°$, $V = 2858$ (3) Å^3, and $Z = 2$. In each compound the starting acetylene has dimerized to form a four-carbon chain and the tantalum has increased its oxidation state from III to V. In each case the molecule resides on a crystallographic inversion center. In 1 each Ta atom has distorted octahedral coordination supplied by four Cl atoms, one P atom, and a $Ph_2P{-}CH{-}$ group that forms a three-membered $\overline{\mathrm{Ta{-}C{-}P}}$ ring with Ta–P = 2.555 (5) Å and Ta–C = 2.326 (13) Å. In 2 the coordination is similar except that there is a $Ph_2P{-}C{-}$ group coordinated and trans to it a Me_2S ligand in place of Cl. The three-membered $\overline{\mathrm{Ta{=}C{-}P}}$ ring has Ta—P = 2.471 (3) Å and Ta=C = 2.018 (10) Å. The reactions leading to these compounds are not understood mechanistically. Systematic names for 1 and 2 are octachloro[μ-[1,2,3,4-tetrakis(diphenylphosphino)-2-butene-1,4-diyl-$C^1,P^1,P^3{:}C^4,P^2,P^4$]]ditantalum and hexachloro[μ-[1,2,3,4-tetrakis(diphenylphosphino)-2-butene-1,4-diylidene-$C^1,P^1,P^3{:}C^4,P^2,P^4$]]bis(dimethyl sulfide)ditantalum, respectively. The structure of 1 was refined with 2480 data to final least-squares residuals $R = 0.061$ and $R_w = 0.068$. The refinement of 2 involved 2971 reflections and gave final residuals $R = 0.061$ and $R_w = 0.074$.

Introduction

Previous studies in this laboratory have examined the reactions of acetylenes with the tantalum and niobium compounds of the type $M_2Cl_6(THT)_3$, where THT represents tetrahydrothiophene.[1-4] In several cases[1-3] the isolated products were mono- or dinuclear complexes containing the acetylene molecules coordinated to one or two metal atoms. With certain acetylenes, however, polymerization occurred[4] to form either cyclic trimers (substituted benzenes) or high molecular weight linear polymers. In addition to these studies we have been exploring the chemistry of tantalum(III) more generally,[5] and in the course of this work we have found that the compound $Ta_2Cl_6(SMe_2)_3$ is a convenient and useful reagent[6] for preparing a variety of tantalum(III) compounds.

In this paper we report the results of an investigation of the reaction of $Ta_2Cl_6(SMe_2)_3$ with the unusual acetylene $Ph_2PC{\equiv}CPPh_2$. The results are quite different from any previously obtained. Neither polymers nor simple (alkyne)metal complexes have been isolated. Instead, complex reactions occur in which the acetylene is dimerized to give a 1,2,3,4-tetraphosphinobut-2-enediyl chain, which then complexes tantalum with the formation of $\overline{\mathrm{P{-}C{-}Ta}}$ or $\overline{\mathrm{P{-}C{=}Ta}}$ rings. The compounds to be described in this paper are 1, octachloro[μ-[1,2,3,4-tetrakis(diphenylphosphino)-2-butene-1,4-diyl-$C^1,P^1,P^3{:}C^4,P^2,P^4$]]ditantalum and 2, hexachloro[μ-[1,2,3,4-tetrakis(diphenylphosphino)-2-butene-1,4-diylidene-$C^1,P^1,P^3{:}C^4,P^2,P^4$]]bis(dimethyl sulfide)ditantalum.

Experimental Section

Bis(diphenylphosphino)acetylene, dppa, was prepared according to the literature method.[7] $Ta_2Cl_6(SMe_2)_3$ was prepared as previously described.[6] Dichloromethane and hexane were distilled over P_2O_5 and potassium benzophenone ketyl, respectively. All manipulations of materials were carried out under anaerobic and anhydrous conditions by using vacuum line, syringe, and Schlenk methods. The infrared spectra were recorded on a Unicam SP1100 spectrometer.

Preparation of $Cl_4Ta{-}CH(PPh_2)C(PPh_2){=}C(PPh_2)CH(PPh_2){-}TaCl_4{\cdot}2(CH_2Cl_2)$, 1. $Ta_2Cl_6(SMe_2)_3$, 100 mg (0.13 mmol), was dissolved in 5 mL of dichloromethane and the solution transferred to a Schlenk tube via syringe. Dichloromethane (15 mL) was carefully layered over the $Ta_2Cl_6(SMe_2)_3$ solution. One equivalent of dppa, 50 mg (0.13 mmol), was dissolved in 5 mL of dichloromethane and the solution layered on top of the dichloromethane stratum in the Schlenk tube. The diffusion of the reactants proceeded over a period of approximately 1 week, which yielded a maroon solution and a small amount of light brown precipitate. The solution was filtered through a Celite pad, and about 8 mL of the filtrate was transferred to another Schlenk tube. The maroon filtrate was covered with a layer of 20 mL of hexane. As diffusion proceeded, the maroon solution turned brown within

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[†] Dedicated to the memory of Rowland G. Pettit.

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Table I. Crystallographic Parameters for 1 and 2

parameter	1	2
space group	$P2_1/n$	$P2_1/n$
a, Å	11.884 (2)	14.851 (4)
b, Å	14.143 (4)	12.245 (6)
c, Å	17.681 (5)	15.848 (4)
β, deg	94.26 (1)	97.32 (2)
V, Å^3	2963 (2)	2858 (3)
d_{calcd}, g/cm^3	1.81	1.73
Z	2	2
fw	1605.99	1463.44
cryst size, mm.	0.20 × 0.31 × 0.25	0.28 × 0.32 × 0.40
μ(Mo Kα), cm^{-1}	43.358	42.81
range 2θ, deg	0-50	0-48
no. of unique data	3143	3463
no. of data, $F_o^2 > 3\sigma(F_o^2)$	2480	2971
no. of variables	326	315
R_1[a]	0.061	0.061
R_2[a]	0.068	0.074
esd[c]	1.622	2.062
largest shift[b]	0.05	0.26

[a] $R_1 = \Sigma \| F_o | - | F_c | / \Sigma | F_o |$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$. [b] Largest parameter shift/esd in final refinement cycle. [c] Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2 / (N_{obsd} - N_{parameters})]^{1/2}$.

24 h, and a fine brown precipitate was formed. Lustrous brown crystals appropriate for X-ray analysis were obtained after 3 days in ca. 5% yield. Crystals of 1 were moderately air sensitive (<15 min in air): Ir (mull) 1590 (w), 1441 (s), 1438 (sh), 1318 (m), 1268 (s), 1390 (m), 1099 (br), 1030 (br), 981 (sh), 805 (s), 765 (sh), 707 (sh), 649 (sh) cm^{-1}.

Preparation of $(Me_2S)Cl_3Ta{=}C(PPh_2)C(PPh_2){=}C(PPh_2)C(PPh_2){=}TaCl_3(SMe_2)$, 2. $Ta_2Cl_6(SMe_2)_3$, 0.5 g (0.66 mmol), was dissolved in 20 mL of dichloromethane. Two equivalents[8] of dppa, 0.52 g (1.32 mmol), were added to the solution, and the reaction mixture was stirred 1 h at 20 °C. The solvent was removed from this maroon solution by vacuum distillation. The resulting purple solid was washed twice with hexane to remove any excess dppa. Dichloromethane (20 mL) was added to the solid and the resulting solution filtered through Celite. A layer of hexane was placed over a portion of the solution as described above. Purple rectangular crystals suitable for X-ray crystallography were obtained in this manner. Crystals of 2 were moderately air sensitive (<15 min in air): Ir (mull) 1440 (s), 1328 (br), 1266 (s), 1097 (br), 1030 (s), 804 (s), 741 (s), 705 (sh), 691 (s), 547 (m) cm^{-1}. The overall yield of 2 was ca. 80%.

X-ray Crystallography. Collection of Data. Crystals of 1 and 2 were mounted in capillary tubes with degassed epoxy resin and sealed under nitrogen. Crystals of 1 were examined by the automatic search routine on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation ($\lambda\bar{\alpha}$ = 0.71073 Å) with a graphite monochromator in the incident beam. Crystals of 2 were inspected by using rotation photographs taken on the CAD-4, followed by the automatic search routine. The ω-scan peak profiles of various strong reflections in each case indicated that the crystals were of good quality. The standard CAD-4 centering, indexing, and data collection programs were used. The temperature during data collection was 25 ± 1 °C. A summary of data collection and refinement parameters is presented in Table I. Lorentz and polarization corrections were applied to the data as were empirical absorption corrections[9] based on ψ scans of several reflections at values of χ near 90°. General procedures for data collection have been previously reported.[10]

During data collection, three standard reflections were measured after every hour of X-ray exposure for each compound. Total losses in intensity for compounds 1 and 2 were 15.4% and 17.6%, respectively. Corrections for anisotropic decay were applied to the data in each case.

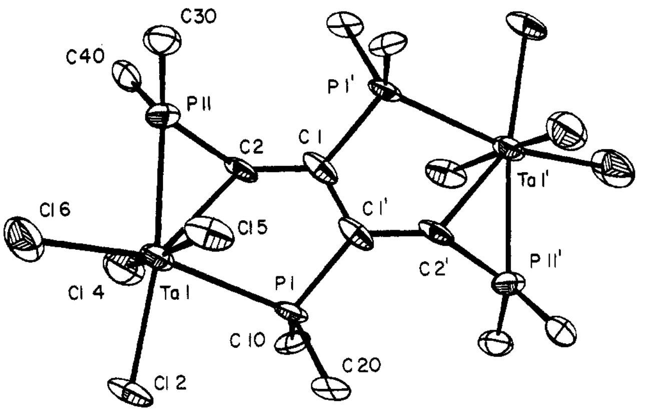

Figure 1. The molecular structure of 1. There is a crystallographic inversion center at the midpoint of the C(1)=C(1)' bond. Atoms are represented by 40% thermal ellipsoids. Phenyl rings have been omitted for clarity.

Solution and Refinement of Structures.[11] Crystals of 1 and 2 were found to be monoclinic. The cell volume was consistent in each case with $Z = 2$. In each set of data there were systematic absences for $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$ that uniquely determined the space group as $P2_1/n$.

Metal atom positions for 1 were obtained by direct methods using the MULTAN program; for 2 they were determined from a three-dimensional Patterson synthesis. Subsequent difference Fourier maps followed by least-squares refinement in each case located all non-hydrogen atoms. Both structures were refined by the full matrix least-squares method. Anisotropic thermal parameters were assigned to all non-hydrogen atoms in each structure, and hydrogen atoms were omitted. The final difference Fourier maps of 1 and 2 showed no peaks of structural significance.

Final positional parameters are listed in Tables II and III, respectively. Listing of structure factors and tables of anisotropic thermal parameters for 1 and 2 are available as supplementary material.

Results

$Cl_4Ta{-}CH(PPh_2)C(PPh_2){=}C(PPh_2)CH(PPh_2){-}TaCl_4{\cdot}2(CH_2Cl_2)$, 1. The dichloromethane molecules reside on general positions and, though not disordered, have rather large amplitudes of thermal vibration. Molecules of 1, illustrated in Figure 1, are located on positions of crystallographic inversion symmetry. The center of symmetry is at the midpoint of the ethylene unit, i.e., between C(1) and C(1)'. The ethylene unit has arisen by dimerization of $Ph_2PC{\equiv}CPPh_2$ to generate a four-carbon chain with a Ph_2P group on each carbon atom: $(Ph_2P)CHC(Ph_2P){=}C(Ph_2P)CH(Ph_2P)$. This then serves as a bridging ligand. Each Ta atom is seven-coordinate, with P(1), C(2), P(11), Cl(6), and Cl(2) approximately coplanar and Cl(4) and Cl(5) above and below this plane. Each Ta atom is part of a three-membered-metallacycle, Ta—C—P, and

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[8] Reactions containing excess dppa up to 4 equiv yielded no other products.

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Table II. Table of Positional Parameters and Their Estimated Standard Deviations for Structure 1[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ta(1)	0.68816 (6)	0.18305 (7)	0.51465 (5)	C(21)	0.718 (2)	−0.085 (1)	0.6471 (9)
Cl(2)	0.8833 (3)	0.1485 (4)	0.5499 (3)	C(22)	0.776 (2)	−0.140 (2)	0.7061 (12)
Cl(4)	0.6285 (4)	0.1504 (4)	0.6343 (3)	C(23)	0.882 (2)	−0.181 (2)	0.6897 (12)
Cl(5)	0.7239 (4)	0.2060 (4)	0.3902 (3)	C(24)	0.928 (2)	−0.162 (1)	0.6209 (13)
Cl(6)	0.7390 (5)	0.3420 (4)	0.5545 (4)	C(25)	0.870 (1)	−0.110 (2)	0.5616 (12)
Cl(60)	0.4577 (9)	0.0914 (8)	0.9215 (6)	C(30)	0.449 (1)	0.307 (1)	0.3944 (10)
Cl(61)	0.5451 (10)	−0.0240 (11)	0.8069 (6)	C(31)	0.406 (2)	0.403 (2)	0.4048 (14)
P(1)	0.6842 (4)	−0.0026 (4)	0.5044 (3)	C(32)	0.370 (2)	0.452 (2)	0.3360 (12)
P(11)	0.4902 (4)	0.2483 (4)	0.4814 (3)	C(33)	0.373 (2)	0.411 (2)	0.2658 (14)
C(1)	0.535 (1)	−0.038 (1)	0.5085 (10)	C(34)	0.418 (2)	0.319 (2)	0.2578 (12)
C(2)	0.514 (1)	0.127 (1)	0.4647 (10)	C(35)	0.457 (2)	0.267 (2)	0.3252 (13)
C(10)	0.728 (1)	−0.039 (1)	0.4124 (11)	C(40)	0.400 (1)	0.289 (1)	0.5527 (11)
C(11)	0.653 (2)	−0.081 (2)	0.3597 (10)	C(41)	0.280 (1)	0.281 (1)	0.5349 (12)
C(12)	0.690 (2)	−0.107 (2)	0.2893 (11)	C(42)	0.207 (2)	0.315 (2)	0.5871 (13)
C(13)	0.801 (2)	−0.090 (2)	0.2707 (12)	C(43)	0.249 (2)	0.351 (2)	0.6602 (18)
C(14)	0.873 (2)	−0.042 (2)	0.3239 (13)	C(44)	0.369 (2)	0.363 (2)	0.6709 (14)
C(15)	0.839 (1)	−0.014 (1)	0.3957 (11)	C(45)	0.444 (2)	0.330 (2)	0.6186 (11)
C(20)	0.764 (1)	−0.074 (1)	0.5757 (9)	C(60)	0.574 (3)	0.048 (4)	0.8915 (18)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table III. Table of Positional Parameters and Their Estimated Standard Deviations for Structure 2[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ta(1)	0.01856 (4)	0.2194 (0)	0.12460 (4)	C(21)	0.0187 (11)	0.145 (1)	−0.1820 (10)
Cl(1)	−0.0389 (3)	0.3705 (3)	0.0421 (3)	C(22)	−0.0037 (14)	0.199 (2)	−0.2574 (12)
Cl(2)	0.0096 (3)	0.3154 (3)	0.2575 (3)	C(23)	0.0077 (13)	0.311 (2)	−0.2639 (12)
Cl(3)	0.1246 (3)	0.0957 (3)	0.1997 (2)	C(24)	0.0480 (12)	0.370 (2)	−0.1934 (12)
P(1)	0.0903 (2)	0.1370 (3)	−0.0090 (2)	C(25)	0.0724 (11)	0.318 (1)	−0.1178 (10)
S(1)	0.1726 (3)	0.3466 (4)	0.1205 (3)	C(30)	−0.2368 (9)	0.203 (1)	0.0579 (9)
P(2)	−0.1376 (3)	0.1500 (3)	0.1255 (2)	C(31)	−0.2270 (12)	0.233 (1)	−0.0246 (9)
C(1)	−0.0566 (9)	0.092 (1)	0.0752 (8)	C(32)	−0.3022 (13)	0.283 (2)	−0.0760 (12)
C(2)	−0.0378 (9)	−0.001 (1)	0.0217 (8)	C(33)	−0.3839 (12)	0.299 (2)	−0.0410 (13)
C(5)	0.1521 (13)	0.483 (2)	0.1574 (13)	C(34)	−0.3921 (11)	0.270 (2)	0.0404 (13)
C(6)	0.2626 (15)	0.309 (2)	0.1964 (19)	C(35)	−0.3168 (11)	0.222 (2)	0.0940 (12)
C(10)	0.2136 (9)	0.119 (1)	−0.0017 (9)	C(40)	−0.1766 (10)	0.078 (1)	0.2139 (10)
C(11)	0.2541 (11)	0.036 (1)	0.0483 (10)	C(41)	−0.2498 (12)	0.003 (1)	0.1997 (12)
C(12)	0.3514 (11)	0.022 (1)	0.0561 (11)	C(42)	−0.2791 (14)	−0.047 (2)	0.2711 (15)
C(13)	0.4008 (11)	0.094 (1)	0.0181 (11)	C(43)	−0.2380 (15)	−0.027 (1)	0.3529 (12)
C(14)	0.3634 (11)	0.177 (2)	−0.0320 (12)	C(44)	−0.1628 (15)	0.041 (2)	0.3643 (12)
C(15)	0.2667 (12)	0.188 (1)	−0.0417 (12)	C(45)	−0.1338 (14)	0.097 (2)	0.2977 (10)
C(20)	0.0577 (9)	0.205 (1)	−0.1117 (9)				

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Table IV. Selected Bond Lengths (Å) in Compound 1[a]

Ta(1)-Cl(2)	2.406 (4)	P(1)-C(1)	1.846 (13)
-Cl(4)	2.327 (4)	P(11)-C(2)	1.76 (2)
-Cl(5)	2.294 (5)	C(1)-C(1)′	1.37 (3)
-Cl(6)	2.419 (5)	C(1)-C(2)	1.49 (2)
-P(1)	2.632 (4)	P(1)-C(10)	1.82 (2)
-P(11)	2.555 (5)	P(1)-C(20)	1.821 (14)
-C(2)	2.326 (13)	P(11)-C(30)	1.78 (2)
		P(11)-C(40)	1.81 (2)

[a] Esds in parentheses.

also a five-membered metallacycle, Ta—C—C═C—P. The six atoms constituting the tetrasubstituted olefin, viz., C(1) and C(1)′, which are connected by a double bond (1.37 (3) Å), and the atoms P(1), P(1)′, C(2), and C(2)′ are essentially coplanar, as shown in Table VI. The important bond distances and angles are listed in Tables IV and V, respectively. Results for the phenyl rings and the CH_2Cl_2 molecule are given in supplementary tables, Tables IVS and VS.

$(\mathrm{Me_2S})\mathrm{Cl_3Ta{=}C(PPh_2)C(PPh_2){=}C(PPh_2)C(PPh_2)}$-$\mathrm{{=}TaCl_3(SMe_2)}$, 2. Each molecule of 2 resides on a crystallographic inversion center located between C(2) and C(2)′. The molecule is shown in Figure 2. The overall structure is quite similar to that of 1 except for the absence of hydrogen atoms on atoms C(1) and C(1)′ and the closer approach of these atoms to their respective tantalum atoms. Quite obviously it also differs qualitatively in having one $(CH_3)_2S$ molecule instead of a terminal Cl atom on each tantalum atom. The important bond lengths and bond angles are given in Tables VII and VIII, respectively, while those in the phenyl groups are given in supplementary tables, Tables VIIS and VIIIS.

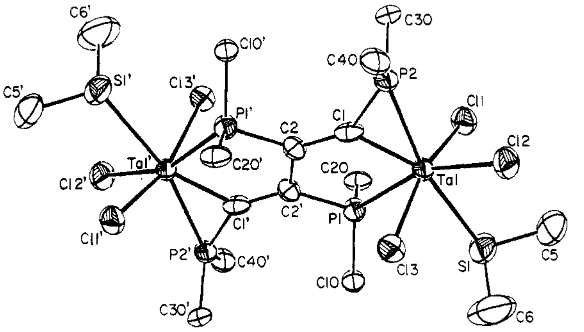


Figure 2. The molecular structure of 2. There is a rigorous inversion center between C(2) and C(2)′. Atoms are represented by 40% thermal ellipsoids. Phenyl rings have been omitted for clarity.

Discussion

The most remarkable features of these compounds are, first, the dimerization of the $Ph_2PC{\equiv}CPPh_2$ molecules

Table V. Bond Angles (Deg) in Compound 1[a]

Cl(2)-Ta(1)-Cl(4)	94.4 (2)	C(2)-P(11)-C(30)	110.2 (9)	P(1)-Ta(1)-P(11)	109.4 (2)		
-Cl(5)	91.9 (2)	-C(40)	122.7 (8)	-C(2)	67.9 (4)	P(11)-C(30)-C(31)	114 (1)
-Cl(6)	84.2 (2)	C(30)-P(11)-C(40)	108.3 (8)	P(11)-Ta(1)-C(2)	42.1 (4)	-C(35)	123 (2)
-P(1)	80.0 (2)	P(1)-C(10)-C(11)	121 (1)	P(1)-C(1)-C(2)	130 (1)		
-P(11)	170.5 (2)	-C(15)	116 (1)	P(1)'-C(1)-C(1)'	111 (2)		
-C(2)	147.3 (4)			C(11)'-C(1)-C(2)	119 (2)		
Cl(4)-Ta(1)-Cl(5)	172.1 (1)			Ta(1)-C(2)-P(11)	75.9 (5)		
-Cl(6)	90.3 (2)			Ta(1)-C(2)-C(1)	122 (1)		
-P(1)	81.9 (2)			P(11)-C(2)-C(1)	134 (1)		
-P(11)	86.7 (2)			Ta(1)-P(1)-C(1)	106.1 (5)	P(11)-C(40)-C(41)	117 (1)
-C(2)	87.5 (4)			C(1)-P(1)-C(10)	107.3 (7)	-C(45)	122 (1)
Cl(5)-Ta(1)-Cl(6)	95.0 (2)	P(1)-C(20)-C(21)	118 (1)	-C(20)	106.0 (7)		
-P(1)	94.5 (2)	-C(25)	120 (1)	C(10)-P(1)-C(20)	107.1 (7)		
-P(11)	87.8 (2)			Ta(1)-P(11)-C(2)	62.0 (5)		
-C(2)	84.6 (4)						
Cl(6)-Ta(1)-P(1)	161.8 (2)						
-P(11)	86.4 (2)						
-C(2)	128.5 (4)						

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VI. Planes of Atoms Adjacent to the Ethylene Unit for Structures 1 and 2

	atom	dist from plane, Å
A. structure 1	P(1)	-0.007
	C(1)	0.026
	C(2)	-0.014
	C(1)'	0.031
	P(1)'	-0.005
	C(2)'	-0.030
B. structure 2	P(1)	-0.008
	C(2)	0.029
	C(1)	-0.023
	C(2)'	0.029
	P(1)'	-0.021
	C(1)'	-0.006

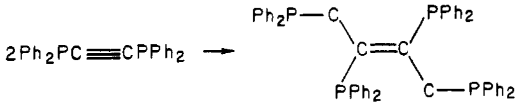
Table VII. Bond Distances (Å) for Compound 2[a]

Ta(1)-Cl(1)	2.362 (6)	S(1)-C(5)	1.806 (15)
-Cl(2)	2.430 (3)	-C(6)	1.742 (15)
-Cl(3)	2.391 (3)	P(2)-C(1)	1.683 (11)
-P(1)	2.685 (3)	-C(30)	1.828 (9)
-S(1)	2.775 (3)	P(2)-C(40)	1.809 (12)
-P(2)	2.471 (3)	C(1)-C(2)	1.464 (15)
-C(1)	2.018 (10)	C(2)-C(2)'	1.39 (2)
P(1)-C(2)	1.842 (11)		
-C(10)	1.835 (10)		
-C(20)	1.836 (10)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

and, second, the formation of three-membered Ta—C—P and Ta═C—P rings, fused to five-membered Ta—C—C═C—P and Ta═C—C═C—P rings.

The dimerization, which may be represented formally as



is alone sufficient to generate the bridging ligand found in compound 2, but for 1 it is also necessary to add a hydrogen atom to each of the terminal carbon atoms. At this time we have no clues as to how this dimerization proceeds nor is the source of the hydrogen atoms known.

Let us turn, then, to the unusual three-membered metallocyclic rings. These are shown in Figure 3. In the case of compound 1 it is reasonable to regard the Ta–C bond as a single bond. By so doing, the tantalum atom is given an oxidation number of V. While we did not see any certain indication of electron density corresponding to a hydrogen atom on the carbon atom C(2), the sum of the three bond angles that are seen is only 329°, which is within experimental error the value expected for three of a tetrahedral set of four bonds. Moreover, the Ta–C bond

Table VIII. Bond Angles (Deg) for Compound 2[a]

Cl(1)-Ta(1)-Cl(2)	92.6 (1)	Ta(1)-P(2)-C(40)	124.4 (4)
-Cl(3)	160.2 (1)	C(1)-P(2)-C(30)	116.3 (5)
-P(1)	90.5 (1)	-C(40)	118.8 (5)
-S(1)	77.8 (1)	C(30)-P(2)-C(40)	108.1 (5)
-P(2)	90.0 (1)	Ta(1)-C(1)-P(2)	83.3 (5)
-C(1)	104.3 (3)	-C(2)	133.4 (7)
Cl(2)-Ta(1)-Cl(3)	88.9 (1)	P(2)-C(1)-C(2)	143.3 (8)
-P(1)	159.4 (1)	P(1)-C(2)-C(1)	131.0 (7)
-S(1)	83.4 (1)	-C(2)'	108 (1)
-P(2)	90.3 (1)	C(1)-C(2)-C(2)'	120 (1)
-C(1)	128.4 (3)	P(1)-C(10)-C(11)	119.0 (8)
Cl(3)-Ta(1)-P(1)	81.52 (9)	-C(15)	121.6 (9)
-S(1)	82.8 (1)	P(1)-C(20)-C(21)	120.2 (9)
-P(2)	109.8 (1)	-C(25)	118.7 (8)
-C(1)	90.0 (3)		
P(1)-Ta(1)-S(1)	77.37 (9)	P(2)-C(30)-C(31)	118.3 (8)
		-C(35)	118.8 (9)
-P(2)	110.01 (8)	P(2)-C(40)-C(41)	120.4 (9)
		-C(45)	120.0 (9)
-C(1)	70.0 (3)		
S(1)-Ta(1)-P(2)	165.9 (1)		
-C(1)	147.3 (3)		
P(2)-Ta(1)-C(1)	42.5 (3)		
Ta(1)-P(1)-C(2)'	102.8 (3)		
-C(10)	119.3 (3)		
-C(20)	116.3 (4)		
C(2)-P(1)-C(10)	107.5 (5)		
-C(20)	104.7 (5)		
C(10)-P(1)-C(20)	105.0 (5)		
Ta(1)-S(1)-C(5)	109.7 (5)		
-C(6)	113.4 (7)		
C(5)-S(1)-C(6)	99.6 (9)		
Ta(1)-P(2)-C(1)	54.2 (3)		
-C(30)	124.2 (4)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

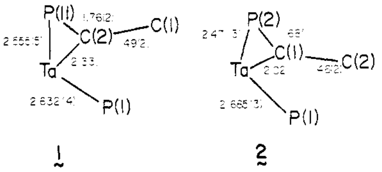


Figure 3. Drawings of the two kinds of three-membered metallocycles found in 1 and 2 with the bond lengths.

Table IX. Comparison of Dimensions in M—CR_2—PR_2' Rings and the Ta=CR—PR_2' Rings

compd	bond length, Å M—P	M—C or M=C	P—C	ref
(1) $(X)[P(C_3H_7)_3]Pt\text{-}CH(C_2H_5)P(C_3H_7)_2$[a]	2.202 (5)	2.17 (2)	1.76 (2)	12
(2) $(X)[P(C_2H_5)_3]Pt\text{-}CH(CH_3)P(C_2H_5)_2$	2.189 (7)	2.19 (2)	1.73 (3)	13
(3) $(X)[P(CH_2Ph)_3]Pt\text{-}CHPh\text{-}P(CH_2Ph)_2$[a]	2.235 (4)	2.15 (1)	1.76 (2)	14
(4) $Cl_2(PMe_2Ph)_2Ir\text{-}CH_2PMePh$	2.276 (6)	2.19 (2)	1.90 (3)	15
(5) compound **1**	2.555 (5)	2.33 (1)	1.76 (2)	
(6) compound **2**	2.471 (3)	2.02 (1)	1.68 (1)	
(7) $(PPh_3)_2Pt{=}C(CH_3)_3P$	2.320 (6)	1.97 (2)	1.67 (2)	16

[a] X = a 2-substituted 1-σ-$B_{10}C_2H_{10}$ unit.

length, 2.326 (13) Å, is comparable to the lengths of other Ta–C single bonds. The Ta-P bond in the small ring is slightly shorter than the other Ta–P bond.

While the type of three-membered M–C–P ring found in **1** is rare, there have been a few previously documented examples, viz., (1)–(4) listed in Table IX. All of these involve the late transition metals, specifically Pt and Ir, and our compound **1** appears to be the first to exhibit this feature for an early transition metal. There are consistent differences in the dimensions of the two types. The P–C distances are comparable (although that in (4) seems strangely out of line), but for Pt and Ir the M–P distances run 0.18–0.27 Å shorter and the M–C distances 0.13–0.18 Å shorter than for the corresponding bonds to tantalum.

It may be noted also that several amino analogues of this type of three-membered ring, viz., M—C—N, have been structurally characterized.[17-20]

The three-membered ring in **2** is entirely unprecedented, as far as we know. Here, we are evidently dealing with a Ta═C double bond. To compensate for this and maintain charge balance, one of the Cl^- ligands of **1** is replaced by the neutral ligand $(CH_3)_2S$, which was introduced into the reaction as part of the starting material, $Ta_2Cl_6(Me_2S)_3$. The oxidation state of the tantalum is again V. The sum of the three bond angles about the carbon atom bound to the tantalum atom is now equal to 360°. The Ta═C distance, 2.02 Å, is similar to previously observed Ta═C distances.[21] It is 0.31 Å shorter than the Ta–C distance in **1**. The P–C distance is also shorter, by 0.08 (2) Å, in **2** than in **1**; some shortening, perhaps 0.04 Å, could be expected because of the change of hybridization from sp^3 to sp^2. There is also a significant decrease, 0.08 (1) Å, in the ring Ta–P bond length.

Since a ring of the type found in **2** is without any exact precedent, the closest comparison we could find was with compound (7) in Table IX. However, since there is a considerable difference between Ta and Pt as well as in the nature of the C–P portion of the ring, this comparison is of uncertain value.

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Registry No. 1, 82808-33-1; 2, 82808-34-2; $Ta_2Cl_6(SMe_2)_3$, 77827-59-9; dppa, 5112-95-8.

Supplementary Material Available: Tables of observed and calculated structure factors, thermal vibration parameters, and bond distances and angles within the phenyl groups (31 pages). Ordering information is given on any current masthead page.

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