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Review

TANTALUM ORGANOMETALLIC COMPOUNDS: ANALYSIS AND CLASSIFICATION OF CRYSTALLOGRAPHIC DATA

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ABBREVIATIONS

bipy	2,2'-bipyridyl
$CCMe_3$	neopentylidyne
$CHCMe_3$	neopentylidene
CHPh	phenylmethylidene
CH_2Ph	phenylmethyl
CH_2PMe_2	dimethylmethylidenephosphine
CH_2SiMe_3	(trimethylsilyl)methyl

C_3H_7	n-propyl
C_4H_6	butadiene
C_4H_8	buta-1,4-diyl
C_5Me_4Et	ethyltetramethylcyclopentadienyl
C_5Me_5	pentamethylcyclopentadienyl
C_6H_4	benzyne
C_7H_{12}	bicyclo[3,3,0]octane
C_8H_8	cyclooctatetraene
cp	cyclopentadienyl
dca	N,N-dicyclohexylacetamidinate
dme	1,2-dimethoxyethane
dmp	N,N'-dimethylpiperazine
dmpe	1,2-bis(dimethylphosphino)ethane
dppbd	1,2,3,4,-bis(diphenylphosphino)-2-butene-1,4-diyl
dppbde	1,2,3,4-bis(diphenylphosphino)-2-butene-1,4-diylidene
dtba	di-tert-butylacetylene
$H_2B(3,5\text{-}Me_2pz)_2$	dihydrobis(3,5-dimethyl-1-pyrazolyl)borate
hx	hexagonal
i-prNC	iso-propylnitrile
L(ax)	axial ligand
Lc	unique capped ligand
Lcf	capped face ligand
Le	capped edged ligand
L(eq)	equatorial ligand
Lqf	capped quadrilateral face ligand
Luf	uncapped face ligand
m	monoclinic
Me	methyl
mes	mesityl
$2,3\text{-}Me_2C_4H_4$	2,3-dimethylbutadiene
Me_2N	dimethylamide
Me_3CCH_2	neopentyl
nph	naphthalene
Obp	2,6-di-tert-butylphenotide
omp	2-oxo-4-methyl-penten(3)
ONOMeNO	N-methyl-N-nitrosohydroxylaminate
or	orthorhombic
O_2CNMe_2	N,N-dimethylcarbamate
Ph	phenyl
Ph_2C_2	diphenylacetylene

PPN	bis(triphenylphosphine)nitrogen(1+)
py	pyridine
pyH	pyridinium
t-Bu	tert-butyl
thf	tetrahydrofuran
tht	tetrahydrothiophene
tr	triclinic

1. INTRODUCTION

Systematic studies in the field of stereoselectivity in organometallic compounds have expanded rapidly in the last decade, partly because many of these compounds are effective catalysts, and because they can themselves be precursors for a wide range of derivatives. An organometallic compound is defined as a compound having at least one carbon-bonded organic ligand. Steric and stereochemical aspects of metallo-organic compounds containing a metal-oxygen or nitrogen bond have been discussed previously (ref.1). Of the more than fifty structural studies of tantalum organometallic compounds only a few have been discussed in specific reviews since 1982 (ref.2). The aim of this review is to present a summary and correlation of all the known tantalum organometallic structural information to date. A similar review of tantalum coordination compounds has also been prepared (ref.3). Comparisons are presented both with this data and with the corresponding data for niobium (ref.4).

The material included in this review was obtained from reports published in primary journals to the end of 1984, or up to volume 101 of Chemical Abstracts. The systems have been subdivided into non-aromatic and aromatic derivatives, representing a major difference from niobium organometallic chemistry, for which there were very few of the former.

2. TANTALUM ORGANOMETALLICS WITH A NON-AROMATIC CARBON ELECTRON DONOR LIGAND

A. Compounds with Coordination Number Four

$[Ta(CCMe_3)(CH_2CCME_3)].Li(dmp)$ (ref.5) and $Ta(Obp)_2(CHSiMe_3)(CH_2SiMe_3)$ (ref.6) are the only examples in which the Ta(V) atom has a coordination number four (Table 1). In the former, the arrangement about the tantalum is nearly tetrahedral, built up of four carbon atoms exhibiting three distinct bond lengths to tantalum, 176(2)pm, 218(2)pm and 226(2)pm (2x) respectively (Figure 1). The shortest of these, Ta-C ($CCMe_3$) has a Ta-C-C angle of 165(1)° which implies triple bond character in the metal-carbon bond. The tetrahedral geometry is the only one found in the chemistry of four coordinate tantalum (ref.3).

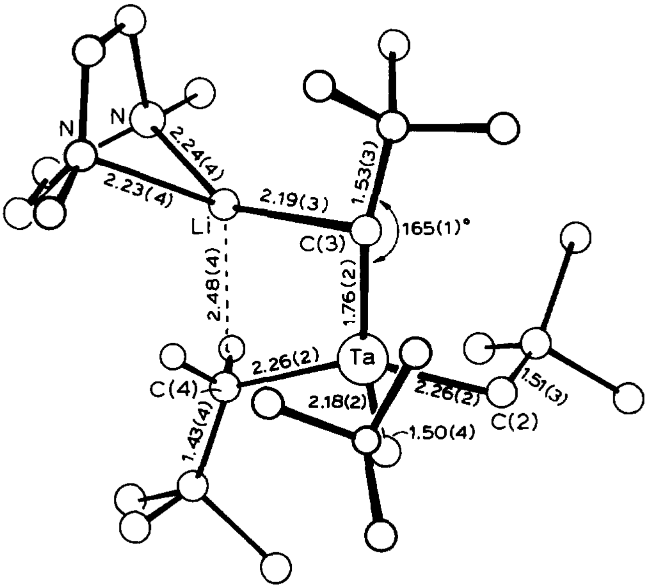

Figure 1. The Crystal Structure of $[(Me_3CCH_2)_3Ta(CCMe_3)].Li(dmp)$. Reproduced with permission from J. Am. Chem. Soc., (ref.5).

B. Compounds with Coordination Number Five

Crystal and structural data for tantalum compounds with a coordination number five are given in Table 1. The crystal structure of $\{[Ta(CHCMe_3)(CH_2CHMe_3)(PMe_3)_2](\mu\text{-}N_2)\}$ (ref.10) is shown as a representative example in Figure 2. The green crystals contain two tantalum(V) atoms in trigonal bipyramidal environments. Each tantalum atom has two axial PMe_3 ligands (Ta-P = 259.0(3,11)pm), and the equatorial sites are occupied by neopentylidene (Ta-C = 193.5(9,3)pm), neopentyl (Ta-C = 229.2(10,7)pm), and the bridging nitrogen ligand (Ta-N = 184.0(8,3)pm). The first number in the parenthesis is an average of the e.s.d. and the second number is a maximum deviation from the average number.

A trigonal bipyramidal coordination around a tantalum atom has also been found in $Ta(CHCMe_3)_2(mes)(PMe_3)_2$ (ref.8), and $Ta(NMe_2)_3(p\text{-tolyl})Br$ (ref.7). By contrast, the central TaN_4C skeleton in $Ta(NMe_2)_4(t\text{-Bu})$ (ref.7) corresponds closely to an idealized square-based pyramid, with the tantalum atom 50(2)pm above the plane of the four nitrogen atoms.

C. Compounds with Coordination Number Six

An almost exactly octahedral coordination is found around the tantalum atom in $[Ta(CO)_6]^-$ (ref.11), and the Ta-C distance of 208.3(6)pm (6x) is

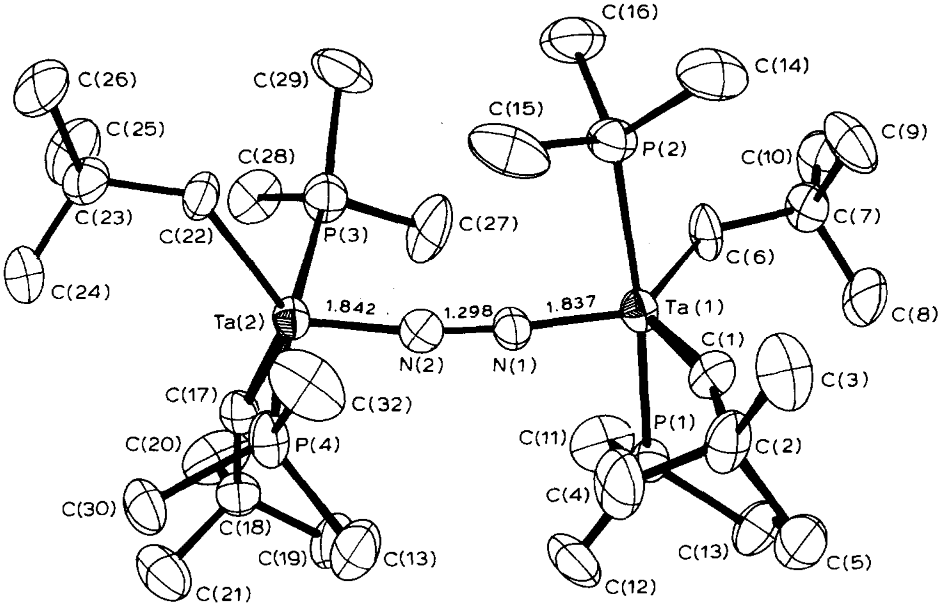

Figure 2. The Crystal Structure of $[(Ta(CHCMe_3)(CH_2CHMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$. Reproduced with permission from Inorg. Chem. (ref.10).

slightly shorter than that found in the niobium analogue (Nb–C = 208.9(5)pm (6x).

In the two dimeric structures $[Ta(CHCMe_3)(PMe_3)C\ell_3]_2$ (ref.13) and $[C\ell_2(dme)Ta(\mu\text{-}CCMe_3)]_2.Zn(\mu\text{-}C\ell)_2]$ (ref.14), a highly distorted octahedral geometry is found about each tantalum atom without any direct Ta-Ta interaction having been found (Table 1). The two $TaC\ell_2PC$ moities in the former are bridged by two chlorine atoms with a Ta-Ta distance of 406.1(2)pm. The bridge system is very asymmetric with two distinct Ta-Cℓ (bridge) distances of 244.8(2)pm and 281.5(2)pm. The longer of the two is situated trans to the neopentylidene ligand (Ta-C = 189.8(2)pm) and clearly demonstrates a trans influence. In the latter compound, the true central atom is zinc, and the two tantalum atoms are part of the ligand system around the zinc (ref.14). Two tantalum fragments, $TaO_2C\ell_2$, are bridged by chlorine and $CCMe_3$ ligands to the central zinc atom (Table 1).

Inspection of the data in Table 1 reveals that the Ta-L(ax) bond distances are longer than those of the Ta-L(eq) bonds. In general, the

TABLE 1. STRUCTURAL DATA FOR TANTALUM ORGANOMETALLIC COMPOUNDS WITH COORDINATION NUMBERS FOUR, FIVE AND SIX[a]

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	CHROMOPHORE	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	L_{eq}-M-L_{eq}[°] L_{eq}-M-L_{ax}[°] L_{ax}-M-L_{ax}[°]	REF.
$\{(Me_3CCH_2)_3Ta^V(CCMe_3)\}$.	or	$P2_12_12_1$	4	TaC_4	1719.6(6)		Me_3CC^b 176(2)	109.5(9,8.9)	5
.Li(dmp)					1751.2(4)		C 218(2)		
					1050.3(3)		C 226(2)(2x)		
$Ta^V(Obp)_2(CHSiMe_3)$.		$P2_1/c$	4	TaC_2O_2	1103.7(4)		C 188.8(29)	110.7(10,16.9)	6
.$(CH_2SiMe_3)^c$					2540.2(15)	126.69(2)	C 216.5(24)		
					1711.3(7)		O 184.9(16,6)		
$Ta^V(NMe_2)_4$(t-Bu)		$P2_1cn$	4	TaN_4C	1428.4(3)		N 203(2,7)	91.6(5,2.6);143.4(5,29.8)	7
					826.1(2)		C^d 224(2)	86.6(7,1.0);119.2(7,2)	
					1421.4(4)				
$Ta^V(CHCMe_3)_2$(mes).	m	C2/c	8	TaC_3P_2	1796.6(3)		(mes)C 230.3(6)	120.00(28,12.35)	8
.$(PMe_3)_2$					1821.7(4)	97.99(2)	C 194.4(7,12)	90.37(21,7.42)	
					1853.1(3)		P^d 256.7(2,2)	166.34(7)	
$Ta^V(Obp)_2(CH_3)_3{}^c$		C_2	4	TaC_3O_2	1979.7(4)		C 213.7(10,1)	90.6(3,8.9)	9
					658.7(7)	96.11(1)	C 224.8(10)	120.0(4,15.9)	
					2325.3(5)		O 193.7(6,8)	164.1(2)	

TABLE 1. Continued 2

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	CHROMOPHORE	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	L_{eq}-M-L_{eq}[°] L_{eq}-M-L_{ax}[°] L_{ax}-M-L_{ax}[°]	REF.
$Ta^V(Dbp)(Ph)_2(OC_6H_3BuC.$		$P\bar{1}$	2	TaC_3O_2	1543.8(6)	73.70(2)	C 215.2(6,7)	90.2(2,8.7)	9
$.Me_2CH_2)^c$					1232.9(4)	67.38(2)	O 191.7(4,8)	119.7(2,8.8)	
					1063.9(3)	69.07(2)		165.4(2)	
$Ta^V(NMe_2)_3$(p-tolyl)Br^c		$P2_1/n$	4	TaN_3BrC	1138.7(3)		C 218(2)	119.2(7,2)	7
					1944.0(8)	102.84(1)	N 194(2,1)	89.9(5,4.3)	
					779.6(2)		N^d 197(2)	173.1(5)	
							Br^d 260.6(3)		
$\{[Ta^V(CHCMe_3)(CH_2CMe_3).$	tr	$P\bar{1}$	2	TaC_2P_2N	971.2(2)	67.278(14)	C 193.5(9,3)	120.00(35,7.32)	10
$.(PMe_3)_2]_2(\mu\text{-}N_2)\}$					1484.5(3)	84.812(15)	C 229.2(10,7)	90.03(26,4.53)	
					1844.8(4)	71.743(12)	μ-N 184.0(8,3)	171.86(9,6)	
							P^d 259.0(3,11)		
$[Ta^{-1}(CO)_6]$PPN	rh	$R\bar{3}$	1	TaC_6	981.4(4)	92.02(8)	C 208.3(6)(6x)	89.1(2)	11

TABLE 1. Continued 3

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	CHROMOPHORE	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	L_{eq}-M-L_{eq}[°] L_{eq}-M-L_{ax}[°] L_{ax}-M-L_{ax}[°]	REF.
$[Ta^V(CHCMe_3)(PMe_3)$.	m	$P2_1/n$	2	$TaCl_4PC$	1092.0(6)		C 189.8(2)	89.8(2)	12,13
$.Cl_3]_2$[e]					1282.7(7)	91.05(2)	P 260.2(2)	99.57(7,4.44)	
					1055.3(6)		Cl[d] 235.2(2,18)		
							μ-Cl 244.8(2)		
							281.5(2)		
$[\{Cl_2(dme)Ta^V(\mu\text{-}CCMe_3)\}_2$. or		Pbca	8	$TaCl_3O_2C$	951.9(2)		O 243.7(13,25)	not given	14
$.Zn(\mu\text{-}Cl)_2]$					1402.6(3)		Cl 239.0(5,0)		
					4464.5(9)		Cl[d] 237.0(4,5)		
							μ-Cl 245.2(4,2)		
							μ-C 183(2,4)		

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value.
b. The chemical identity of the coordinated atom or ligand.
c. At 111K.
d. The atom (ligand) coordinated in an axial position.
e. At 110 K. Ta.....Ta distance = 406.1(2)pm.

Ta-L distances are lengthened as the coordination number of the tantalum increases. The Ta-C bond distances are lengthened in the order $CCMe_3$ < $CHCMe_3$ < CH_2CMe_3, and this reflects both electronic and steric factors.

Except for the hexacarbonyl anion, where the tantalum has an oxidation number of -1, the oxidation number +5 predominates in Table 1.

D. Compounds with Coordination Number Seven

Structural data are summarised in Table 2 for these derivatives. From a structural point of view, the mononuclear derivatives in Table 2 can be divided into three groups. In $Ta(O_2CNMe_2)_4(CH_2SiMe_3)$ (ref.7), $Ta(CHPMe_2)(CH_2PMe_2)(PMe_3)_3$ (ref.15), $TaC\ell_2(dca)(CH_3)$ (ref.16), and $TaC\ell_2(ONMeNO)_2(CH_3)$ (ref.17), the tantalum atoms are surrounded by seven donor atoms in the form of a distorted pentagonal bipyramid.

The crystal structure of $Ta(CHPMe_2)(CH_2PMe_2)(PMe_3)_3$ is shown in Figure 3 as a representative example. The tantalum is surrounded by five ligands, three unidentate and two bidentate. The equatorial plane contains the two bidentates, $CHPMe_2$ and CH_2PMe_2, each of them bound by a carbon atom (Ta-C = 201.5(4)pm and 232.4(4)pm) and by a phosphorus atom (Ta-P = 251.6(1)pm and 243.5(1)pm). The fifth equatorial site is occupied by a PMe_3 ligand (Ta-P = 259.6(1)pm).

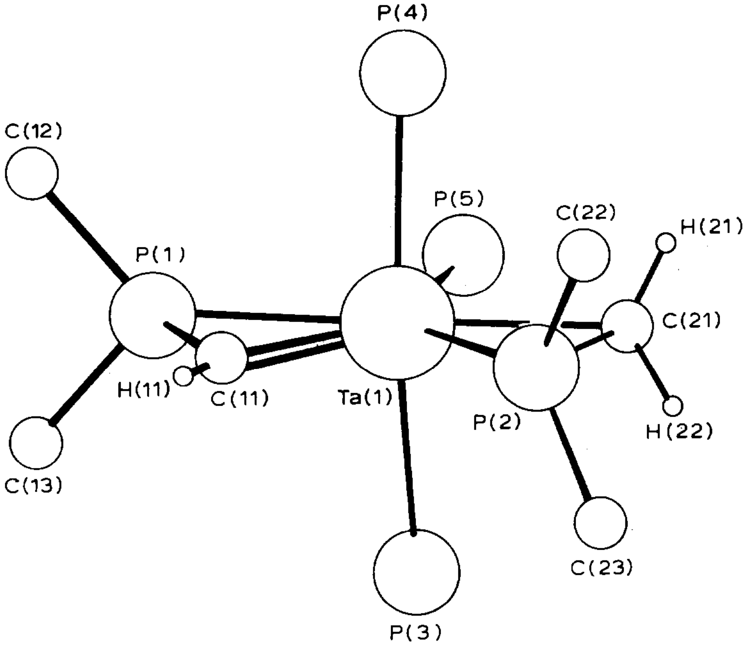

Figure 3. The Crystal Structure of $Ta(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)(\eta^2\text{-}CHPMe_2)$. Reproduced with permission from J. Chem. Soc., Chem. Commun. (ref.15).

In this type of structure the axial sites are less sterically crowded than the equatorial sites, and therefore the M-L (axial) bond distances are, in general, shorter than the M-L (equatorial) ones. The data in Table 2 shows that only $Ta(O_2CNMe_2)_4(CH_2SiMe_3)$ and $TaC\ell_2(dca)(CH_3)$ follow this trend, while in the other two examples (refs.15 and 17) the mean Ta-L(ax) bond lengths are longer than the mean Ta-L(eq) bond lengths. This suggests that the variation of the Ta-L bond distances in these complexes is not a simple function of steric requirements within the polyhedra.

In another three examples (Table 2), $TaH(CO)_2(dmpe)_2$ (ref.18), $Ta(CH_3)_3C\ell[HB(3,5\text{-}Me_2pr)_3]$ (ref.19), and $Ta(CH_3)_3C\ell[H_2B(3,5\text{-}Me_2pz)_2]$ (ref.20), the polyhedra around the tantalum has a capped octahedral geometry. The crystal structure of $Ta(CH_3)_3C\ell[HB(3,5\text{-}Me_2pz)_3]$ (ref.19) is nearly regular octahedron as shown in Figure 4, with the capped face (Lcf) formed by the C(5), C(6) and C(4) atoms, and the uncapped face (Luf) formed by the three nitrogen atoms. The C(7) atom occupies the unique capping position (Lc). In all three cases (refs. 18,19 and 20), the mean

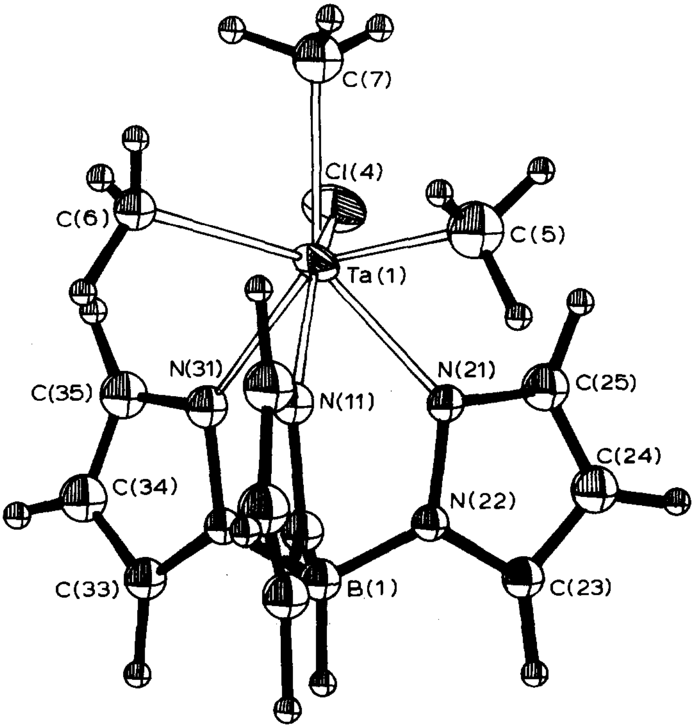

Figure 4. The Crystal Structure of $Ta(CH_3)_3C\ell[HB(3,5\text{-}Me_2pz)_3]$.
Reproduced with permission from Inorg. Chem., (ref.19).

TABLE 2 STRUCTURAL DATA FOR TANTALUM ORGANOMETALLIC COMPOUNDS WITH COORDINATION NUMBER SEVEN AND EIGHT[a]

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	Chromophore	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	$M\text{-}L_c$[b] (pm)	L-M-L [°]
$Ta^V(O_2CNMe_2)_4(CH_2SiMe_3)$		$P\bar{1}$	2	TaO_6C	1532.1(8)	92.70(2)	O^c193.8(5,6)		171.5(2)[e]
					980.1(6)	117.95(2)	O^d212.9(5,21)		89.9(2,7.7)
					918.7(5)	88.57(2)	C^d217.1(7)		72.0(2,11.1);
									143.1(2,12.0)
$Ta^{III}(CHPMe_2)(CH_2PMe_2)\cdot$	m	$P2_1/n$	4	TaP_5C_2	1014.3(3)		P^c255.2(1,1)		174.3(1)
$\cdot(PMe_3)_3$					1876.9(3)	93.61(2)	P^d251.6(1,80)		
					1304.0(2)		C^d216.9(4,155)		
$Ta^VC\ell_2(dca)(CH_3)$	m	$P2_1/c$	4	$TaN_4C\ell_2C$	1352.1(8)		$C\ell^c$243.0(6)		157.5(5)[e]
					1308.4(8)	93.78(9)	N^c204.0(17)		93.3(5,21.1)
					1791.6(8)		$C\ell^d$231.7(6)		72.5(6,12.1),139.4(6,8.3)
							N^d216.5(17,22)		
							C^d221.7(20)		
$Ta^VC\ell_2(ONMeNO)_2(CH_3)$	m	$P2_1/n$	4	$TaO_4C\ell_2C$	978(1)		$C\ell^c$235.3(9,1)		179.2(3)[e]
					1510(1)	97.18(6)	O^d208.6(21,22)		90.0(6,3.1)
					774(1)		C^d224.8(28)		71.9(9,4.9);143.9(9,3.8)

TABLE 2 Continued 2

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	Chromo-phore	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	$M\text{-}L_c$[b] (pm)	L-M-L [°]	Ref.
$Ta^{1}H(CO)_2(dmpe)_2$	m	$P2_1/c$	2	TaP_4C_2H	896.3(5)		C^f215(5)	H not refined	87.8(11)^h	18
					1246.7(4)	125.53(6)	P^f251.4(11,17)		82.5(8,6.7),163(3)	
					1255.2(5)		C^g187(12)		104.2(3)	
							P^g251.9(11,17)			
$Ta^V(CH_3)_3C\ell\cdot$	m	$P2_1/n$	4	$TaN_3C_3C\ell$	942.5(6)		N^f226.5(9,29)	C 225(1)	77.7(3,2.2)^h	19
$\cdot\{HB(3,5\text{-}Me_2pz)_3\}$					1256.7(5)	106.00(4)	C^g222(1,2)		78.6(3,2.3),149.2(3,5.5)	
					1431.5(5)		$C\ell^g$238.0(3)		115.3(3,3.5)	
$Ta^V(CH_3)_3C\ell\{H_2B(3,5\text{-}Me_2\cdot$		$P2_1/c$		$TaC_3N_2C\ell H$	810.3(2)		H^f242	C 226.3(9)	79.8(3)^h	20
$\cdot pz)_2\}$					2506.3(4)	111.26(2)	N^f223.9(10,2)		80.6(5,3.1);145.4(5,5.3)	
					942.5(2)		C^g222.8(19,12)		117.8(5,12.1)	
							$C\ell^g$235.6(7)			
$Ta^{1}(CO)_3(PMe_3)_3C\ell$	m	$P2_1/n$	8	$TaC_3P_3C\ell$	1768.4(3)		C^i202.8(10,7)	Cℓ 254.5(2)	not given	21
					1390.4(5)	117.60(2)	C^j205.9(10)			
					1852.2(5)		P^j263.3(3,38)			
$Ta^{III}C\ell_4(py)(PhCCPh)\cdot$	tr	$P\bar{1}$	2	$TaC\ell_4C_2N$	1134.5(8)	101.12(3)	C^i206.7(8,2)	N 242.5(7)	81.35(17,1.03)^k	22
$\cdot(pyH)$					1233.5(4)	106.82(4)	$C\ell^j$243.8(2,21)		161.30(28,22)	
					935.2(4)	87.07(4)			85.76(23,1.31); 111.05(23,3.23)	

TABLE 2 continued 3

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	Chromo-phore	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	M-L_c^{b} (pm)	L-M-L [°]	Ref.
$Ta^{V}C\ell_2(CH_3)_3(bipy)$	m	$P2_1/m$	2	$TaC_3N_2C\ell_2$	754.9(8)		C^{i}220(5,4)	$C\ell$ 254.0(10)	78.6(5,1.9)$^{\ell}$	23
					1242.2(12)	109.7(2)	$C\ell^{j}$236.7(14)		143.2(14,2.4)	
					855.8(9)		N^{j}229.1(21)		77.0(10,2.0);123.9(8,9.2)	
							C^{j}236.7(14)			
$Ta_2{}^{III}C\ell_4(\mu\text{-}C\ell)_2\cdot$	m	$C2/c$	4	$TaC\ell_4C_2O$	1518.1(9)		$\mu\text{-}C^{i}$231.5(11,101)	O 228.2(8)	m	24
$\cdot(\mu\text{-dtba})(thf)_2$					1018.5(8)	101.48(6)	$C\ell^{j}$234.5(4,17)			
					1730.1(2)		$\mu\text{-}C\ell^{j}$248.9(3,7)			
$[\{Ta^{III}C\ell_2(tht)(Me_3CCOMe)\}_2\cdot$	m	$P2_1/c$	2	$TaC\ell_4C_2S$	1095.2(9)		$C\ell^{c}$236.5(3)		n	25a
$\cdot(\mu\text{-}C\ell)_2]$					1171.6(4)	107.45(3)	S^{c}263.4(3)			
					1309.7(6)		C^{d}203.1(15,2)			
							$\mu\text{-}C\ell^{d}$261.6(4,120)			
$Ta^{V}{}_2(dppbd)_2\cdot C\ell_8(CH_2C\ell_2)_2$		$P2_1/n$	2	$TaC\ell_4P_2C$	1188.4(2)		C 232.6(13)		o	25b
					1414.3(4)	94.26(1)	$C\ell$ 236.1(5,67)			
					1768.1(5)		P 259.3(5,39)			

TABLE 2 continued 4

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	Chromophore	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	M-L$_c$^{b} (pm)	L-M-L	Ref.
$Ta^V_2(dppbdc)_2C\ell_6\cdot(SMe_2)_2$		$P2_1/n$	2	$TaC\ell_3P_2CS$	1485.1(4)		C 201.8(10)		p	25b
					1224.5(6)	97.32(2)	Cℓ 239.4(4,36)			
					1584.8(4)		P 257.8(3,107)			
							S 277.5(3)			
$Ta_2^{III}C\ell_6(i\text{-}PrNC)_6$		$P2_1/c$	4	TaC_6N_2	1801.4(8)		C 222(2,11)		q	26
					1186.2(4)	98.23(3)	Cℓ 246.8(6,16)			
					1794.8(5)					
				$TaC\ell_4N_2$			N 201(2)(2x)			
							Cℓ 242.3(6,54)			

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value. b. Unique capped ligand (L_c). c. axial ligand (L_{ax}). d. Equatorial ligand (L_{eq}). e. The values of the L_{ax}-Ta-L_{ax}; L_{ax}-Ta-L_{eq}; cis-, trans-L_{eq}-Ta-L_{eq}, angles. f. Uncapped face ligand (L_{uf}). g. Capped face ligand (L_{cf}). h. The values of the L_{uf}-Ta-L_{uf}, L_{uf}-Ta-L_{cf}, and L_{cf}-Ta-L_{cf} angles.
i. capped edge ligand (L_e). j. Capped quadrilateral face ligand (L_{qf}). k. The values of the L_c-Ta-L_{qf};L_c-Ta-L_e and L_e-Ta-L_{qf} angles. The L_e-Ta-L_e = 37.38(32)°; L_{qf}-Ta-L_{qf} = 88.72(8,4.73)°(cis); and 162.59(8,1.55)° (trans). ℓ. The values of the L_c-Ta-L_{qf};L_c-Ta-L_e and L_e-Ta-L_{qf} angles. The L_e-Ta-L_e = 73.8(19)°; L_{qf}-Ta-L_{qf} = 89.3(6,27.1)°(cis); and 146.8(6)° (trans). m. The values of the Ta-Cℓ-Ta = 65.04(7)°; (μ-)Cℓ-Ta-(μ-)Cℓ=78.19(13)°; (μ-)Cℓ-Ta-(μ)-C = 96.93(28,13.3)°.
o. The values of angles are: Cℓ-Ta-Cℓ = 91.2(2,6.9) and 172.1(1)°; Cℓ-Ta-P = 86.2(2,8.3) and 166.1(2,4.4)°; Cℓ-Ta-C = 86.0(2,1.5) and 137.9(4,9.4)°; P-Ta-P = 109.4(2); and P-Ta-C = 42.1(4) and 67.9(4)°. p. The values of angles are : Cℓ-Ta-Cℓ = 90.7(1,1.9) and 160.2(1)°; Cℓ-Ta-P = 92.4(1,17.4) and 159.4(1)°; Cℓ-Ta-S = 81.3(1,3.5)°; Cℓ-Ta-C = 97.1(1,7.2) and 128.4(3)°; P-Ta-P = 110.01°; P-Ta-S = 77.37 and 165.9(1)°; P-Ta-C = 42.5(3) and 70.0(3)°; and S-Ta-C = 147.3(3)°. q. The values of the Cℓ-Ta-Cℓ = 90.6(2)°; Cℓ-Ta-C = 71.6(8)-159.4(5)°; C-Ta-C = 68.2(7)-139.6(7)°, and (i-PrNC) C-Ta-C(i-PrNC) = 38.5(6)°.

metal-ligand bond distances (Table 2) increase in the order Lc < Lcf < Luf. This demonstrates that the capped position is in fact more sterically crowded than the uncapped face.

The capped trigonal prismatic geometry has been found in $Ta(CO)_3(PMe_3)_3Cl$ (ref.21) $TaCl_4(py)(Ph_2C_2)(pyH)$ (ref.22), $TaCl_2(CH_3)_3(bipy)$ (ref.23), and $Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-dtba})(thf)_2$ (ref.24), Table 2. The environment of the central atom is constructed with the unique capping position ligand, Lc, being chlorine in the first and the third cases, nitrogen in the second, and oxygen in the last case. Another four atoms occupy the capped quadrilateral face, Lqf, and two atoms occupy the remaining edge, Le. The two Ta(II) atoms in the last derivative (ref.24) are 267.7(1)pm apart, representing the shortest such distance in tantalum organometallic chemistry, and they are bridged by two chlorine atoms and two carbon atoms of the dtba ligand.

In another dimer (ref.25), each Ta(III) atom has a 1,5,1-pentagonal bipyramidal environment, the equatorial plane of which consists of two carbon atoms (Me_3CCCMe) with Ta-C distances of 202.9(13)pm and 203.3(16)pm, and three chlorine atoms, of which two are bridging (Ta-Cl = 249.6(3) and 273.6(4)pm) and the other terminal (Ta-Cl = 236.2(3)pm). The apices are occupied by a fourth terminal chlorine (Ta-Cl = 236.5(3)pm) and a sulphur atom from the tetrahydrothiophene ligand. The Ta-Ta distance in this compound is too long, at 414.4(1)pm to allow for any bonding interactions.

Two non-equivalent tantalum atoms, one six coordinate and the other eight coordinate, have been found in $Ta_2Cl_6(i\text{-}prNC)_6$ (ref.26), Table 2. Again, there is no evidence for bonding interactions between the metal atoms at a distance of 423.6(1)pm.

Examination of the data in Table 2 reveals that the mean Ta-C bond distances for unidentate ligands increases in the order: 201pm (CO) < 217pm (CH_2SiMe_3) < 222pm (i-prCN) < 224pm (CH_3). For bidentate ligands the order of increase is: 203pm (Me_3CCCMe) < 207pm (Ph_2C_2) < 217pm (CH_2PMe_2). The mean value of the Ta-L bond distance increases with increasing van der Waals radii of the donor atoms, thus: O < N < Cl < P. The mean values of the Ta-L (bridge) bond distances are longer than those of the corresponding terminal donors, for instance the Ta-Cl (bridge) distance of 255pm is about 13pm longer than the terminal (242pm), and the Ta-C (bridge) distance of 232pm is about 19pm longer than the terminal (213pm).

3. TANTALUM ORGANOMETALLICS WITH AN AROMATIC CARBON ELECTRON-DONOR LIGAND

A. Mononuclear Cyclopentadienyl Compounds

The crystal and structural data gathered in Table 3 show that there are five examples with cyclopentadiene as ligand, nine with pentamethyl-

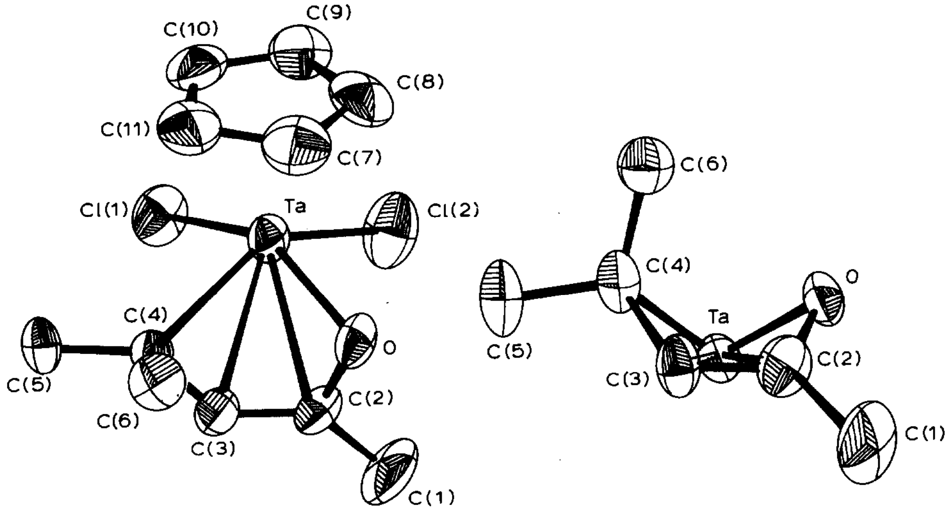

Figure 5. The Crystal Structure of $(\eta^5\text{-cp})\mathrm{Ta(omp)C\ell_2}$, and View of the Oxoalkyltantalum Moiety. Reproduced with permission from J. Organomet. Chem., (ref.28).

cyclopentadiene as ligand, and one where naphthalene is present as the aromatic ligand.

The crystal structure of $(\eta^5\text{-cp})\mathrm{Ta(omp)C\ell_2}$ (ref.28) is shown in Figure 5. The tantalum coordination pattern might be described as a square pyramid with an effectively planar cyclopentadienyl ligand at the apex. The Ta-C(cp) bond distances are in the range 239.6 to 243.8(17)pm, which is much narrower than those in $(\eta^5\text{-cp})\mathrm{Ta(CO)C\ell_2(PMe_2Ph)_2}$ (224 to 247(2)pm) (ref.27), and $(\eta^5\text{-cp})\mathrm{Ta}(\eta^2\text{-}\mathrm{C_2H_4})\mathrm{C\ell_2(PMe_2Ph)_2}$ (237 to 262(3) pm) (ref.29). The mean Ta-C(cp) distance (241.3(17)pm) is intermediate between those of the latter two derivatives (refs. 27 and 29). By contrast, the Ta-Cℓ bond distance of the former (ref.28) is shorter at 241.4(5)pm than the other two examples (Table 3). The larger variation of the Ta-C bond lengths and the longer Ta-Cℓ bond in the latter two derivatives suggest that the steric requirements are more severe in these cases.

The structure of $(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Ta(C_4H_8)C\ell_2}$ (ref.35) is shown in Figure 6 where $\mathrm{C_4Ta}$ heterocyclic ring has been described as having an "open-envelope" conformation, with a dihedral angle between the strictly planar C(1)-Ta-C(1') and the C(1)-C(2)-C(2')-C(1') plane of 116.2(6)°. The mean Ta-C(cp) bond distance of 239.5(9)pm is the shortest found in monopentamethylcyclopentadienyl tantalum compounds (Table 3). A similar

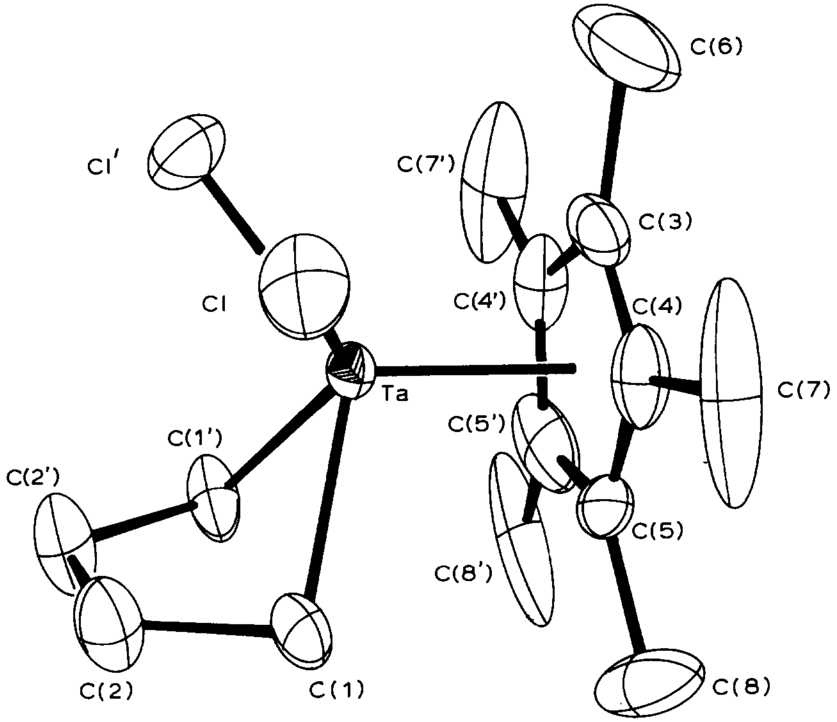

Figure 6. The Crystal Structure of $(\eta^5\text{-}C_5Me_5)Ta(C_4H_8)C\ell_2$. Reproduced with permission from Inorg. Chem. (ref.35).

structure is found for $(\eta^5\text{-}C_5Me_5)Ta(C_7H_{12})C\ell_2$ (ref.35), in which the corresponding dihedral angle of 122.64° is even larger than that of the C_4H_8 analogue.

Inspection of the data in Table 3 reveals that the mean Ta-C bond distances increases in the order: 232pm (η^4-nph) $<$ 242pm, (η^5-cp) $<$ 243pm (η^5-C_5Me_5); and, 207.1pm(η^2-Ph_2C_2) $<$ 207.5pm (η^2-C_6H_4) $<$ 219.5pm (η^2-C_7H_{12}); and, 184.9pm (CPh) $<$ 188.3pm (CHPh) $<$ 221.0pm (CH_2Ph). These observations indicate that electronic effects have a dominant influence on Ta-C bond lengths. However, steric factors are also important as can be seen in the lengths of Ta-P bonds which increase in the order: 253.8pm (PMe_3) $<$ 259.9pm (dmpe) $<$ 264.4pm (PMe_2Ph).

As the mean Ta-C(cp) bond lengths increase so do the Ta-cp(centroid) distances, as might be expected. For instance, the mean Ta-C and Ta-cp distances in $(\eta^5\text{-cp})Ta(CO)C\ell_2(PMe_2Ph)_2$ are 236 and 207pm respectively, compared to 245.2 and 213.7pm for the corresponding distances in $(\eta^5\text{-}C_5Me_5)Ta(\eta^2\text{-}C_2H_4)(CH_3)_2$.

It is interesting to note that mononuclear monocyclopentadienyl tantalum

TABLE 3 STRUCTURAL DATA FOR MONONUCLEAR TANTALUM COMPOUNDS WITH CYCLOPENTADIENYL AS A LIGAND[a]

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	L-M-cp centroid [°]	L-M-L [°]	Ref.
$[(\eta^5\text{-cp})\mathrm{Ta^{III}(CO)C\ell_2}\cdot$	hx	$P6_5$	6	1366.1(2)		OC[b] 201(2)	P[b] 106.0(0,4)	83.4(1)[c]	27
$\cdot(\mathrm{PMe_2Ph})_2]\text{.thf}$						Cℓ 252.9(4,11)	Cℓ 101.7(0,4.2)	73.2(5),15.6(5)	
				2642.0(11)		P 264.2(4,9)	Cℓ 170.8	79.2(1.5,6)	
						(cp)C 236(2,12)		147.8(1)	
$(\eta^5\text{-cp})\mathrm{Ta^{II}(omp)C\ell_2}$	m	$P2_1/c$	4	824.41(194)		O 200.5(6)	not given	84.18(16)[d]	28
				1483.39(67)	130.02(11)	C 235.7(13,95)		87.05(35),143.70(26)	
				1362.98(312)		Cℓ 241.4(5,26)		86.84(32),138.45(37)	
						(cp)C 241.3(17,25)			
$(\eta^5\text{-cp})\mathrm{Ta^{III}}(\eta^2\text{-}\mathrm{C_2H_4})\mathrm{C\ell_2}\cdot$	or	$Fdd2$	8	2109.8(9)		C 238(2,1)	P 101.3(0,5)	82.4(2)[e]	29
$\cdot(\mathrm{PMe_2Ph})_2$				2984.8(9)		Cℓ 247.3(4)	Cℓ 100.9	79.2(2,2.3)	
				769.4(3)		P 264.9(3)	Cℓ 176.4	151.1(2)	
						(cp)C 249(3,12)			
$(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Ta^{V}(PMe_3)_2H_4}$[f]		$P\bar{1}$	4	858.1(2)	90.34(2)	P 253.2(5,3)	P 117.3(1,2)	116.1(2)[f]	30
				1424.4(4)	99.96(2)	C 241.4(17,40)			
				1726.7(14)	90.05(2)			f	
						P 253.2(5,4)	P 120.1(1,3)	112.4 (2)	
						C 242.3(17,37)			
$(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Ta(CHPh)(CH_2Ph)_2}$		$P2_1/c$	4	1309.3(5)		C 188.3(14)	not given	103.3(6,1.9)	31
				794.6(4)	100.64(4)	C 221.0(15,23)			
				2529.9(13)		(η^5)C 243.8(18,42)			

TABLE 3 Continued 2

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	L-M-cp centroid [°]	L-M-L [°]	Ref.
$(\eta^5\text{-}C_5Me_5)Ta(\eta^2\text{-}C_6H_4)(CH_3)_2$	tr	$P\bar{1}$	2	887.89(12)	71.769(12)	217.5(6,6)	(CH_3)C 107.14(0,58)	99.35(21,12.46)^g	32,33
				923.65(14)	76.101(12)	207.5(4,16)	(η^2)C 114.21	107.72(26)	
				1131.74(18)	73.142(11)	245.2(4,48)	(η^5)C 152.49		
$(\eta^5\text{-}C_5Me_5)Ta(CHCMe_3)\cdot$		$P2_1/n$	4	1655.7(7)		(η^2)C 225.6(3,29)	P 116.7	89.4(1)^h	13
$\cdot(\eta^2\text{-}C_2H_4)(PMe_3)^h$				1393.2(5)	103.53(3)	C 194.6(3)	C 122.1	76.0(1),113.3(1)	
				939.3(3)		H 204.2(5)		109.5(1,4.4)	
						P 250.7(4)			
						(η^5)C 245.9(3,19)			
$(\eta^5\text{-}C_5Me_5)Ta^V(C_4H_8)C\ell_2$	or	Pnam	4	1007.36(18)		C 221.7(8)	C 107.49	89.30(8)^i	34,35
				1128.34(20)		$C\ell$ 236.6(2)	$C\ell$ 116.22	82.49(21)	
				1352.39(24)		(η^5)C 239.5(9,33)		134.43(21)	
$(\eta^5\text{-}C_5Me_5)Ta^V(C_7H_{12})C\ell_2$	m	$P2_1/n$	4	920.5(1)		C 219.5(6,5)	C 107.65(0,31)	88.57(7)	35
				1362.3(2)	96.63(1)	$C\ell$ 236.8(2,7)	$C\ell$ 117.49(0,1.77)	82.20(18,1.18)	
				1414.4(3)		(η^5)C 241.8(6,51)		132.77(18,1.47)	
$(\eta^5\text{-}C_5Me_5)TaC\ell_2\cdot$	m	$P2_1/c$	4	1702.12(15)		C 207.1(6,4)	C 114.62(0,88)	97.08(16)^j	36
$\cdot(PhCCPh)$				932.27(14)	90.510(15)	$C\ell$ 235.3(2,2)	$C\ell$ 115.19(0,52)	37.66(22)	
				1384.50(23)		(η^5)C 242.0(6,17)		105.20(16,16.21)	

TABLE 3 Continued 3

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	L-M-cp centroid [°]	L-M-L [°]	Ref.
$(\eta^4\text{-nph})TaC\ell(dmpe)_2$	m	$P2_1/c$	4	1034.3(3)		Cℓ 259.6(1)		$74.26(4,1.97)^{\ell}$	39,40
				1028.1(3)	97.39(1)	P 259.9(1,32)	P 78.97(19,23)	77.05(4,1.16)	
				2464.2(7)		(η^4)C 231.7(5,88)		150.95(4,3.09)	
$(\eta^5\text{-cp})TaC\ell_2(C_4H_6)$		$P2_1/n$	4	661.5(1)		Cℓ 241.4(3,9)	C 113.4	$89.5(1)^{m}$	41
				1096.2(1)	97.02	C 225.7(12,1)	C 120.1	73.3(4)	
				1438.4(2)		C 241.7(12,7)			
						(cp)C 240.9(12,16)			
$(\eta^5\text{-cp})Ta(2,3\text{-}Me_2C_4H_4)_2$	or	Pnma	4	894.7(1)		C 227.6(8,16)	C 108.5	75.7(3,5)	41
				1229.1(2)		C 249.8(8,25)	C 137.2		
				1351.2(2)		(cp)C 243.7(13,45)			
$(\eta^5\text{-}C_5Me_5)Ta(2,3\text{-}Me_2C_4H_4)_2$		$P2_1$	2	1046.8(2)		C 225(2,6)	C 103.1	76.2(6,4.5)	41
				1244.2(2)	106.68(2)	C 257(3,4)	C 142.2		
				802.0(1)		(cp)C 249(2,6)			

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value. b. The chemical identity of coordinatd atom (ligand) ... columns.
c. The values of Cℓ-Ta-Cℓ, Cℓ-Ta-CO; Cℓ-Ta-P and P-Ta-P angles. d. The values of Cℓ-Ta-Cℓ, Cℓ-Ta-O and Cℓ-Ta-C angles. e. The values of Cℓ-Ta-Cℓ, Cℓ-Ta-P and P-Ta-P angles. f. There are two independent molecules. The value of P-Ta-P angle. g. The values of $(CH_3)C\text{-}Ta\text{-}C(C_6H_4)$ and $(CH_3)C\text{-}Ta\text{-}C(CH_3)$ angles. h. At 20K. The values of $P\text{-}Ta\text{-}C(CHCMe_3)$, $P\text{-}Ta\text{-}C\ (\eta^2\text{-}C_2H_4)$; $(\eta^2\text{-}C_2H_4)C\text{-}Ta\text{-}C\ (CHCMe_3)$ angles.
i. The values of Cℓ-Ta-Cℓ and C-Ta-C angles. j. The values of Cℓ-Ta-Cℓ, C-Ta-C and Cℓ-Ta-C angles. k. The values of C-Ta-P, C-Ta-Cℓ and Cℓ-Ta-P angles. ℓ. The values of Cℓ-Ta-P, and P-Ta-P angles. m. The values of Cℓ-Ta-Cℓ and C-Ta-C angles.

organometallic complexes are based predominantly upon pentamethylcyclopentadiene, (Table 3), while the corresponding niobium complexes are predominantly of cyclopentadiene itself (ref.4). The Ta-C(cp) bond distances lie in the range 224.0 to 262.0pm (mean value 242.1pm), which is wider than the range found for niobium (236.4 to 248.0pm with a mean value of 242.5pm). A similar trend is observed for the M-Cℓ bond distances; the Ta-Cℓ distances range from 235.2 to 259.6pm (mean value 244.4pm) compared to 246.3 to 250.5pm (mean value 248.1pm) for the niobium analogues.

In the chemistry of the coordination compounds of niobium and tantalum, it was found (ref.3) that in general Ta-L distances are somewhat shorter than the Nb-L distances. As can be seen from the above discussion, the organometallic complexes follow the same trend. The wider range of distances observed for the tantalum complexes probably reflects the generally less symmetric environments about tantalum than niobium.

B. Mononuclear Biscyclopentadienyl Compounds

Monoclinic purple crystals of $(\eta^5\text{-cp})_2\text{Ta(CO)H}$ has the crystal structure (Figure 7) in which the tantalum is η^5-bonded to two cp rings with an angle between the two cp ring planes (cp-Ta-cp) equal to 144.8°. This angle is

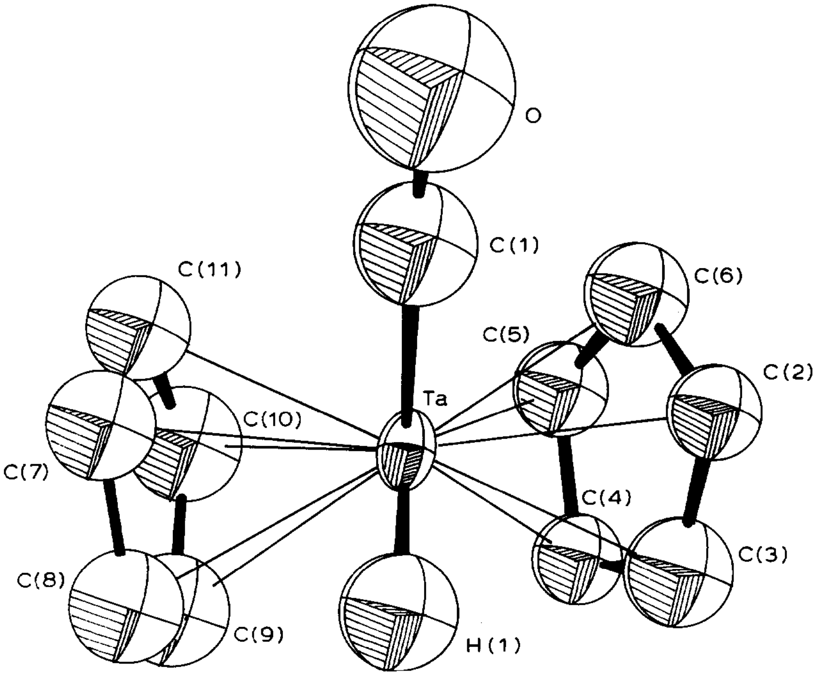

Figure 7. The Molecular Structure of $(\eta^5\text{-cp})_2\text{Ta(CO)H}$.
Reproduced with permission from J. Am. Chem. Soc., (ref.42).

the largest found for both the tantalum compounds (Table 4) and the niobium compounds (ref.4). The hydrogen and CO ligand are bonded to the tantalum atom at distances of 145pm and 194pm respectively, which are again the shortest for both the tantalum compounds and the niobium compounds. Similarly, the mean Ta-C(cp) bond distance of 235(4)pm is also the shortest for both Ta (Table 4) and Nb (ref.4). This is probably due to the large dihedral angle between the cp rings and the relatively small size of the H and CO ligands.

The crystal structure of $(\eta^5\text{-cp})_2Ta(\eta^2\text{-}C_8H_8)(C_3H_7)$ (ref.50) is shown in Figure 8. The cyclopentadienyl rings are approximately planar and staggered, with dihedral angle between them of 50.1°. It is interesting to note the planar carbon skeleton of the C_8H_8 ligand. The bond distances and the angles (Table 4) lie in the range observed for other biscyclopentadienyl tantalum compounds.

Examination of the data in Tables 3 and 4 reveals that the mean Ta-C(cp) bond distance of 228.4pm for the biscyclopentadienyl derivatives (Table 4) is about 37pm shorter than that for the monocyclopentadienyl derivatives (Table 3). Also, the range of values in the former (230 to 246pm) is narrower than in the latter (224 to 262pm). Again, as in the case of the

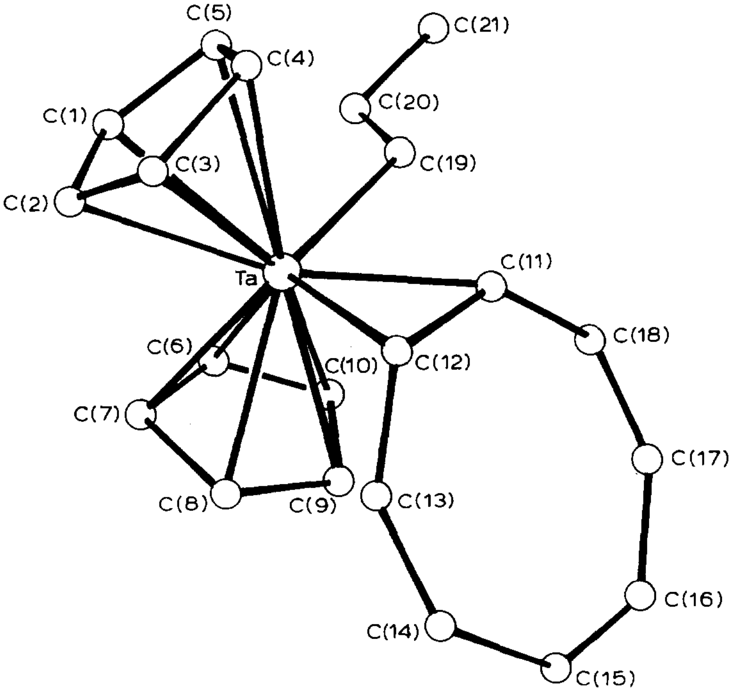

Figure 8. The Crystal Structure of $(\eta^5\text{-cp})_2Ta(\eta^2C_8H_8)(C_3H_7)$.
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TABLE 4. STRUCTURAL DATA FOR BISCYCLOPENTADIENYL TANTALUM COMPOUNDS[a]

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	Ta-cp centroid (pm)	cp^b-Ta-cp^b L-Ta-cp^b [°]	L-Ta-L [°]	Ref.
$(\eta^5$-cp$)_2$Ta(CO)H	m	$P2_1/n$	4	614.7(3)		H^c145	205(0,2)	144.8	97	42
				1386.4(6)	100.53(3)	C 194(4)		H^c 98.2(0,10.3)		
				1180.1(5)		cp 235(4,5)		C^c104.2(0,2.0)		
$(\eta^5$-cp$)_2$Ta(CH_3).	m	$P2_1/c$	4	654.4(4)		(CH_2)C 202.6(10)	210.1	135.7	95.6(3)	43
.(CH_2)				1168.5(2)	117.13(5)	(CH_3)C 224.6(12)				
				1533.9(11)		cp not given				
$(\eta^5$-cp$)_2$Ta(CH_2Ph).	m	$P2_1/c$	4	883.6(2)		(CH) C 207(1)	not given	132.6(6)	95.2(5)	44
.(CHPh)				1595.2(5)	100.20(4)	(CH_2)C 230(1)		(CH)C 106.9(5,2.4)		
				1361.7(9)		cp 242(1,2)		(CH_2)C 104.5(5,1.3)		
$[(\eta^5$-cp$)_2$Ta^{III}.	m	$P2_1/c$	4	934.7(2)		P 253.5(1,1)	203.5	138.9	72.21(4)	45
.(dmpe)].				1389.1(3)	96.84(5)	cp 236.2(5,48)				
.Cℓ.CH_3CN				1573.3(3)						
$(\eta^5$-cp$)_2$Ta.	m	$P2_1/c$	4	659.57(8)		C 203.0(6)	210.5(0,12)	130.86	97.63(18)	46,47
.$(CHCMe_3)$Cℓ				1544.18(19)	103.023(10)	Cℓ 247.9(2)		C 108.25(0,1.61)		
				1433.63(19)		cp 241.7(7,41)		Cℓ 104.75(0,1.04)		

TABLE 4. Continued 2

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	Ta-cp centroid (pm)	cp^b-Ta-cp^b L-Ta-cp^b [°]	L-Ta-L [°]	Ref. .
$(\eta^5\text{-cp})_2TaH_3$[d]		$P4_1 2_1 2$	8	1096.5(5)		H 177.4(9,5)	206.5(0,4)	139.9	62.9(5,1)	48
				-		cp 239.3(5,15)			125.8(5)	
				1481.7(7)						
$(\eta^5\text{-}C_5H_4CH_3)_2\cdot$	or	Pnma	4	1201.0(4)		Cℓ 244.2(4,3)	206(0,5)		84.5	49
$\cdot TaC\ell_2$				1505.5(6)		cp not given				
				690.4(4)						
$(\eta^5\text{-cp})_2Ta\cdot$	m	$P2_1/n$	4	957(7)		C 229(1)	205(0,1)		77(1)	50
$\cdot(\eta^2\text{-}C_8H_8)\cdot C_3H_7$				1519(1)	97.05(15)	(η^2)C 233(2,1)				
				1160(1)		cp 236(2,5)				

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value.

b. Centroid of cp.

c. The chemical identity of the coordinating atom or ligand columns.

d. At 90K; at room temperature: a = 1102.6(14)pm and C = 1501.8(19)pm.

monocyclopentadienyl compounds, the mean Ta-C(cp) distance of 238.4pm is shorter than the Nb-C(cp) distance of 240.3pm (ref.4) in the clino-sandwich biscyclopentadienyl compounds.

C. Oligonuclear Compounds

Crystal and structural data for oligonuclear tantalum organometallic compounds are summarised in Table 5. There are five examples of homobinuclear tantalum compounds, and two trinuclear compounds with one tantalum atom and two manganese or zinc atoms as central atoms.

Monoclinic violet crystals of $[(\eta^5\text{-}C_5Me_4Et)_2Ta_2C\ell_3H_2(CH_3)]$ (ref.51), is the only example where two approximately tetrahedrally coordinated tantalum atoms are joined by a Ta-Ta bond (285.4(1)pm) without any additional bridging atom (Figure 9). The tetrahedral fragments are $Ta(\eta^5\text{-}C_5Me_4Et)C\ell(C\ell/C)$, where the $(C\ell/C)$ moiety signifies disordered eclipsed $C\ell$ and methyl ligands (ref.51). As can be seen in Figure 9, there are two independent molecules which differ by degree of distortion and metal-metal separation (Table 5). The coexistence of two species of the same coordination number about a central atom, but with different degrees of distortion in the same crystal is typical of the general class of distortion isomerism (ref.61). Two independent molecules differing by

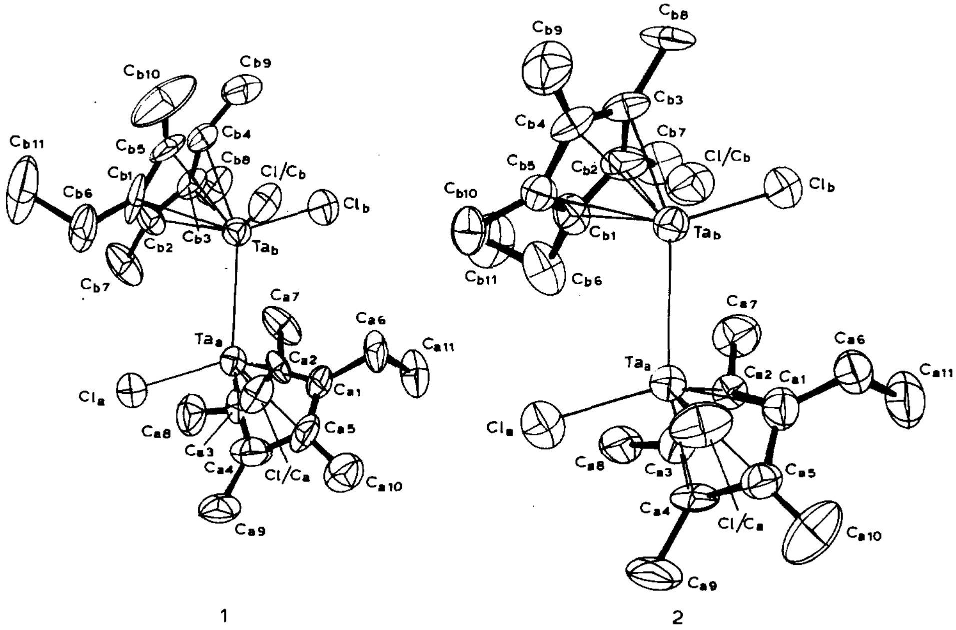

Figure 9. The Two Independent Molecules of $[(\eta^5\text{-}C_5Me_4Et)_2Ta_2C\ell_3H_2(CH_3)]$. Reproduced with permission from J. Am. Chem. Soc., (ref.51).

degree of distortion have also been found in $(\eta^5\text{-}C_5Me_5)Ta(PMe_3)_2H_4$ (ref.30), Table 3., and it represents another example of distortion isomerism.

Figure 10 shows the crystal structure of $(\eta^5\text{-}C_5Me_4Et)_2Ta_2C\ell_4(H)(NCHMe)$ (ref.52). The molecule contains non-equivalent $[(\eta^5\text{-}C_5Me_4Et)TaC\ell_2]$ and $[(\eta^5\text{-}C_5Me_4Et)TaC\ell]$ fragments which are unsymmetrically triple bridged by a chloride $\{Ta(1)\text{-}C\ell(4) = 255.3(3)pm;\ Ta(2)\text{-}C\ell(4) = 261.7(3)pm)\}$, a hydride ligand $\{Ta(1)\text{-}H = 218(9)pm;\ Ta(2)\text{-}H = 170(9)pm\}$, and a $\mu\text{-}\eta^1\text{-}N,\ \eta^2\text{-}C,N\text{-}(NCHMe)$ ligand $\{Ta(1)\text{-}N = 190.1(8);\ Ta(2)\text{-}N = 205.9(8)pm;\ Ta(2)\text{-}C(1) = 219.5(10)pm\}$. The Ta(1)-Ta(2) bond distance of 297.9(1) is longer than those found in $(\eta^5\text{-}C_5Me_4Et)_2Ta_2C\ell_3H_2(CH_3)$ (ref.51), but shorter than in other binuclear compounds (Table 5).

Two tantalum atoms triple bridged have been found in another three examples. These are, $\{[(\eta^5\text{-}C_5Me_4Et)TaC\ell_2]_2(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHPMe_3)\}$ (ref.54); $\{[(\eta^5\text{-}C_5Me_4Et)TaC\ell_2]_2(\mu\text{-}H)(\mu\text{-}CHO)\}$ (ref.56); and $\{[(\eta^5\text{-}C_5Me_4Et)TaC\ell_2]_2\cdot\cdot(\mu\text{-}C\ell)_3$ (ref.58). The triple bridge consists of hydride, oxygen, and the carbon atom of $CHPMe_3$ in the first case; of hydride, and $\mu\text{-}\eta^2\text{-}C,O\text{-}(CHO)$ in the second; and three chlorides in the last case (Table 5).

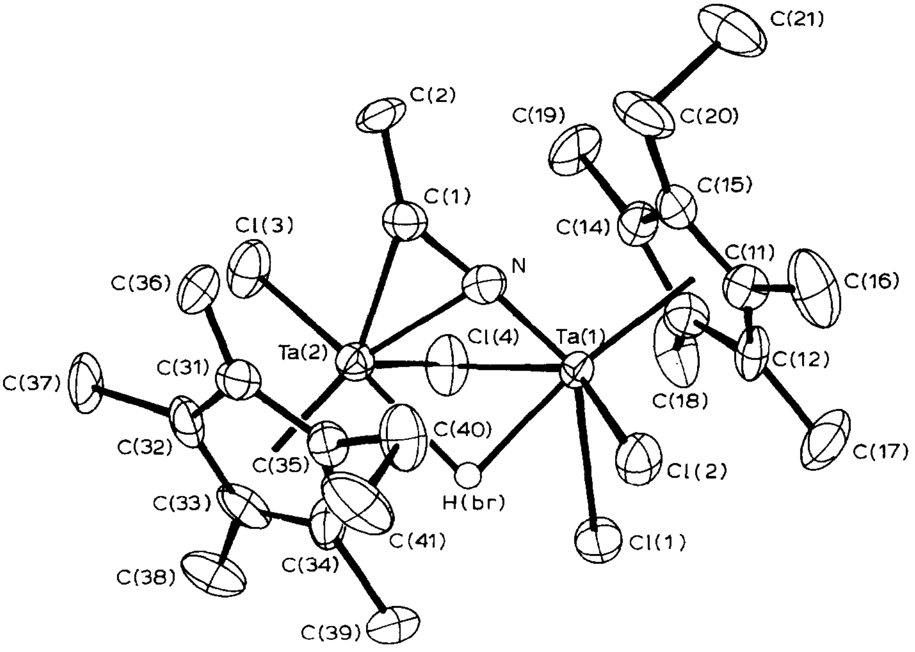

Figure 10. The Crystal Structure of $[(\eta^5\text{-}C_5Me_4Et)_2Ta_2C\ell_4.H(NCHMe)]$.
Reproduced with permission from J. Organomet. Chem., (ref.52).

TABLE 5. STRUCTURAL DATA FOR OLIGONUCLEAR TANTALUM ORGANOMETALLIC COMPOUNDS[a]

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	M-M M-cp centroid (pm)	M-L-M L-M-cp centroid [°]	REF.
$\{(\eta^5\text{-}C_5Me_4Et)_2Ta^{III}{}_2$	m	$P2_1/c$	8	2008.4(6)		Cl^b 235.9(5)	281.5(1)	-	51
$Cl_3H_2(CH_3)\}^c$				1697.2(4)	96.86(2)	(cp)C 245(2,5)	212	Cl^b 110.0(0,2.0)	
				1586.9(4)		C/Cl^c 235.4(5)		f	
						H^d e			
						Cl 237.0(5)	285.4(1)	-	
						(cp)C 242(2,2)	210	Cl 110.1(0,3)	
						C/Cl^c 234.4(6)		f	
						H^d e			
$\{(\eta^5\text{-}C_5Me_4Et)_2Ta_2Cl_4$	or	$Pbc2_1$	4	993.6(4)		Cl 241.9(3,53)	297.9(1)	g	52
.H(NCHMe)\}				1889.6(5)		(cp)C 244.1(11,58)	212.2(0,21)	Cl 106.7(0,1.4),142.3	
				1500.5(3)		C 219.5(10)		N 109.1;126.1	
						H^d 194(9,14)		H 86;176	
						N^d 198.0(8,79)		C 108.5	
						Cl^d 258.5(3,32)			

TABLE 5. continued 2

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	M-M M-cp centroid (pm)	M-L-M L-M-cp centroid (°)	REF.
$\{[(\eta^5\text{-}C_5Me_4Et)TaC\ell_2]_2$	or	$P2_12_12_1$	4	1793.7(8)		Cℓ 242.6(5,19)	299.2(1)	h	53,54
$(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHMe_3)\}$				1245.2(4)		(cp)C 248.5(19,71)	216.8(0,4)	Cℓ 104.7(0,3.6)	
				1402.2(5)		O^d 192.6(11,32)		O 101.2(0,9)	
						C^d 227.0(17,84)		H 109;177	
						H^d not given		C 112.2;172.5	
$\{[(\eta^5\text{-}C_5Me_4Et)TaC\ell_2]_2\cdot$	tr	$P\bar{1}$	2	1111.4(3)	82.98(2)	Cℓ 236.2(4,25)	318.6(1)	98.6(5);99.2(4)	55,56
$\cdot(\mu\text{-}H)(\mu\text{-}CHO)\}$				1485.6(4)	103.91(2)	(cp)C 243.6(13,35)	211.3(0,2)	Cℓ 107.9(0,4.0)	
				885.8(2)	105.56(2)	O^d209.1(9,3)		O 105.7;156.0	
						C^d210.2(12,17)		C 110.1(0,4.0)	
						H^d not given		H 180;^{i}	
$\{[(\eta^5\text{-}C_5Me_5)Ta^VC\ell_2]_2\cdot$	m	$P2_1/c$	2	1683.9(3)		Cℓ 232.5(9,9)	370.8(2)	92.2(3,6)	57,58
$\cdot(\mu\text{-}C\ell)_3\}_2{}^{+\ j}$				1522.5(4)	111.18(3)	(cp)C 247.0(14,70)		not given	
$\cdot\{[TaC\ell_5(\mu\text{-}O)TaC\ell_3]_2\cdot$				1706.5(7)		$C\ell^d$ 256.9(9,108)		k	
$\cdot(\mu\text{-}C\ell)_2\}^{2-}$									
$(\eta^5\text{-}C_5H_4Me)_2TaH.$	m	$P2_1/n$	4	1551.9(3)		H 152(9)		ℓ	59
$\cdot\{Zn(\eta^5\text{-}cp)\}_2$				846.1(4)	99.99(4)	Zn 258.9(2,1)			
				1552(1)		(cp)C 237(1,7)			

TABLE 5 continued 3

COMPOUND	CRYSTAL CLASS	SPACE GROUP	Z	a(pm) b(pm) c(pm)	α(°) β(°) γ(°)	M-L (pm)	M-M M-cp centroid (pm)	M-L-M L-M-cp centroid (°)	REF.
$(\eta^5\text{-cp})_2(CO)Ta(\mu\text{-}H)$.	m	$P2_1/a$	4	1487.2(3)		OC not given			60
$.Mn_2(CO)_9$				1075.6(2)	114.04(1)	(cp)C not given			
				1559.1(3)		Mn 344.1(1)			
						H^d 191(5)			

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value.

b. The chemical identity of the coordinating atom or ligand. c. There are two independent molecules; the C/Cℓ terminology signifies that the CH_3 group was disordered with the chloride ligand. d. The bridge atom (ligand). e. Proposed that the hydride ligands are bridging.

f. The value of Cℓ-Ta-Cℓ angle is 99.1(2.7) and 97.3(2,6)°, respectively. g. The Ta-Cℓ-Ta = 70.35(8)°; Ta-N-Ta = 97.5(4)°; Ta-H-Ta = 99(4)°; Cℓ-Ta-C = 76.8(1) -146.1(1)°; Cℓ-Ta-N = 80.7(3)-143.9(3)°; Cℓ-Ta-H (bridge) = 69.6(25) - 147.5(32)°; N-Ta-H (bridge) = 72.7(28,3.3)°; N-Ta-C = 39.3(4)°; Cℓ-Ta-C = 108.4(3)°. h. The Ta-C-Ta = 82.3(6)°; Ta-O-Ta = 101.9(5); Ta-H-Ta = 92°; Cℓ-Ta-Cℓ = 89.6(2,6.9)°; Cℓ-Ta-C = 83.6(5,4.0) and 140.9(5)°; Cℓ-Ta-O = 96.0(3,2.1) and 150.8(3,7)°; and C-Ta-O = 75.4(6,2.6)°. i. The Cℓ-Ta-Cℓ = 98.0(2,4.1)°; Cℓ-Ta-C (bridge) = 98.0(3,5.8) and 129.3(3,2)°; Cℓ-Ta-O (bridge) = 87.6(3,7.7) and 139.0(3)°, and (bridge) C-Ta-O (bridge) = 41.8(4,2)°. j. The X-ray data in the Table presented for cation. k. The Cℓ-Ta-Cℓ = 93.9(4,5)°; Cℓ-Ta-Cℓ (bridge) = 77.3(3)-150.6(3)°; (bridge) Cℓ-Ta-Cℓ (bridge) = 73.8(3,2.8)°. ℓ. The Zn-Ta-Zn = 62.8(1)° and Zn-Ta-H = 54(3)°.

From the data in Table 5 it can be seen that the most common η^5-ligand is tetramethylethylcyclopentadiene. The mean Ta-C (C_5Me_4Et) bond distance of 243.9pm is about 0.9pm longer than the value of 243.0pm found for Ta-C(C_5Me_5) in the mononuclear tantalum compounds (Table 3). The Ta-L(bridge) bond distances are longer than the Ta-L(terminal) distances. For instance the mean Ta-Cℓ (bridge) distance is 257.3pm compared to 237.6pm for the Ta-Cℓ (terminal) distance; the Ta-H (bridge) distance is 194pm compared to 152pm for the Ta-H (terminal) distance. It is interesting that the mean Ta-Cℓ (terminal) distance (Table 5) is shorter than that found in the mononuclear derivatives (Tables 3 and 4).

In $(\eta^5\text{-}C_5H_4Me)_2TaH(Zn(\eta^5\text{-cp})_2)$ (ref.59) the cp_2TaHZn unit has an approximate mirror plane passing through the metal atoms. The cp_2Ta fragment has a normal geometry with a bonding angle of 137.5°. The two Ta-Zn distances (258.8 and 259.0(2)pm) indicate that both interactions are of a single bond type. The cp rings are bound to the zinc atom in a η^5 fashion, with Zn-cp (centroid) distances of 206(6) and 203(4)pm.

In the cubic, purple crystals of $(\eta^5\text{-cp})_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_9$ (ref.60) the $cp_2Ta(CO)$ and $Mn_2(CO)_9$ moieties are bridged by the hydride ligand (Ta-H = 191(5)pm, Mn-H = 171(9)pm). The Ta-H-Mn bridge angle is 138.2(3)°, and the distance between the two metal atoms is 344.1(1)pm.

4. CONCLUSIONS

The crystal and structural data gathered in this review represent nearly fifty tantalum organometallic compounds. There are two groups of compounds discussed, the aromatic group having $\eta^5(\eta^4)$ coordinated ligands, and the non-aromatic group in which no such ligand is present. The predominant electronic configurations for the tantalum are d^0 and d^2.

The data for the non-aromatic derivatives shows that the various geometries are represented by increasing number of examples in the order: six-coordinate (tetragonally distorted) < five coordinate (mostly square pyramidal) < seven coordinate with all three common geometries (pentagonal bipyramidal, capped octahedral, and capped trigonal biprismatic) present. There are two examples in which tantalum is in a tetrahedral environment, and even one example of dodecahedral geometry.

The structures of the aromatic derivatives can be classified as mostly mononuclear, with one or two cyclopentadienyl type ligands, and binuclear. There are only two examples of heterotrinuclear complexes.

There are two examples, $(\eta^5\text{-}C_5Me_5)Ta(PMe_3)_2H_4$ (ref.30) and $[(\eta^5\text{-}C_5Me_4Et)_2Ta_2Cℓ_3H_2(CH_3)]$ (ref.51) in which two crystallographically independent molecules are present, differing only by degree of distortion. These are examples of distortion isomerism which is also observed for many other central atoms.

Two non-equivalent tantalum atoms, one six and the other eight coordinate have been found in $Ta_2C\ell_2(i\text{-}prNC)_6$ (ref.26). The coexistence of an organometallic cation and a coordination complex anion has been found for $\{[(\eta^5\text{-}C_5Me_5)TaC\ell_2]_2(\mu\text{-}C\ell)_3\}^{2+}\{[TaC\ell_5(\mu\text{-}O)TaC\ell_3]_2(\mu\text{-}C\ell)_2\}^{2-}$ (ref.58).

From the data in Tables 1 and 2 it can be seen that the mean value of the Ta-L bond distance increases with increasing coordination number when L = C, C(bridge), N, Cℓ, and Cℓ (bridge), but decreases when L = O or P as the donor atom. For example, the mean value of Ta-C, {Ta-C (bridge)}, distances increase in the order: 211.5pm (four coordinate) < 213.0pm (five coordinate) < 218.3pm, {182.5pm} (six coordinate) < 213.0pm, {231.5pm} (seven coordinate); Ta-Cℓ, {Ta-Cℓ (bridge)} distances: 237.1pm, {254.2pm} (six coordinate) < 241.5pm, {255.3pm} (seven coordinate). By contrast, the mean values of Ta-O, Ta-P distances decrease in the order: 230.3pm, 260.2pm (six coordinate) > 205.3pm, 254.5pm (seven coordinate).

A summary of the structural data for aromatic derivatives of tantalum are given in Table 6, together with the data for niobium analogues (ref.4) for comparison. Inspection of this data reveals that, in general:

(a) the mean value of M-L distances in the biscyclopentadienyl complexes are smaller than those of the monocyclopentadienyl derivatives, and Ta-L < Nb-L;

(b) the Ta-L distances are spread over a wider range than the corresponding Nb-L distances;

(c) the mean M-L bond distances are shorter than the mean M-L (bridge) distances.

The shortest Ta-Ta distance of 267.7(1)pm is found in the binuclear non-aromatic groups, while the shortest distance in the aromatic derivatives is 281.5(1)pm. In both cases the tantalum is in the oxidation state +3. The former distance is also within the range of 254.5 to 272.6pm found in Ta(III) coordination compounds (ref.3), while the latter is not.

This survey, together with the corresponding survey of the coordination compounds (ref.3) illustrates the rich variety found in almost two hundred tantalum compounds for which structures have been defined by X-ray crystallography or related techniques. Very recently, reviews of niobium coordination complexes (ref.62) and niobium organometallics (ref.4) have been completed, in which an even richer chemistry has been found for over two hundred and fifty derivatives. A similar study on the chemistry of vanadium coordination and organometallic complexes is currently in progress by the present authors. About eighty structures have been determined to date for organo-vanadium compounds (ref.63), and they demonstrate both the similarities and differences between vanadium and its niobium and tantalum homologues.

TABLE 6. SUMMARY OF THE TANTALUM-ATOM (LIGAND) AND NIOBIUM-ATOM (LIGAND) BOND DISTANCES (pm)[a]

Coord. Atom (Ligand)		Mononuclear		Homobinuclear
		Mono cp	Bis cp	
C(cp)	Nb	236.4-248.0(242.5)	234.0-246.0(240.3)	232.0-248.8(242.2)
	Ta	224.0-262.0(242.1)	230.0-245.7(238.4)	
C(C_5Me_5)	Ta	237.1-251.8(243.0)		240.0-253.3(247.0)
C(C_5Me_4Et)	Ta			230.0-253.2(243.3)
C(Ph_2C_2)	Nb	216.0-229(220.6)	225-232(229)	211-240(225)
	Ta	206.7-207.5(207.1)		
C(CO)	Nb	200.0-211.5(206)	202-204(203)	196-211.5(206.5)
	Ta	201	194	
C[b]	Nb	210-251(231)	227.7-234.6(230.6)	209-235(222)
	Ta	185-242(220)	207-233.0(220.2)	219.5-235.4(229.7)
H	Nb		150-176(164)	(167-190(179))[c]
	Ta	211.9	145-177.7(169.3)	(170-218(194))[c]
Cl	Nb	246.3-250.5(248.1)	246.4-248.3(247.4)	232.0-237.0(234.5) (255.7-257.0(256.5))[c]
	Ta	236.2-259.6(244.4)	243.9-247.9(245.4)	231.9-247.2(237.6) (246.1-269.0(257.3))[c]
P	Ta	250.7-265.0(259.4)	253.4-253.6(253.5)	

a. The mean value is in parenthesis. The values for Nb compounds taken from ref.4.
b. excluding all ligands listed above.
c. The values for a bridge atom (ligand).

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