The Synthesis and Structure of Group 5 Metal Alkyl and Alkylidene Complexes containing 2,6-Dialkylphenoxide Ligands: *X*-Ray Crystal Structures of $[Ta(OC_6H_3Me_2\text{-}2,6)_2(CH_2Ph)_3]$, $[Ta(OC_6H_3Me_2\text{-}2,6)_4Me]$, and $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2(=CHSiMe_3)(CH_2SiMe_3)]$†

Linda R. Chamberlain and Ian P. Rothwell*
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, U.S.A.
Kirsten Folting and John C. Huffman
Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, U.S.A.

A number of alkyl and alkylidene complexes of niobium and primarily tantalum containing 2,6-dialkylphenoxide ligation, $OC_6H_3R_2$-2,6 (R = Me, Pr^i, or Bu^t) have been synthesized and characterized. For the sterically less demanding 2,6-dimethyl- and 2,6-di-isopropyl-phenoxides a series of compounds $[Ta(OC_6H_3R_2\text{-}2,6)_2(CH_2R')_3]$ (R′ = H, SiMe$_3$, or Ph) can be readily obtained by alkylation of the corresponding mixed chloro-aryloxide. The remaining two aryloxides are more resistant to further substitution. Spectroscopic evidence supports the σ-bonded compounds adopting a trigonal-bipyramidal structure with *trans*-axial aryloxide ligands. This structure was confirmed by a single-crystal *X*-ray diffraction study on $[Ta(OC_6H_3Me_2\text{-}2,6)_2(CH_2Ph)_3]$. The di- and mono-alkyls $[Ta(OC_6H_3Me_2\text{-}2,6)_3(CH_2Ph)_2]$ and $[Ta(OC_6H_3Me_2\text{-}2,6)_4Me]$ have also been isolated and the latter shown to adopt a square-pyramidal structure in the solid state with an axial methyl group. In contrast the reaction of $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl_3]$ with $Li(CH_2SiMe_3)$ or $Mg(CH_2Ph)_2$ leads to the mixed alkyl–alkylidene complexes $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2(=CHR')(CH_2R')]$ (R′ = SiMe$_3$ or Ph). The presence of the alkylidene functional group was confirmed both spectroscopically and by a single-crystal *X*-ray diffraction study on the trimethylsilyl derivative. A related complex, $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(=CHSiMe_3)(CH_2SiMe_3)]$, was obtained by photolysis of $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2SiMe_3)_3]$.

We have recently reported that bulky 2,6-dialkylphenoxide ligands can support a variety of organometallic chemistry at both Group 4 and 5 metal centres. In particular CH bond activation,[1] photochemical[2] and thermal[3] α-hydrogen abstraction to produce alkylidene functional groups, and aryl isomerization *via* benzyne intermediates[4] has been demonstrated with Ta^V aryloxide complexes. We wish to report here a more extensive study of the synthesis, structure, and reactivity of a number of Group 5 metal alkyl and alkylidene complexes containing aryloxide coligation, in particular 2,6-dimethyl-, 2,6-di-isopropyl-, and 2,6-di-t-butyl-phenoxides. In the following paper we discuss in more detail the electronic spectra and photochemical reactivity of these complexes.[5]

Results and Discussion

Synthesis of Compounds.—Selected ^1H and ^{13}C n.m.r. data for the compounds obtained in this study are collected in Table 1. The synthetic methods used will be discussed separately for the three types of 2,6-dialkylphenoxides.

(*a*) 2,6-*Dimethylphenoxide Complexes.*—Treatment of either $[M(OC_6H_3Me_2\text{-}2,6)_5]$ or $[M(OC_6H_3Me_2\text{-}2,6)_3Cl_2]$ (M = Nb or Ta)[6] with the alkylating agents LiMe, $Li(CH_2SiMe_3)$, or $Mg(CH_2Ph)_2$ in hydrocarbon solvents has allowed us to isolate the mixed alkyl–aryloxides (**1**)—(**5**) shown in Table 1. Excellent yields of the trialkyls (**1**)—(**3**) are readily obtained when the dichlorides are reacted with three equivalents of the lithium reagents, equation (1), or 1.5 equivalents of $Mg(CH_2Ph)_2$.

$$[M(OC_6H_3Me_2\text{-}2,6)_3Cl_2] + 3Li(CH_2R') \longrightarrow [M(OC_6H_3Me_2\text{-}2,6)_2(CH_2R')_3] + 2LiCl + Li(OC_6H_3Me_2\text{-}2,6) \quad (1)$$

The two remaining aryloxy ligands in (**2**) and (**3**) are resistant to substitution by $Li(CH_2SiMe_3)$ or $Mg(CH_2Ph)_2$. However, on continued exposure to methyl-lithium in hydrocarbon solvents, (**1**) produces a black mixture indicative of the formation of the thermally unstable pentamethyl, $[MMe_5]$ (M = Nb or Ta).[7]

During reaction of $[Ta(OC_6H_3Me_2\text{-}2,6)_3Cl_2]$ with either $Li(CH_2SiMe_3)$ or $Mg(CH_2Ph)_2$ in C_6D_6, spectroscopic evidence (^1H n.m.r.) for the presence of the intermediate dialkyls was obtained. Furthermore, the dibenzyl (**4**) could be obtained in good yield using only one equivalent of $Mg(CH_2Ph)_2$. However, when $[Ta(OC_6H_3Me_2\text{-}2,6)_3Cl_2]$ is reacted with two equivalents of $LiCH_3$ (suspended in C_6H_6) a mixture of the mono-, bi-, and tri-methyl compounds is given from which the complex $[Ta(OC_6H_3Me_2\text{-}2,6)_4Me]$ (**5**) is readily separated due to its insolubility in pentane. Reaction of (**5**) with two more equivalents of LiMe gives (**1a**). The formation of (**5**) from the dichloride indicates that $Li(OC_6H_3Me_2\text{-}2,6)$ generated during the formation of (**1a**) back-reacts to produce $[Ta(OC_6H_3Me_2\text{-}2,6)_4Cl]$ which then becomes alkylated. Monoalkyl compounds related to (**5**) were not detected when using $Li(CH_2SiMe_3)$ or $Mg(CH_2Ph)_2$. The trialkyls (**1**) and (**2**) were also produced by reacting $[M(OC_6H_3Me_2\text{-}2,6)_5]$ (M = Nb or Ta) with three equivalents of the corresponding lithium reagent.

(*b*) 2,6-*Di-isopropylphenoxide Complexes.*—The sparingly

---

† Tribenzylbis(2,6-dimethylphenoxo)-, tetrakis(2,6-dimethylphenoxo)methyl-, and bis(2,6-di-t-butylphenoxo)(trimethylsilylmethyl)(trimethylsilylmethylene)-tantalum(v).

Supplementary data available (No. SUP 56644, 5 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: cal = 4.184 J.

Table 1. Hydrogen-1 and ^{13}C n.m.r. data (in [$^2H_6$]benzene, 99.5% ^{2}H)

Compound	δ(^{1}H)	δ(^{13}C)
(**1a**) $[Ta(OC_6H_3Me_2\text{-}2,6)_2Me_3]$	0.97 (s, 9 H, Ta–CH_3), 2.48 (s, 12 H, $C_6H_3\mathit{Me}_2$), 6.9—7.2 (m, 6 H, C_6H_3)	57.4 (Ta–CH_3), 17.6 ($C_6H_3\mathit{Me}_2$)
(**1b**) $[Nb(OC_6H_3Me_2\text{-}2,6)_2Me_3]$	1.12 (s, 9 H, Nb–CH_3), 2.26 (s, 12 H, $C_6H_3\mathit{Me}_2$), 6.8—7.1 (m, 6 H, C_6H_3)	47.1 (Nb–CH_3), 17.6 ($C_6H_3\mathit{Me}_2$)
(**2**) $[Ta(OC_6H_3Me_2\text{-}2,6)_2(CH_2SiMe_3)_3]$	1.19 (s, 6 H, Ta–$C\mathit{H}_2SiMe_3$), 0.14 (s, 27 H, $SiMe_3$), 2.57 (s, 12 H, $C_6H_3\mathit{Me}_2$), 6.7—7.2 (m, 6 H, C_6H_3)	70.5 (Ta–CH_2), 1.4 ($SiMe_3$), 18.6 ($C_6H_3\mathit{Me}_2$)
(**3**) $[Ta(OC_6H_3Me_2\text{-}2,6)_2(CH_2Ph)_3]$	2.63 (s, 6 H, Ta–$C\mathit{H}_2Ph$), 2.31 (s, 12 H, $C_6H_3\mathit{Me}_2$), 6.8—7.3 (m, aromatics)	34.0 (Ta–$\mathit{C}H_2Ph$), 20.8 ($C_6H_3\mathit{Me}_2$)
(**4**) $[Ta(OC_6H_3Me_2\text{-}2,6)_3(CH_2Ph)_2]$	2.81 (s, 4 H, Ta–$C\mathit{H}_2Ph$), 2.08 (s, 18 H, $C_6H_3\mathit{Me}_2$), 6.8—7.3 (m, aromatics)	53.9 (Ta–$\mathit{C}H_2Ph$), 17.1 ($C_6H_3\mathit{Me}_2$)
(**5**) $[Ta(OC_6H_3Me_2\text{-}2,6)_4Me]$	1.94 (s, 3 H, Ta–CH_3), 2.19 (s, 24 H, $C_6H_3\mathit{Me}_2$), 6.7—7.0 (m, 12 H, C_6H_3)	43.0 (Ta–CH_3), 16.6 ($C_6H_3\mathit{Me}_2$)
(**6**) $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Me_3]$	0.93 (s, 9 H, Ta–CH_3), 1.24 (d, 24 H, $CHMe_2$), 3.60 (spt, 4 H, $C\mathit{H}Me_2$), 6.9—7.3 (m, 6 H, C_6H_3)	58.8 (Ta–CH_3), 24.3 ($CH\mathit{Me}_2$), 28.0 ($\mathit{CH}Me_2$)
(**7**) $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2SiMe_3)_3]$	1.08 (s, 9 H, Ta–CH_2), 0.11 (s, 27 H, $SiMe_3$), 1.34 (d, 24 H, $CH\mathit{Me}_2$), 3.81 (spt, 4 H, $C\mathit{H}Me_2$), 6.9—7.3 (m, 6 H, C_6H_3)	71.7 (Ta–CH_2), 3.1 ($SiMe_3$), 24.8 ($CHMe_2$), 27.4 ($\mathit{C}HMe_2$)
(**8**) $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2Ph)_3]$	2.73 (s, 6 H, Ta–$C\mathit{H}_2Ph$), 1.28 (d, 24 H, $CH\mathit{Me}_2$), 3.33 (spt, 4 H, $C\mathit{H}Me_2$), 6.8—7.2 (m, aromatics)	61.5 (Ta–$\mathit{C}H_2Ph$), 24.2 ($CH\mathit{Me}_2$), 27.3 ($\mathit{C}HMe_2$)
(**9**) $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2({=}CHSiMe_3)\text{-}(CH_2SiMe_3)]$	8.68 (s, 1 H, Ta=CH), 0.24, 0.21 (s, 9 H + 9 H, $Si\mathit{Me}_3$), 1.17, 1.20 (d, 12 H, $CH\mathit{Me}_2$), 3.47 (spt, 4 H, $C\mathit{H}Me_2$), 6.9—7.3 (m, 6 H, C_6H_3)	226.6 (Ta=CH), 48.3 (Ta–CH_2), 2.6, 3.9 ($SiMe_3$), 23.1, 23.9 ($CH\mathit{Me}_2$), 28.5 ($\mathit{C}HMe_2$)
(**10**) $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2({=}CHSiMe_3)\text{-}(CH_2SiMe_3)]$	8.60 (s, 1 H, Ta=$C\mathit{H}$), 1.35 (s, 2 H, Ta–$C\mathit{H}_2SiMe_3$), 0.21, 0.39 (s, 9 H + 9 H, $SiMe_3$), 1.41 (s, 36 H, Bu^t), 6.7—7.2 (m, 6 H, C_6H_3)	234.6 (Ta=CH), 56.7 (Ta–CH_2), 2.4, 3.6 ($SiMe_3$), 31.6 ($C\mathit{Me}_3$), 33.1 ($\mathit{C}Me_3$)
(**11**) $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2({=}CHPh)\text{-}(CH_2Ph)]$	9.22 (s, 1 H, Ta=CH), 3.20 (s, 2 H, Ta–$C\mathit{H}_2Ph$), 1.30 (s, 36 H, Bu^t), 6.7—7.4 (m, aromatics)	255.0 (Ta=CH), 70.8 (Ta–CH_2), 34.6 ($\mathit{C}Me_3$), 30.9 ($C\mathit{Me}_3$)

soluble chloride $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3Cl_2]$ reacts with three equivalents of LiMe, $Li(CH_2SiMe_3)$, or $Mg(CH_2Ph)_2$ to give good yields of the corresponding trialkyls (**6**), (**7**), and (**8**). Again the trimethyl compound undergoes decomposition upon further treatment with LiMe. No attempt to isolate partially alkylated intermediates was made although they could be detected by ^{1}H n.m.r. Upon photolysis solutions of $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2SiMe_3)_3]$ (**7**) undergo a clean conversion to the mixed alkyl–alkylidene complex $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2({=}CHSiMe_3)(CH_2SiMe_3)]$ (**9**) with the elimination of one equivalent of $SiMe_4$, equation (2). In contrast, photolysis of

$$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2SiMe_3)_3] \xrightarrow{h\nu} [Ta(OC_6H_3Pr^i_2\text{-}2,6)_2({=}CHSiMe_3)(CH_2SiMe_3)] + SiMe_4 \quad (2)$$

(**9**)

either $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2Ph)_3]$ (**8**) or $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Me_3]$ (**6**) did not lead to any isolable alkylidene compounds but instead $PhCH_2CH_2Ph$ and methane respectively with unidentified metal products.[5] Attempts to prepare the alkylidene complex (**9**) by heating toluene solutions of (**7**) at 150 °C failed, yielding only traces of $SiMe_4$ and decomposition products.

(*c*) 2,6-*Di-t-butylphenoxide Complexes*.—The synthesis, structure, and reactivity of the trimethyl complex $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Me_3]$ obtained from $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl_3]$ and LiMe (3:1) has been reported.[8,9] In contrast, alkylation of the trichloride with $Li(CH_2SiMe_3)$ or $Mg(CH_2Ph)_2$ results in the room-temperature formation of the alkyl–alkylidene compounds (**10**) and (**11**) with the elimination of one equivalent of $SiMe_4$ or toluene respectively, equations (3) and (4).

$$[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl_3] + 3Li(CH_2SiMe_3) \longrightarrow [Ta(OC_6H_3Bu^t_2\text{-}2,6)_2({=}CHSiMe_3)(CH_2SiMe_3)] + 3LiCl + SiMe_4 \quad (3)$$

(**10**)

$$[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl_3] + 1.5Mg(CH_2Ph)_2 \longrightarrow [Ta(OC_6H_3Bu^t_2\text{-}2,6)_2({=}CHPh)(CH_2Ph)] + 1.5MgCl_2 + PhMe \quad (4)$$

(**11**)

The ease with which α-hydride abstraction takes place for derivatives of 2,6-di-t-butylphenoxide is clearly a result of the extreme steric pressure exerted at the metal by this ligand. A somewhat related complex has been reported by Andersen,[10] formed using the sterically demanding amido ligand, $N(SiMe_3)_2$.

The trimethylsilylmethylidene complex (**10**) thermally undergoes intramolecular activation of the carbon–hydrogen bonds of the t-butyl groups of the aryloxide ligands to give good yields of the bis-cyclometallated complex (**12**), as shown in equation (5).[3]

$$[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2({=}CHSiMe_3)(CH_2SiMe_3)] \xrightarrow{80\ ^\circ C} [Ta(OC_6H_3Bu^tCMe_2CH_2)_2(CH_2SiMe_3)] + SiMe_4 \quad (5)$$

(**12**)

The overall formation of this product can involve a number of possible pathways.[3] However, it appears likely that the first step of the reaction involves the addition of one of the t-butyl CH bonds across the tantalum–carbon double bond. Support for this idea comes from the observed room-temperature ring closure of the related methylidene complex, $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2({=}CH_2)Me]$.[2,9]

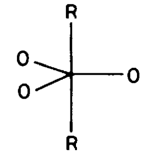
Hydrogen-1 *and Carbon*-13 *N.M.R. Spectroscopic Properties*.—All of the trialkyl compounds exhibit temperature-independent ^{1}H n.m.r. spectra with one set of alkyl and aryloxide signals. Furthermore, the methylene protons in the trimethylsilyl and benzyl derivatives resonate as sharp singlets. These data are consistent with all of these complexes adopting a trigonal-bipyramidal (t.b.p.) geometry with *trans*-axial aryloxide ligands as confirmed in the solid state previously for $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Me_3]$[8,9] and in this study for (**3**) (see below). However, if another, lower symmetry co-ordination environment is present in solution then the molecules must be fluxional on the n.m.r. time-scale.

For the dibenzyl complex (**4**) one sharp set of benzyl and 2,6-dimethylphenoxide peaks is present in the ^{1}H n.m.r. spectrum at room temperature. On cooling solutions of the complex the benzyl methylene protons remain as a sharp singlet but the methyl resonances of the aryloxide broaden and resolve into

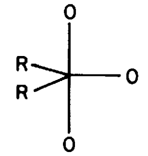
Table 2. Data for crystal structure analyses[a]

	(3)	(5)	(10)
Formula	$C_{37}H_{39}O_2Ta$	$C_{33}H_{39}O_4Ta$	$C_{36}H_{63}O_2Si_2Ta$
M	696.66	680.62	765.01
Space group	$P2_1/n$	$P4/n$	$P2_1/c$
a/Å	13.720(4)	14.156(4)	11.37(4)
b/Å	15.399(4)	14.156(4)	25.402(15)
c/Å	14.952(4)	7.636(1)	17.113(7)
β/°	99.94(2)		126.69(2)
Z	4	2	4
U/Å^3	3 111.43	1 530.20	3 847.52
D_c/g cm^{-3}	1.487	1.477	1.321
Crystal size (mm)	0.08 × 0.12 × 0.12	*b*	0.10 × 0.12 × 0.12
Crystal colour	yellow	colourless	yellow
μ/cm^{-1}	35.193	35.805	29.098
Temp. (°C)	−155	−160	−164
Background counts (s)	5	10	4
2θ range (°)	6—45	6—45	6—40
Data collected	4 688	2 826	3 962
Unique data	4 075	1 766	3 605
Unique data	3 515[c]	1 684[c]	2 450[d]
$R(F)$	0.033	0.023	0.080
$R'(F)$	0.034	0.025	0.068
Goodness of fit	0.863	0.751	1.277
Largest Δ/σ	0.05	0.05	0.05

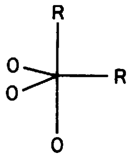
[a] Data common to all three structures: Mo-K_α radiation (λ = 0.710 69 Å); detector aperture 3.0 mm wide × 4.0 mm high (22.5 cm from crystal), sample to source distance 23.5 cm, take off angle 2.0°, scan speed 4.0° min^{-1}, scan width (2.0 + 0.692 tan θ)°. [b] Crystal dimensions were: face −1 −1 0, *d* = 0.0400, face 1 1 0, *d* = 0.0400, face 0 0 1, *d* = 0.0400, face 0 0 −1, *d* = 0.0400, face 1 −1 0, *d* = 0.0410, face −2 2 1, *d* = 0.0400 mm. [c] $F_0 > 3.0\sigma(F)$. [d] $F_0 > 2.33\sigma(F)$.



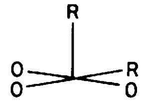
(a)



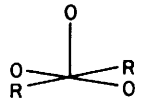
(b)



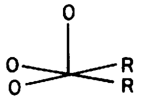
(c)



(d)



(e)



(f)

two signals of intensity 2 : 1. Of the six possible diastereoisomers of this complex based on idealized t.b.p. and square-pyramidal geometries, these data are consistent with the presence in solution of either isomer (**b**) or (**e**) for complex (**4**). From the coalescence temperature (T_c) the free energy of activation for exchange of non-equivalent aryloxide ligands in complex (**4**) can be estimated as $\Delta G^\ddagger = 12.3 \pm 0.5$ kcal mol^{-1} (−25 °C).

The monomethyl complex (**5**) shows only one type of aryloxide methyl group in the ^{1}H n.m.r. spectrum even at low temperatures. This observation is consistent with the observed solid-state structure of the complex (see below), containing a square-pyramidal co-ordination about tantalum with an axial methyl group.

For the complexes (**9**)—(**11**) the presence of the alkylidene functional groups is readily detected in the ^{1}H n.m.r. spectrum by the characteristically low-field resonance of the α-CH proton. The rest of the ^{1}H n.m.r. resonances are unexceptional except for the isopropyl resonances of the aryloxide ligands in (**9**). Although only one type of Pr^i group is present with a single C*H*Me$_2$ septet, the methyl groups appear as two non-equivalent (diastereotopic) doublets. This is consistent with the lack of a plane of symmetry through the isopropyl group in these four-co-ordinate compounds.

In the ^{13}C n.m.r. spectrum of the compounds in Table 1, the Ta–C carbon is found typically to resonate in the 40—70 p.p.m. region usual for early transition metal alkyls, while the alkylidene carbons, Ta=C, in complexes (**9**)—(**11**) are observed at 220—260 p.p.m. downfield of SiMe$_4$, Figure 1. This low-field position of early transition metal alkylidene carbons is characteristic.

Solid-state Structures.—In order more fully to characterize these types of complexes the solid-state structures of the tribenzyl (**3**), monomethyl (**5**), and the alkylidene complex (**10**) have been determined by *X*-ray crystallography. Crystallographic data are collected in Table 2 while Table 3 contains the fractional co-ordinates of the three molecules.

[Ta(OC$_6$H$_3$Me$_2$-2,6)$_2$(CH$_2$Ph)$_3$]. An ORTEP view of the molecule along with the atom numbering scheme is shown in Figure 2. Table 4 contains selected bond distances and angles. It can be seen that the molecule adopts a geometry about the metal best described as trigonal bipyramidal with *trans*-axial aryloxide ligands. This geometry is similar to that found for the compounds [Ta(OC$_6$H$_3$Bu$^t{}_2$-2,6)$_2$Me$_3$] and [Ta(OC$_6$H$_2$Bu$^t{}_2$-2,6-OMe-4)$_2$Me$_3$] but there are some interesting differences.[9] Although in both cases the O–Ta–O angle is distorted from linearity (*ca.* 165°), in the case of these last two molecules the aryloxide oxygens are bent *towards* a unique methyl group in order to relieve the steric crowding caused by the 2,6-di-t-butyl substituents. However, for the less crowded complex (**3**) obtained in this study the aryloxide oxygens bend *away* from a unique alkyl group, C(34). We believe this deformation from the expected, true t.b.p. geometry is again due to steric interaction between the 2,6-dimethyl substituents and the alkyl groups. The plane of the benzene rings of the aryloxides is such that one methyl group of each aryloxide in (**3**) is pointing at the unique Ta–CH$_2$Ph function, and hence the deformation from linearity helps relieve this steric pressure.

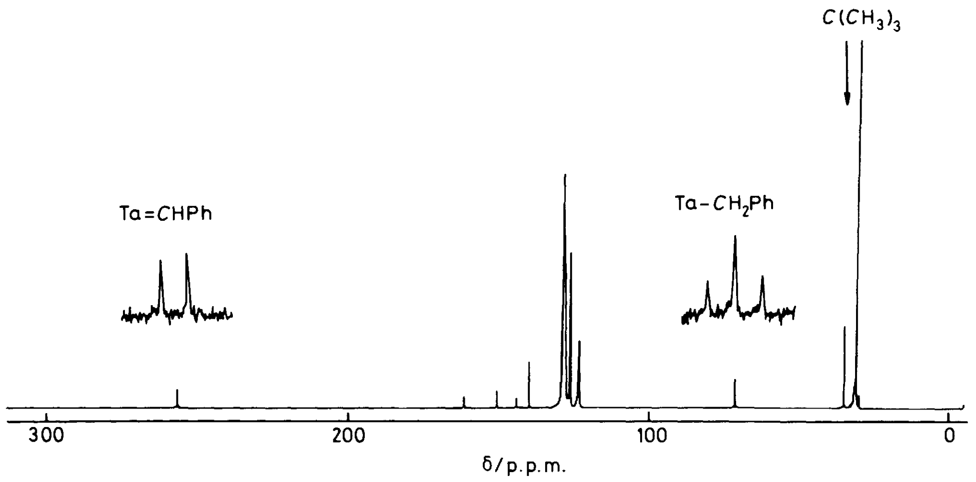


Figure 1. ^{13}C-{^{1}H} n.m.r. spectrum of [Ta(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$(=CHPh)(CH$_2$Ph)] (**11**) in [^{2}H$_6$]benzene. The result of proton coupling to the benzyl and benzylidene α-carbons is shown

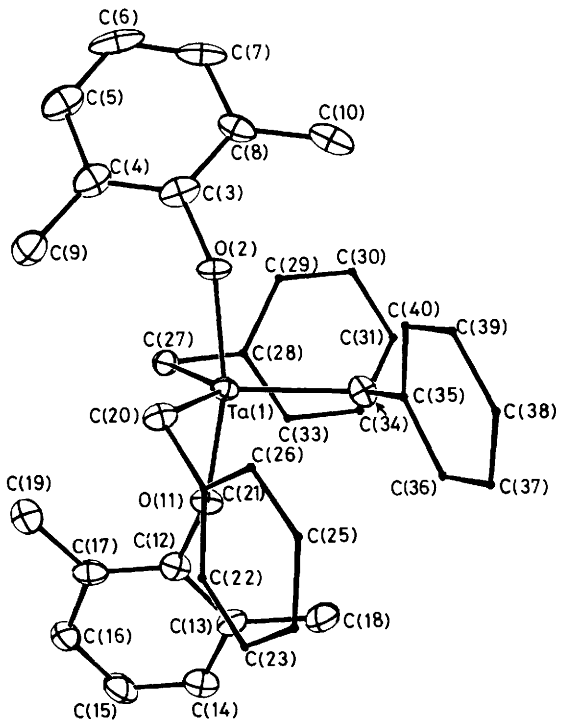


Figure 2. ORTEP view of [Ta(OC$_6$H$_3$Me$_2$-2,6)$_2$(CH$_2$Ph)$_3$] (**3**). The thermal ellipsoids due to the CH$_2$Ph phenyl rings have been reduced for clarity

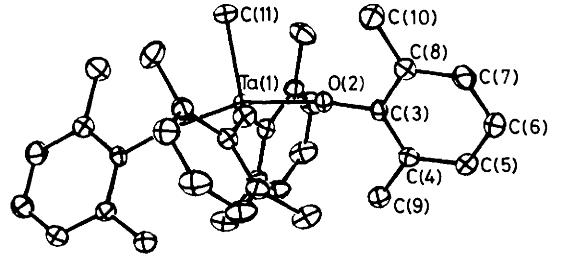


Figure 3. ORTEP view of [Ta(OC$_6$H$_3$Me$_2$-2,6)$_4$Me] (**5**)

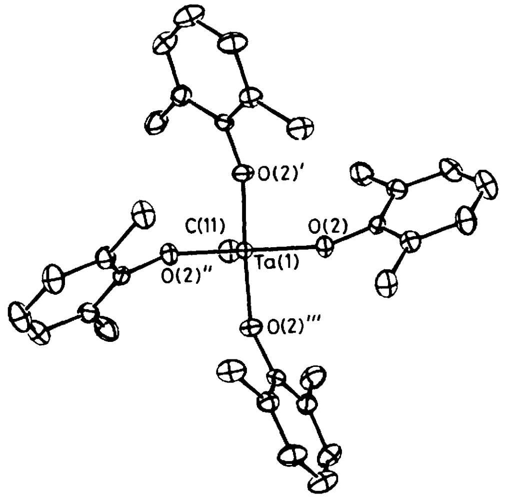


Figure 4. ORTEP view of [Ta(OC$_6$H$_3$Me$_2$-2,6)$_4$Me] (**5**) looking down the Ta–CH$_3$ axis

[Ta(OC$_6$H$_3$Me$_2$-2,6)$_4$Me] (**5**). ORTEP Views of the molecule along with the numbering scheme are shown in Figures 3 and 4. Table 5 contains some selected bond distances and angles. It can be seen that the molecule adopts a square-pyramidal geometry about tantalum with the methyl group being axial. Indeed, there is crystallographic C_4 symmetry (with disordered Ta–CH$_3$ hydrogens) making all of the aryloxide ligands equivalent. The only other structurally characterized compound of stoicheiometry [TaX$_4$R] is the complex [Ta(NMe$_2$)$_4$Bu^t] studied by Chisholm *et al.*[11] Here again a square-pyramidal geometry with axial alkyl group was observed with the C–Ta–N angles of 100—106° being slightly larger than the 95.1° found in complex (**5**).

[Ta(OC$_6$H$_3$Bu^t-2,6)$_2$(=CHSiMe$_3$)(CH$_2$SiMe$_3$)] (**10**). Due to the extremely high solubility of this complex it was found to be very difficult to obtain crystals suitable for *X*-ray diffraction studies. The results that we have obtained, although not as good as hoped for, clearly represent the correct molecular structure of the complex. An ORTEP view of the molecule is given in Figure 5, while Table 6 contains selected bond distances and angles. The pseudo-tetrahedral co-ordination about the metal is distorted by the opening up of the angle between the two bulky

Table 3. Final positional parameters (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $[Ta(OC_6H_3Me_2\text{-}2,6)_2(CH_2Ph)_3]$ (**3**)							
Ta(1)	1 304.5(2)	−449.8(2)	2 995.5(2)	C(21)	2 879(5)	201(4)	1 842(5)
O(2)	63(3)	84(3)	2 508(3)	C(22)	3 773(5)	−124(5)	2 304(5)
C(3)	−780(5)	532(5)	2 627(5)	C(23)	4 493(5)	−439(5)	1 837(5)
C(4)	−695(5)	1 341(5)	3 041(5)	C(24)	4 330(5)	−437(5)	896(5)
C(5)	−1 571(6)	1 753(5)	3 149(5)	C(25)	3 451(6)	−116(5)	423(5)
C(6)	−2 479(5)	1 368(6)	2 889(5)	C(26)	2 733(5)	209(4)	898(5)
C(7)	−2 535(5)	580(6)	2 456(5)	C(27)	806(5)	−362(4)	4 318(4)
C(8)	−1 702(5)	137(5)	2 298(5)	C(28)	369(5)	−1 248(5)	4 267(4)
C(9)	287(5)	1 786(5)	3 336(5)	C(29)	−638(5)	−1 391(5)	3 928(4)
C(10)	−1 774(5)	−698(5)	1 781(5)	C(30)	−1 015(5)	−2 213(5)	3 789(5)
O(11)	2 531(3)	−759(3)	3 702(3)	C(31)	−412(6)	−2 933(5)	3 989(5)
C(12)	3 251(5)	−860(5)	4 459(4)	C(32)	579(6)	−2 810(5)	4 346(5)
C(13)	3 707(5)	−1 667(5)	4 576(5)	C(33)	950(5)	−1 989(5)	4 482(5)
C(14)	4 406(5)	−1 787(5)	5 363(5)	C(34)	1 009(5)	−1 663(4)	2 271(4)
C(15)	4 641(5)	−1 132(5)	5 990(5)	C(35)	1 230(5)	−1 602(4)	1 328(4)
C(16)	4 215(5)	−327(5)	5 821(5)	C(36)	2 071(5)	−2 020(4)	1 118(5)
C(17)	3 500(5)	−166(5)	5 050(5)	C(37)	2 263(5)	−2 023(5)	235(5)
C(18)	3 465(6)	−2 374(5)	3 891(6)	C(38)	1 646(6)	−1 588(5)	−443(5)
C(19)	3 084(5)	721(5)	4 884(5)	C(39)	842(5)	−1 145(5)	−224(5)
C(20)	2 084(5)	545(5)	2 328(5)	C(40)	637(5)	−1 145(5)	637(5)
(*b*) $[Ta(OC_6H_3Me_2\text{-}2,6)_4Me]$ (**5**)							
Ta(1)	7 500*	7 500*	9 778.2(3)	C(7)	11 091(3)	6 327(3)	9 347(5)
O(2)	8 821(1)	7 515(2)	9 355(3)	C(8)	10 201(2)	6 599(2)	9 908(4)
C(3)	9 682(2)	7 201(2)	8 805(4)	C(9)	9 454(3)	8 188(3)	6 094(5)
C(4)	10 037(2)	7 519(2)	7 199(4)	C(10)	9 806(3)	6 280(3)	11 639(5)
C(5)	10 931(3)	7 223(3)	6 695(5)	C(11)	7 500*	7 500*	12 581(9)
C(6)	11 459(3)	6 633(3)	7 762(5)				
(*c*) $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2({=}CHSiMe_3)(CH_2SiMe_3)]$ (**10**)							
Ta(1)	9 553(1)	1 188.3(4)	2 101(1)	C(22)	11 940(29)	1 433(10)	4 867(18)
C(2)	10 962(32)	1 702(12)	2 321(21)	C(23)	5 852(28)	1 902(10)	1 925(18)
Si(3)	11 708(9)	2 371(3)	2 916(5)	C(24)	6 688(35)	2 309(13)	1 769(23)
C(4)	13 708(33)	2 320(12)	4 046(21)	C(25)	4 448(33)	2 172(12)	1 722(21)
C(5)	10 635(33)	2 665(12)	3 332(21)	C(26)	5 288(27)	1 418(10)	1 198(18)
C(6)	11 625(31)	2 850(11)	2 051(20)	O(27)	10 294(17)	534(6)	2 114(11)
C(7)	7 782(27)	1 318(9)	567(17)	C(28)	10 795(25)	14(9)	2 392(16)
Si(8)	8 055(8)	1 403(3)	−309(5)	C(29)	9 737(28)	−386(9)	2 151(18)
C(9)	9 208(31)	883(11)	−409(20)	C(30)	10 200(29)	−881(10)	2 490(18)
C(10)	6 120(39)	1 357(14)	−1 592(25)	C(31)	11 783(30)	−1 001(10)	3 064(19)
C(11)	8 873(43)	2 044(15)	−284(28)	C(32)	12 822(28)	−627(10)	3 233(18)
O(12)	8 828(17)	1 392(6)	2 792(11)	C(33)	12 382(28)	−116(10)	2 902(18)
C(13)	8 306(25)	1 449(9)	3 378(16)	C(34)	8 013(30)	−294(10)	1 460(19)
C(14)	9 278(26)	1 232(11)	4 350(17)	C(35)	7 532(29)	−117(10)	441(19)
C(15)	8 683(24)	1 283(9)	4 866(16)	C(36)	7 089(30)	−801(11)	1 226(20)
C(16)	7 321(31)	1 482(11)	4 480(20)	C(37)	7 434(29)	81(10)	1 847(18)
C(17)	6 482(33)	1 700(12)	3 559(22)	C(38)	13 531(27)	309(10)	3 078(18)
C(18)	6 878(28)	1 675(10)	2 951(18)	C(39)	13 037(27)	577(10)	2 116(17)
C(19)	10 836(28)	1 008(9)	4 822(18)	C(40)	13 803(29)	712(10)	3 821(19)
C(20)	11 585(32)	843(12)	5 902(21)	C(41)	15 017(30)	34(11)	3 477(19)
C(21)	10 718(28)	497(10)	4 276(18)				

* Fixed parameter.

aryloxides to 126.7(7)° while that between the two carbon atoms is closed down slightly to 100.1(11)°. The metal co-ordination is related in some ways to that reported for $[Ta(\eta\text{-}C_5H_5)_2({=}CHPh)(CH_2Ph)]$ [12] and $[Ta(\eta\text{-}C_5H_5)_2({=}CH_2)Me]$.[13]

Aryloxide Co-ordination.—For the three compounds obtained in this study the Ta–O distances vary over a very short range from 1.85 to 1.92 Å. Of the known Ta^V compounds containing terminal aryloxide ligands the shortest Ta–O distance found is 1.836(4) Å in $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2Cl_3]$ [6] while the longest so far reported is 1.945(6) Å in $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2Me_3]$.[8,9] The Ta–O distance to bridging

Table 4. Selected bond distances (Å) and angles (°) for the complex $[Ta(OC_6H_3Me_2\text{-}2,6)_2(CH_2Ph)_3]$ (**3**)

Ta(1)–O(2)	1.919(4)	Ta(1)–C(27)	2.204(6)
Ta(1)–O(11)	1.887(4)	Ta(1)–C(20)	2.204(7)
O(2)–Ta–O(11)	165.5(2)	C(20)–Ta–C(27)	127.8(3)
O(2)–Ta–C(20)	89.9(2)	C(20)–Ta–C(34)	115.9(3)
O(2)–Ta–C(27)	85.5(2)	C(27)–Ta–C(34)	116.2(3)
O(2)–Ta–C(34)	95.9(2)	Ta–O(2)–C(3)	150.6(4)
O(11)–Ta–C(20)	88.5(2)	Ta–O(11)–C(12)	158.9(4)
O(11)–Ta–C(27)	84.1(2)	Ta–C(2)–C(21)	114.9(5)
O(11)–Ta–C(34)	97.6(2)	Ta–C(27)–C(28)	94.8(4)
		Ta–C(34)–C(35)	111.5(4)

Table 5. Selected bond distances (Å) and angles (°) for the complex $[Ta(OC_6H_3Me_2\text{-}2,6)_4Me]$ (**5**)

Ta(1)–O(2)	1.899(4)	Ta(1)–C(11)	2.155(10)
O(2)–Ta–O(2)′	88.44(4)	O(2)–Ta–C(11)	99.5(1)
Ta–O(2)–C(3)	157.8(3)		

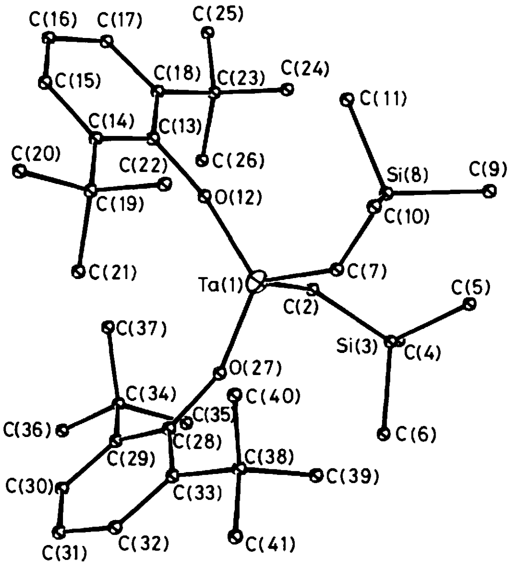


Figure 5. ORTEP view of $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2({=}CHSiMe_3)(CH_2SiMe_3)]$ (**10**)

aryloxide ligands is considerably longer, *cf.* 2.084(8) Å in $[Ta_2(OC_6H_4Me\text{-}4)_{10}]$.[14] One important aspect of high-valent early transition metal fluoride, alkoxide, aryloxide, and dialkylamide chemistry is the presence of considerable heteroatom *p* to metal *d* π-bonding.[15–17] This results in a significant shortening of the bond to these groups over what would be expected for a single bond. This π-bonding can also exert a considerable influence on other aspects of both structure and reactivity.[18,19] An illustration of this is seen in the dramatic increase in the Nb–O distances of 1.900(2) Å in $[Nb(OC_6H_3Me_2\text{-}2,6)_5]$[20] to 2.181(4) Å in the 18-electron complex $[Nb(Me_2PCH_2CH_2PMe_2)_2(CO)_2(OC_6H_3Me_2\text{-}3,5)]$[21] where niobium–oxygen π-bonding cannot take place.

Another important and related characteristic of the co-ordination of alkoxides, and aryloxides in particular, is the large M–O–C angles found. For the three compounds reported here the value of the Ta–O–C(aryl) angle varies from 150° for one of the aryloxides in (**3**) to 170° in the alkylidene complex. Indeed we and others have observed essentially linear aryloxide and alkoxide co-ordination in a number of cases.[15,22–26] It therefore appears that, besides the sometimes obvious steric effect of the 2,6-substituents, the co-ordination properties of those aryloxides are consistent with previous studies.

Alkyl and Alkylidene Co-ordination.—The tantalum–alkyl distances in the three structures also vary over a narrow range, 2.16—2.20 Å. These distances are in the range found for other related tantalum alkyl complexes.[27] The tantalum–alkylidene distance of 1.89(3) Å found in complex (**10**) is 0.28 Å shorter than the distance to the alkyl group in the same complex. This degree of shortening due to the double bond character in this group is similar to that reported for the related compounds $[Ta(\eta\text{-}C_5H_5)_2({=}CHR')(CH_2R')]$ (R′ = H or Ph).[12,13] The conformation of the $Ta{=}CHSiMe_3$ bond is worthy of note. In the complexes $[Ta(\eta\text{-}C_5H_5)_2({=}CHR')(CH_2R')]$ (R′ = Ph or $SiMe_3$)[12,28] it was found that the orientation of the alkylidene group was such that non-equivalent C_5H_5 ligands and diastereotopic methylene protons in the CH_2R' group were generated. Analysis of the variable-temperature ^1H n.m.r. spectra of the benzyl compounds by Schrock *et al.*[12] allowed an estimate of the rotational barrier around the Ta=C double bond to be made. It can be seen from the structure of (**10**), Figure 5, that the orientation of the $Ta{=}CHSiMe_3$ substituents is such that non-equivalent aryloxide ligands and a diastereotopic $Ta{-}CH_2SiMe_3$ methylene group are also to be expected. However, these groups are found to be equivalent in the ^1H n.m.r. spectra of (**10**) and (**11**) even at low temperatures. Hence, it appears that rotation about the tantalum–carbon double bond is much more facile in these compounds. This undoubtedly reflects the less rigid orbital requirements of a $Ta(aryloxy)_2$ unit compared to $Ta(\eta\text{-}C_5H_5)_2$.

Table 6. Selected bond distances (Å) and angles (°) for the complex $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2({=}CHSiMe_3)(CH_2SiMe_3)]$ (**10**)

Ta(1)–O(12)	1.85(2)	Ta(1)–C(2)	1.89(3)
Ta(1)–O(27)	1.85(2)	Ta(1)–C(7)	2.17(2)
O(12)–Ta–O(27)	126.7(7)	Ta–O(12)–C(13)	169(1)
O(12)–Ta–C(2)	107.4(9)	Ta–O(27)–C(28)	159(1)
O(12)–Ta–C(7)	108.0(8)	Ta–C(2)–Si(3)	140(2)
O(27)–Ta–C(2)	108.3(8)	Ta–C(7)–Si(8)	126(1)
O(27)–Ta–C(7)	103.0(8)		

Experimental

Starting Materials and Reaction Procedures.—All reactions were performed under a dry, oxygen-free nitrogen atmosphere using standard dry-box and Schlenk techniques. Solvents were distilled from sodium benzophenone prior to use and stored under nitrogen over molecular sieves. Methyl-lithium (low halide) was purchased from Aldrich and solid, ether-free LiMe obtained by removal of the solvent under vacuum before being stored in the dry-box. The reagents $Li(CH_2SiMe_3)$ and $Mg(CH_2SiMe_3)_2$[7] were stored in the dry-box as solids. The aryloxides $[M(OC_6H_3Me_2\text{-}2,6)_5]$ (M = Nb or Ta), $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]$, and $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl_3]$ were obtained as outlined previously.[6]

Physical Measurements.—Hydrogen-1 n.m.r. spectra were recorded in either $[^2H_6]$benzene (99.5% ^2H) or $[^2H_8]$toluene (99.5% ^2H) on a Varian XL-200 spectrometer and referenced internally to the protio impurities of the deuteriated solvents. Carbon-13 n.m.r. spectra were recorded in $[^2H_6]$benzene also on a Varian XL-200 spectrometer operating at 50.4 MHz.

Microanalyses were performed either by Galbraith Laboratories, Inc., Knoxville, Tennessee or by the Purdue University Microanalytical Laboratory.

Reaction Procedures.—Due to the similarity of the synthetic method used for the preparation of a number of these compounds, an illustrative procedure is given for each type.

(*i*) *Trialkyl Compounds* (**1**)—(**3**), (**6**)—(**8**). $[Ta(OC_6H_3Me_2\text{-}2,6)_2Me_3]$ (**1a**). To a suspension of yellow $[Ta(OC_6H_3Me_2\text{-}2,6)_3Cl_2]$ (0.50 g, 0.8 mmol) in benzene (20 cm^3) was added LiMe (0.055 g, 2.5 mmol). The reaction mixture was stirred at 25 °C for 6 h, filtered, and the solvent removed from the colourless solution *in vacuo* to leave the product as a white crystalline solid. Recrystallization from hexane gave the product as pale yellow needles. Yield 0.24 g, 63% (Found: C, 48.95; H, 5.70. $C_{19}H_{27}O_2Ta$ requires C, 48.75; H, 5.70%). The 2,6-dimethylphenoxide complexes (**1**)—(**3**) could all be readily recrystallized from hexane on cooling. However, the 2,6-di-isopropylphenoxide derivatives obtained using $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]$ were isolated as low-melting solids or liquids exhibiting great solubility in all hydrocarbon solvents.

(*ii*) $[Ta(OC_6H_3Me_2\text{-}2,6)_3(CH_2Ph)_2]$ (**4**). To a suspension of $[Ta(OC_6H_3Me_2\text{-}2,6)_3Cl_2]$ (5.0 g, 8.0 mmol) in benzene (40 cm^3) was added $Mg(CH_2Ph)_2$ (2.18 g, 10.0 mmol). The reaction mixture was stirred for 24 h, the colour changing from yellow to light orange. Filtration, removal of solvent, and recrystallization from hexane gave the product as a light orange solid. Yield 3.4 g, 58% (Found: C, 62.7; H, 5.65. $C_{38}H_{41}O_3Ta$ requires C, 62.8; H, 5.70%).

(*iii*) $[Ta(OC_6H_3Me_2\text{-}2,6)_4Me]$ (**5**). To a suspension of $[Ta(OC_6H_3Me_2\text{-}2,6)_3Cl_2]$ (0.5 g, 0.8 mmol) in benzene (20 cm^3) was added LiMe (0.035 g, 1.6 mmol). After 1 h the mixture was filtered and solvent removed *in vacuo* to leave a colourless oil. Addition of pentane caused precipitation of the product as a white powder, which was recrystallized from hexane. Yield 0.04 g, 7%.

(*iv*) $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2({=}CHSiMe_3)(CH_2SiMe_3)]$ (**9**). A cooled benzene solution of $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2SiMe_3)_3]$ (0.5 g in 10 cm^3) was irradiated for 4 h through Pyrex using a 450-W Ace-Hanovia medium-pressure Hg lamp housed in a cooled quartz jacket. Removal of solvent and generated $SiMe_4$ gave the product as a pale yellow liquid, completely soluble in hydrocarbon solvents.

(*v*) $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2({=}CHSiMe_3)(CH_2SiMe_3)]$ (**10**). To a cooled (−78 °C) solution of $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl_3]$ (0.5 g, 0.7 mmol) in toluene (25 cm^3) was added $Li(CH_2SiMe_3)$ (0.21 g, 2.2 mmol) in toluene (15 cm^3). The mixture was stirred for 30 min before being warmed up slowly to room temperature. The resulting yellow suspension was filtered and the solvent removed *in vacuo* to leave the product as a pale yellow powder. Yield 0.43 g, 78% (Found: C, 56.85; H, 7.9. $C_{36}H_{63}O_2Si_2Ta$ requires C, 56.5; H, 8.3%). The benzylidene complex (**12**) was prepared by an essentially identical procedure.

Crystal Structure Determinations and Refinements.—Crystallographic data are collected in Table 5. General operating procedures and programs used have been described previously.[29,30]

(*a*) $[Ta(OC_6H_3Me_2\text{-}2,6)_2(CH_2Ph)_3]$ (**3**). Crystals suitable for a diffraction study were grown from hexane by cooling. A suitable small crystal was selected, transferred to the goniostat, and cooled to −155 °C. The crystal was characterized as described previously.[29,30] A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited monoclinic symmetry and systematic extinctions corresponding to the space group $P2_1/n$. Data were collected in the usual manner using a θ–2θ scan with parameters given in Table 2 of this paper. 4 688 Reflections were collected and reduced to a unique set of 4 075. No absorption correction was carried out.

The structure was solved by using standard heavy-atom techniques. The Ta atom was located by means of a Patterson function and the remaining atoms were located in successive difference Fourier syntheses phased by the heavy atom. All hydrogen atoms were located after initial refinement of the non-hydrogen atoms. The structure was refined by full-matrix least-squares methods using anisotropic thermal parameters on the non-hydrogen atoms and isotropic thermal parameters on the hydrogen atoms.

The final difference map contained three peaks of *ca.* 1.0 e $Å^{-3}$; these peaks were identified as residuals from the Ta atom, otherwise the map was essentially featureless.

(*b*) $[Ta(OC_6H_3Me_2\text{-}2,6)_4Me]$ (**5**). Crystals suitable for study were readily obtained by cooling saturated hexane solutions of (**5**) to −15 °C. A nearly equidimensional fragment was cleaved from a larger crystal in a nitrogen-filled glove-box and transferred to the goniostat using standard inert-atmosphere handling techniques. After transfer, the crystal was cooled to −160 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima which could be indexed as tetragonal, space group $P4/n$. The structure was solved by direct methods and Fourier techniques, and refined by full-matrix least-squares methods. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen atoms. These (with the exception of the disordered H on the terminal methyl group) were refined isotropically. A difference Fourier synthesis on these results indicated a peak of 1.1 e $Å^{-3}$ at the Ta site, and the next largest peak (0.42 e $Å^{-3}$) was in the proper position for a disordered H on the terminal Me. The latter was included in the final refinement, allowing both the thermal parameter and the occupancy to vary. The position refined properly, with an occupancy of 79%. While one would expect three hydrogens (each of occupancy 25%), only the one peak was apparent. Thus, the position reported for H(10) in the supplementary material is suspect, even though the refinement indicates it to be real.

(*c*) $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2({=}CHSiMe_3)(CH_2SiMe_3)]$ (**10**). Due to the extremely high solubility of this complex great difficulty was experienced in obtaining crystals suitable for *X*-ray diffraction. Eventually a few large crystals were obtained by very slow cooling of a pentane solution of (**10**) to −15 °C. The results obtained, although clearly not as good as one would wish, represent the best we have been able to achieve for this compound. A suitable crystal was obtained by cleaving a larger crystal and transferring to the goniostat using standard inert-atmosphere handling techniques. A systematic search of a limited hemisphere of reciprocal space located diffraction maxima which could be indexed as monoclinic, space group $P2_1/c$.

The structure was solved by direct methods (MULTAN 78) and refined by full-matrix least-squares methods. Attempts to refine the structure anisotropically did not improve the residuals significantly, and several atoms converged to non-positive definite thermal parameters. For this reason only the tantalum atom was allowed to vary anisotropically, all others remaining isotropic. Hydrogen atoms were visible in a difference Fourier map phased on the non-hydrogen parameters and their contribution was included as fixed atoms in idealized positions for the final refinement.

A final difference Fourier map was featureless with two peaks of density 1.3 e $Å^{-3}$ located adjacent to the Ta and all other peaks less than 0.9 e $Å^{-3}$.

Acknowledgements

We thank the National Science Foundation for financial support.

References

1 I. P. Rothwell, *Polyhedron*, 1985, **4**, 177.

2 L. Chamberlain, A. P. Rothwell, and I. P. Rothwell, *J. Am. Chem. Soc.*, 1984, **106**, 1847.

3 L. Chamberlain, I. P. Rothwell, and J. C. Huffman, *J. Am. Chem. Soc.*, 1982, **104**, 7338.

4 L. Chamberlain and I. P. Rothwell, *J. Am. Chem. Soc.*, 1983, **105**, 1665.

5 L. Chamberlain and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, following paper.

6 L. Chamberlain, I. P. Rothwell, and J. C. Huffman, *Inorg. Chem.*, 1984, **23**, 2575.
7 R. R. Schrock, *J. Organomet. Chem.*, 1976, **122**, 209.
8 L. Chamberlain, J. Keddington, J. C. Huffman, and I. P. Rothwell, *Organometallics*, 1982, **1**, 1538.
9 L. Chamberlain, I. P. Rothwell, and J. C. Huffman, *J. Am. Chem. Soc.*, 1986, **108**, 1502.
10 R. A. Andersen, *Inorg. Chem.*, 1979, **18**, 3622.
11 M. H. Chisholm, L. S. Tan, and J. C. Huffman, *J. Am. Chem. Soc.*, 1982, **104**, 4879.
12 R. R. Schrock, L. W. Messerle, C. D. Wood, and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1978, **100**, 3793.
13 R. R. Schrock and P. R. Sharp, *J. Am. Chem. Soc.*, 1978, **100**, 2389.
14 L. N. Lewis and M. F. Garbauskas, *Inorg. Chem.*, 1985, **24**, 363.
15 M. H. Chisholm, *Polyhedron*, 1983, **2**, 681.
16 T. W. Coffindaffer, I. P. Rothwell, and J. C. Huffman, *Inorg. Chem.*, 1983, **22**, 2906.
17 M. F. Lappert, P. P. Power, A. R. Sanger, and R. C. Srivastava, 'Metal and Metalloid Amides,' John Wiley and Sons, New York, 1980.
18 P. Kubacek and R. Hoffman, *J. Am. Chem. Soc.*, 1981, **103**, 4320.
19 M. H. Chisholm, J. C. Huffman, I. P. Rothwell, P. G. Bradley, N. Kress, and W. H. Woodroof, *J. Am. Chem. Soc.*, 1981, **103**, 4945.
20 T. W. Coffindaffer, D. Powell, and I. P. Rothwell, unpublished work.
21 T. W. Coffindaffer, I. P. Rothwell, K. Folting, J. C. Huffman, and W. E. Steib, *J. Chem. Soc., Chem. Commun.*, 1985, 1519.
22 S. L. Latesky, A. K. McMullen, I. P. Rothwell, and J. C. Huffman, *Organometallics*, 1985, **4**, 902.
23 S. L. Latesky, A. K. McMullen, J. Keddington, I. P. Rothwell, and J. C. Huffman, *Inorg. Chem.*, 1985, **24**, 995.
24 S. L. Latesky, A. K. McMullen, I. P. Rothwell, and J. C. Huffman, *J. Am. Chem. Soc.*, 1985, **107**, 5981.
25 T. V. Lubben, P. T. Wolczanski, and G. D. Van Duyne, *Organometallics*, 1984, **3**, 977.
26 P. B. Hitchcock, M. F. Lappert, and A. Singh, *J. Chem. Soc., Chem. Commun.*, 1983, 1499.
27 'Comprehensive Organometallic Chemistry,' eds. E. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon Press, New York, 1982.
28 M. F. Lappert and C. R. C. Milne, *J. Chem. Soc., Chem. Commun.*, 1978, 925.
29 J. C. Huffman, L. N. Lewis, and K. G. Caulton, *Inorg. Chem.*, 1980, **19**, 2755.
30 M. H. Chisholm, K. Folting, J. C. Huffman, and C. C. Kirkpatrick, *Inorg. Chem.*, 1984, **23**, 1021.

Received 21*st October* 1985; *Paper* 5/1834