

PHENOXOTANTALUM(V) COMPLEXES

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Summary

The reaction of the compounds TaXCl_4 ($\text{X} = \eta^5\text{-C}_5\text{H}_5$, $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ or Cl) with *o*-diphenols $4\text{-RC}_6\text{H}_3(\text{OH})_2$ ($\text{R} = \text{H}$, Me , Bu^t) gave the dialkoxides $\text{XCl}_2\text{Ta}(\text{O}_2\text{C}_6\text{H}_3\text{R})_2$, whereas the reaction with 4,4'-isopropylidenediphenol gave the monoalkoxides $[\text{TaXCl}_3]_2[(\text{OC}_6\text{H}_4)_2\text{CMe}_2]$. Osmometry shows the cyclopentadienyl derivatives with $\text{X} = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ and $\text{R} = \text{Me}$, Bu^t to be dimeric in benzene, but the halogeno complex with $\text{X} = \text{Cl}$ and $\text{R} = \text{Bu}^t$ to be trimeric. The new alkoxide complexes have been characterised by IR and ^1H and ^{13}C NMR spectroscopy.

Introduction

There is increasing interest in the chemistry of monocyclopentadienyl derivatives of the first group transition metals [1]. Many coordinatively unsaturated organo complexes of this type can be readily obtained by use of bulky ligands. Various alkoxo ligands have been used to stabilize high oxidation states and there have been numerous studies of the catalytic activity of these compounds in alkene [2] and methyl metacrylate [3] polymerization and particularly in alkene metathesis [4]. The ability of the alkoxo groups to form double or triple μ -oxo bridges leads to coordinatively saturated complexes when the alkoxo group substituent is not especially bulky. We describe here results observed in reactions of 4-R-substituted *o*-diphenols with TaXCl_4 ($\text{X} = \eta^5\text{-C}_5\text{H}_5$, $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ or Cl).

Results and discussion

The compound $\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4$, I, was made by two methods, the first involving $\text{Sn}(\text{C}_5\text{H}_4\text{SiMe}_3)\text{Bu}_3^n$ (prepared by a modification of the procedure reported for $\text{Sn}(\text{C}_5\text{H}_5)\text{Bu}_3^n$ [5]) and the second $\text{C}_5\text{H}_4(\text{SiMe}_3)_2$ [6], as the source of the trimethylsilylcyclopentadienyl ligand. Dropwise addition of the tin or silicon re-

* This paper is dedicated to Prof. R. Usón on his 60th birthday.

TABLE 1

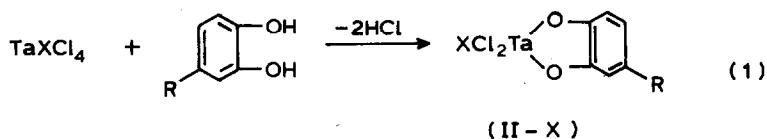
ANALYTICAL COMPOSITION AND PHYSICAL DATA FOR PHENOXY-TANTALUM(V) COMPLEXES

Complex	Colour	Analysis (Found (calcd.)(%))		Yield (%)	Molec. weight ^a Found. (calcd.)
		C	H		
I	Yellow-dark	20.7 (20.9)	3.0 (2.8)	80	-
II	Green	30.7 (31.0)	2.2 (2.1)	75	-
III	Green	32.7 (32.8)	2.7 (2.5)	75	-
IV	Green	37.2 (37.4)	3.6 (3.6)	90	-
V	Green-dark	34.0 (33.8)	3.6 (3.4)	80	-
VI	Red-dark	35.1 (35.2)	3.7 (3.7)	90	1000(511)
VII	Red-dark	38.9 (39.1)	4.4 (4.6)	85	1138(553)
VIII	Orange	20.1 (18.2)	1.8 (1.0)	65	-
IX	Orange	21.6 (20.5)	2.3 (1.5)	65	-
X	Orange	28.6 (26.6)	2.9 (2.7)	67	1390(518)
XI	Brown	32.4 (32.3)	2.6 (2.6)	95	-
XII	Green	33.8 (34.6)	3.7 (3.7)	90	-

^a In benzene solution

agents to a toluene solution of TaCl₅ led to the formation of complex I which was isolated in 80% yield.

Reactions of TaXCl₄ (X = η⁵-C₅H₅, η⁵-C₅H₄SiMe₃, Cl) with LiOBu^t and with alcohols such as Bu^tOH; 2,3,5-Me₃C₆H₂OH and 2,3,5-Bu^t₃C₆H₂OH in various molar ratios gave solutions from which solids containing a mixture of halo-alkoxo complexes with various degrees of substitution were obtained. However, new chelate diphenoxo tantalum(V) complexes were obtained by heating a toluene solution of a mixture of TaXCl₄ (X = η⁵-C₅H₅, η⁵-C₅H₄SiMe₃, Cl) and various 4-R-*o*-diphenols in 1/1 molar ratio, according to eq. 1.



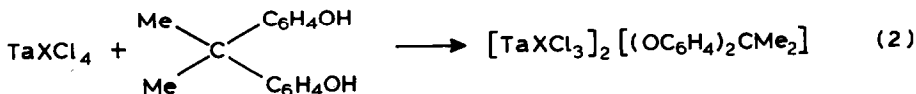
(X = η⁵-C₅H₅ ; R = H(II) ; Me(III) ; Bu^t(IV) ;

X = η⁵-C₅H₄SiMe₃ ; R = H(V) ; Me(VI) ; Bu^t(VII) ;

X = Cl ; R = H(VIII) ; Me(IX) and Bu^t(X))

Complexes II–IV are only slightly soluble in toluene and benzene and moderately soluble in methanol, whereas V–X are readily soluble in toluene, benzene and chloroform. They are not very stable in air, since they are readily hydrolyzed, and reaction takes place in polar solvents; the possibility of isolating adducts with N and O donors is being studied.

A similar reaction with 4,4'-isopropylidenediphenol in a 2/1 molar ratio gave very insoluble solids which were identified as the monoaryloxo compounds (eq. 2).



(X = $\eta^5\text{-C}_5\text{H}_5$ (XI) ; $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ (XII))

Complexes XI–XII are only slightly soluble in methanol.

All the compounds gave satisfactory analyses (see Table 1).

Infrared spectra

All the spectra show the characteristic absorption bands of the η^5 -cyclopentadienyl group [7], the most significant being the bands at $850\text{--}860\text{ cm}^{-1}$ for the η^5 -cyclopentadienyl ring and that at $1260\text{--}1275\text{ cm}^{-1}$ for the trimethylsilyl group [8]. They also show bands due to the internal vibrations of the alkoxy groups. Other bands assignable to the metal–chlorine bonds and to the C–O–Ta system are shown in Table 2. The $\nu(\text{Ta-Cl})$ stretching vibrations appear between 305 and 360 cm^{-1} [9], although in complexes involving $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$, the presence of absorptions due to the SiMe_3 group [10] makes definitive assignment more difficult. The region between 900 and 1125 cm^{-1} contains two or more bands which must be assigned to $\nu(\text{C-O})$ vibrations and there are always two in the region $470\text{--}590\text{ cm}^{-1}$ which can be assigned to $\nu(\text{M-O})$ [11]. Many studies of these two regions have been made in

TABLE 2

SELECTED IR BANDS (Nujol mulls) (cm^{-1}) FOR PHENOXO-TANTALUM(V) COMPLEXES

Complex	$\nu(\text{Ta-Cl})$	$\nu(\text{C-O})$	$\nu(\text{Ta-O})$
I	315 vs,b	930 m; 1025 s	545 m; 475 w
II	320 s,b	1125 m; 1015 m 950 m; 900 m	590 w; 475 w
III	320 vs,b	1075 w; 975 m; 900 w	585 m; 470 m
IV	310 s	1100 s,b; 1025 s, b 915 m	580 w; 525 w
V	325 vs	1090 s,b; 915 s	515 m
VI	305 s,b	1120 s,b; 1050 s,b 950 s	565 w; 505 m
VII	345 vs,vb	1210 m; 1060 s 930 s; 890 m	590 s; 540 s; 470 m
VIII	360 vs,b	1125 s; 1105 s 1015 m; 935 m	585 w; 555 w; 470 w
IX	355 vb	1135 m; 980 m 900 m,b	560 w; 495 vw

order to distinguish between terminal and bridge alkoxo groups [12] but complexity of the absorption bands observed precludes definitive assignment for our complexes, which probably contain both terminal and bridge systems.

NMR spectra and structural assignment

Table 3 gives ^1H NMR data, Table 4 the ^{13}C NMR data.

The ^1H spectrum of complex I shows a multiplet between δ 6.50 and 6.68 ppm for the cyclopentadienyl protons and a singlet due to the SiMe_3 group at δ 0.10 ppm in benzene- d_6 . The ^{13}C spectrum of this compound shows only two resonances for the ring carbon atoms instead of the expected three observed for similar complexes [13]. The less intense signal at δ 127.5 ppm must be assigned to the substituted carbon atom, whereas the more intense at δ 126.7 ppm corresponds to the remaining four carbon atoms which are unexpectedly equivalent or so similar that they cannot be distinguished by our spectrometer. The SiMe_3 carbon atoms give a singlet at δ 0.27 ppm. From these data it seems that I may have a four-legged piano stool structure, although some type of association by chlorine bridges cannot be discounted.

The IR spectra of the alkoxo cyclopentadienyl complexes II–VII suggest the presence of only terminal metal–chlorine bonds, but bridging alkoxo groups could be present. Molecular weights measurements in benzene gave values of 1000 (calcd. 511) and 1138 (calcd. 553) for VI and VII, respectively, confirming the dimeric nature of these compounds. This is also confirmed by the NMR studies, and in this

TABLE 3

^1H NMR DATA FOR PHENOXO-TANTALUM(V) COMPLEXES (δ (ppm) with respect to TMS (multiplicity))

Complex	Solvent	C_5H_5	$\text{C}_5\text{H}_4\text{R}$	SiMe_3	$\text{R}'\text{C}_6\text{H}_3\text{O}_2$	$\text{R}'\text{C}_6\text{H}_3\text{O}_2$		CMe_2
						$\text{R}'=\text{Me}$	$\text{R}'=\text{Bu}^t$	
I	CDCl_3 C_6D_6		^a	0.38(s)				
			6.68(m)	0.10(s)				
			6.50(m)					
II	CD_3OD	6.70(s)			6.91(m)			
III	CD_3OD	6.60(s)			6.40(m)	1.80(s)		
IV	CD_3OD	6.67(s)			6.80(m)		1.22(s)	
V	C_6D_6		7.66(m)					
			6.40(m)	0.22(s)	6.56(m)			
VI	C_6D_6		6.63(b)					
VII	C_6D_6		6.07(b)	0.19(s)	6.45(d)	1.83(s)		
			6.68(m)	0.23(s)				1.18(s)
VIII	CDCl_3		6.43(t)	0.25(s)	6.56(b)			1.06(s)
IX	CDCl_3				6.45(b)			
X	CDCl_3				6.93(b)	2.37(m)		
					6.90(b)		1.37(m)	
XI	CDCl_3	6.68(s)		0.38(s)	^a			1.54(s)
					7.00(d)			
XII	CD_3OD		^a		6.62(d)			1.50(s)

^a Overlapped with solvent.

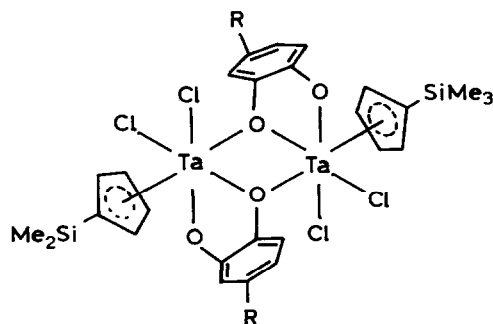
TABLE 4
 ^{13}C -(^1H) NMR SPECTRA FOR TANTALUM(V) COMPLEXES

Complex	Solvent	$\text{C}_5\text{H}_4\text{R}$		$\text{R}-\text{SiMe}_3$	$\text{O}_2\text{H}_3\text{C}_6\text{R}'$						R'		
		C(1)	C(2,3,4,5)		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Me	Bu ^t	
I	CH_2Cl_2	127.5	126.7	-0.30									
V		124.4	121.9	0.18	121.1	119.7	115.6	^a	^a	115.1			
VI	C_6H_6	122.6	121.1	0.19	^a	119.7	118.1	^a	^a	114.8	19.5		
VII		124.0	120.9	0.37 0.57	144.9	119.7	118.3	138.3	^a	112.9			C ^t 32.7 Me 32.0; 32.2
VIII					120.6	120.6	117.7	153.6	148.7	119.2			
IX	CH_2Cl_2				^a	123.7	118.1	136.6	^a	119.2	21.6		
X					^a	146.2	116.1	148.9	118.6	119.6			C ^t 34.8 Me 31.9

^a Not observed.

respect complex VII deserves special mention. The ^1H spectrum of VII shows complex signals for the cyclopentadienyl protons in benzene- d_6 , two singlets for t-butyl at δ 1.18 and 1.06 ppm and also for SiMe_3 at δ 0.23 and 0.25 ppm, but both t-Bu and SiMe_3 give only singlets at δ 1.02 ppm and δ 0.16 ppm, respectively, when the spectrum is recorded in $\text{MeOH}-d_4$. This behaviour confirms that an alkoxo bridge dimer is present in benzene, and that MeOH cleaves the bridge to give mononuclear species by coordination of the solvent.

The ^{13}C NMR spectrum correspondingly shows two resonances due to the ring carbon atoms, the less intense at δ 124.0 ppm being attributed to the substituted carbon atom and the more intense at δ 120.9 ppm to the remaining ring carbon atoms, but two singlets are observed for the SiMe_3 group, at δ 0.37 and 0.57 ppm, and also for the t-butyl substituent, at δ 32.0 and 32.2 ppm. A dimeric structure containing two alkoxo bridges formed by two different oxo groups could account for this behaviour.



Probably the same structure can be assigned to all complexes II–VII although split signals were not always observed. The ^1H spectra of complexes II–IV and XI show a singlet for the cyclopentadienyl protons at δ 6.60–6.70 ppm, whereas a complex resonance is observed for the ring $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ protons at δ 6.07–7.66 ppm for complexes V–VII and XII. A singlet due to the SiMe_3 protons at δ 0.19–0.38 ppm is also observed for complexes V, VI and XII. The phenyl protons of the alkoxo ligand give a multiplet between δ 6.40 and 7.00 ppm. The methyl group of the alkoxo ligand gives a singlet, at δ 1.80 and 1.83 ppm, respectively, for III and VI and the t-butyl protons also give a singlet at δ 1.22 ppm for IV.

The $\{^1\text{H}\}$ - ^{13}C NMR spectra show only two resonances for the ring carbon atoms for all $\text{C}_5\text{H}_4\text{SiMe}_3$ complexes and a singlet between δ 0.18 and 0.57 ppm for the SiMe_3 carbon atoms; two Me resonances at δ 19.5 and 20.3 ppm, are observed for complex VI.

The phenyl carbon atoms of the catecholate groups give various resonances between δ 112.9 and 153.6 ppm whose chemical shifts are reasonably consistent with values based on expected displacements produced by effect of the substituents on the aromatic ring [14].

No crystals suitable for X-ray diffraction studies could be obtained.

The ^1H NMR spectra of the halogeno complexes VIII–X also show a multiplet due to the phenyl protons of the alkoxo ligand between δ 6.45 and 6.93 ppm. Complexes IX–X show complex resonances for methyl and t-butyl groups in both ^1H and ^{13}C NMR spectra. The molecular weight in benzene for complex X was 1390 (theor. 518), so that this complex, and probably also VIII and IX, must be formulated as trimers. The observed NMR behaviour can be interpreted in terms of the existence of a mixture of different isomers with alkoxo bridges.

No assignment can be made for XI–XII.

Experimental

All the experiments were carried out under vacuum, or under N_2 or Ar atmosphere using Schlenk techniques. Solvents were purified by distillation under N_2 from sodium benzophenone, except for toluene which was dried over calcium hydride.

$\text{Ta}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_4$ [5b], $\text{C}_5\text{H}_5\text{SiMe}_3$ and $\text{C}_5\text{H}_4(\text{SiMe}_3)_2$ [6] were prepared as previously described. Commercial catechol (Riedel) and 4-Me- and 4-Bu^t-catechol (Fluka) were used without purification, but 4,4'-isopropylidene diphenol (Alfa) and TaCl_5 (Fluka) were purified by sublimation.

C and H analyses were made with a 240B Perkin–Elmer microanalyzer. IR spectra were recorded in a 599 Perkin–Elmer spectrophotometer as Nujol mulls between CsI plates. ^1H and ^{13}C NMR spectra were run in a FT-80A Varian spectrometer. Molecular weight measurements were carried out with a Knauer vapor pressure osmometer.

$\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4$ (I)

Method A. A toluene (20 ml) solution of $\text{Sn}(\text{C}_5\text{H}_4\text{SiMe}_3)\text{Bu}_3^n$ (5.42 ml, 13.9 mmol) was added dropwise to an orange toluene (250 ml) solution of TaCl_5 (5.00 g, 13.9 mmol). A deep yellow solid rapidly separated. Stirring at room temperature

was continued for 4 h, then the yellow solid was filtered off, repeatedly washed with n-pentane, and identified as complex I. Yield 4.30 g, 80%.

Method B. A toluene solution (20 ml) of $C_5H_4(SiMe_3)_2$ (4.40 g, 20.9 mmol) was slowly added to an orange toluene (500 ml) solution of $TaCl_5$ (7.5 g, 20.9 mmol). After 12 h stirring at room temperature the brown solution was filtered then evaporated almost to dryness to give a yellow crystalline solid. The solid was filtered off, repeatedly washed with n-pentane, and identified as complex I. Yield: 7.50 g, 80%.

$Ta(\eta^5-C_5H_5)Cl_2(4-R-C_6H_3O_2)$, $R = H, Me, Bu'$ (II–IV)

$4-RC_6H_3(OH)_2$ (1.29 mmol) was added to a toluene (100 ml) suspension of $Ta(\eta^5-C_5H_5)Cl_4$ (0.50 g, 1.29 mmol). The mixture was stirred for 8 h at 90–95°C during which HCl was evolved. The resulting green solids were filtered off washed with n-pentane, and characterized as complexes II–IV. Yields 75%.

$Ta(\eta^5-C_5H_4SiMe_3)Cl_2(4-R-C_6H_3O_2)$, $R = H, Me, Bu'$ (V–VII)

2.00 mmol of $4-RC_6H_3(OH)_2$ were added to a toluene (25 ml) solution of $Ta(\eta^5-C_5H_4SiMe_3)Cl_4$ (0.92 g, 2.0 mmol). The mixture was stirred for 4 h, at 90–95°C, and the solution was then filtered and evaporated to ~ 5 ml. Addition of petroleum ether and cooling gave deep green ($R = H$) or red ($R = Me, Bu'$) crystals, which were identified as complexes V–VII. Yields 95%.

$TaCl_3(4-R-C_6H_3O_2)$, $R = H, Me, Bu'$ (VIII–X)

$4-RC_6H_3(OH)_2$ (6.95 mmol) was added to a toluene (150 ml) solution of $TaCl_5$ (2.5 g, 6.95 mmol). The solution was stirred for 4 h at 90–95°C then filtered. Concentration of the filtrate to ca. 5 ml and addition of hexane (5 ml) gave orange microcrystals of the title compounds VIII–X. Yields 65%.

$[TaCpCl_3]_2[(C_6H_4O)_2CMe_2]$ $Cp = \eta^5-C_5H_5, \eta^5-C_5H_4SiMe_3$ (XI–XII)

$Me_2C(C_6H_4OH)_2$ (0.17 g, 0.75 mmol) was added to toluene (70 ml) solutions of $TaCpCl_4$ (1.50 mmol) and the mixture was stirred for 6 h under reflux. When evolution of HCl was complete the insoluble brown or green solids were filtered off, washed twice with petroleum ether (50–60°C), and identified as complexes XI–XII. Yields 90%.

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