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Studies of the alkylation of niobium and tantalum halides containing 2,6-diarylphenoxide ancillary ligation

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The mixed halo(aryloxide) compounds [Nb{$OC_6H(C_6H_4Me\text{-}4)_2\text{-}2,6\text{-}Ph_2\text{-}3,5$}$_2Cl_3$], [Ta($OC_6HPh_4$-2,3,5,6)$_2Br_3$] and [Nb($OC_6HPh_4$-2,3,5,6)$_2I_3$] have been isolated and structurally characterized. Although the chloride and bromide compounds are square pyramidal with an axial aryloxide, the tris(iodide) compound was determined to adopt a trigonal bipyramidal geometry in the solid state with *trans*, axial aryloxides. The reaction of the tantalum tris(chlorides) [Ta($OC_6H_3Ph_2$-2,6)$_2Cl_3$] or [Ta(OC_6HPh_4-2,3,5,6)$_2Cl_3$] with RMgCl (R = CH_2Ph or CH_2SiMe_3) forms the corresponding mono-, bis- and tris-(alkyls), all shown to adopt a trigonal bipyramidal geometry in the solid state with *trans*, axial aryloxides. In contrast the mono(cycloalkyl) compounds [Ta($OC_6H_3Ph_2$-2,6)$_2$(C_nH_{2n+1})Cl] (n = 5, 6) were found to adopt square pyramidal structures in the solid state with the alkyl group axial (metal pseudo-equatorial) and mutually *cis* aryloxides. The alkylation of the corresponding niobium substrate [Nb(OC_6HPh_4-2,3,5,6)$_2Cl_3$] with Me_3SiCH_2MgCl produced a complex mixture of products. Careful analysis including the use of ^{29}Si NMR identified the d^0-alkyl products [Nb(OC_6HPh_4-2,3,5,6)$_2Cl_2$(CH_2SiMe_3)], [Nb(OC_6HPh_4-2,3,5,6)$_2$Cl(CH_2SiMe_3)$_2$] and [Nb(OC_6HPh_4-2,3,5,6)$_2$(CH_2SiMe_3)$_3$], the alkylidene compounds [Nb(OC_6HPh_4-2,3,5,6)$_2$Cl(=$CHSiMe_3$)] and [Nb(OC_6HPh_4-2,3,5,6)$_2$(CH_2SiMe_3)(=$CHSiMe_3$)] and the d^1-alkyl [Nb(OC_6HPh_4-2,3,5,6)$_2$(CH_2SiMe_3)$_2$]. Treating a benzene solution of [Nb(OC_6HPh_4-2,3,5,6)$_2$(CH_2SiMe_3)$_2$]/[Nb(OC_6HPh_4-2,3,5,6)$_2$(CH_2SiMe_3)(=$CHSiMe_3$)] and PMe_3 at 85 °C under 1200 psi of H_2 produced deep-green crystals of the d^1-di(hydride) [Nb(OC_6HCy_2-2,6-Ph_2-3,5)$_2$(H)$_2$(PMe_3)$_2$].

Introduction

The mixed chloro(aryloxide)s of niobium and tantalum [M(OAr)$_x$Cl$_{5-x}$] are important starting materials for exploring the inorganic/organometallic chemistry of these elements.[1] One area of investigation involves the activation of unsaturated organic substrates by highly reducing, low valent aryloxides of niobium and tantalum formed by chemical reduction of chloro(aryloxide) precursors.[2,3] The second involves the stoichiometric and catalytic reactivity of d^0-alkyl and hydrido aryloxides,[4] and in particular their use as precursors/catalysts for arene hydrogenation. In this latter context we have demonstrated that activation of the trichloride derivatives [M(OAr)$_2$Cl$_3$] (M = Nb, Ta) with alkylating agents in hydrocarbon solvents followed by exposure to pressures of hydrogen generates catalysts for the hydrogenation of simple arenes and aryl-phosphines.[5] In this paper we report upon a study of the stepwise alkylation of a series of niobium and tantalum chloro(aryloxide) substrates. Some emphasis is placed on the structure of isolated five-coordinated compounds and the interplay between trigonal bipyramidal and square pyramidal structures. In the case of niobium the hydrogenolysis of alkyl products has been investigated and a new, paramagnetic di-hydride isolated and characterized.

Results and discussion

Synthesis and characterization of halide starting materials

The bis(aryloxide) compounds [M(OAr)$_2$Cl$_3$] (M = Nb, Ta) are typically isolated by simple addition of two equivalents of parent phenol to a hydrocarbon solution of the metal pentachloride. By this method the trichlorides **1–4** (Scheme 1) as well as other *meta* and *para* substituted 2,6-diphenylphenoxides have been isolated and characterized.[6] In order to investigate the impact of substituents within the *ortho*-phenyl rings we have also synthesized 2,6-di(4-methylphenyl)-3,5-diphenylphenol and prepared the corresponding niobium trichloride **5** (Scheme 1). The compound can be seen to adopt a square based pyramidal geometry about the niobium metal center (Fig. 1, Table 1) with an axial aryloxide. This is the same geometry found for other reported mononuclear trichlorides.[6] However, during our study of the methylation of **3** with MeMgI we have isolated a small amount of the tri-iodide [Nb(OC_6HPh_4-2,3,5,6)$_2I_3$] **6**, presumably arising from a metathesis reaction between the chloride ligands and MgI_2 within the Grignard reagent. This compound was characterized by X-ray crystallography and shown (Fig. 2, Table 2) to contain a trigonal bipyramidal geometry about the metal center with axial aryloxide ligands. This, therefore, prompted us to synthesize the tantalum tri-bromide [Ta(OC_6HPh_4-2,3,5,6)$_2Br_3$] **7** for comparison (Scheme 1). In this case a square based pyramid was adopted (Fig. 3, Table 3) similar to that found for the

Table 1 Selected bond distances (Å) and angles (°) for [Nb(OC_6H(C_6H_4Me-4)$_2$-2,6-Ph_2-3,5)$_2Cl_3$] **5**

Nb–O(10)	1.815(2)	Nb–O(20)	1.862(2)
Nb–Cl(1)	2.3483(8)	Nb–Cl(2)	2.3405(7)
Nb–Cl(3)	2.3434(8)		
O(10)–Nb–O(20)	104.00(7)	O(10)–Nb–Cl(1)	101.12(6)
O(10)–Nb–Cl(2)	102.05(6)	O(10)–Nb–Cl(3)	102.33(6)
O(20)–Nb–Cl(1)	154.37(5)	O(20)–Nb–Cl(2)	92.54(5)
O(20)–Nb–Cl(3)	84.34(5)	Cl(1)–Nb–Cl(2)	87.11(3)
Cl(1)–Nb–Cl(3)	85.45(4)	Cl(2)–Nb–Cl(3)	155.45(3)
Nb–O(10)–C(11)	179.6(2)	Nb–O(20)–C(21)	152.5(2)

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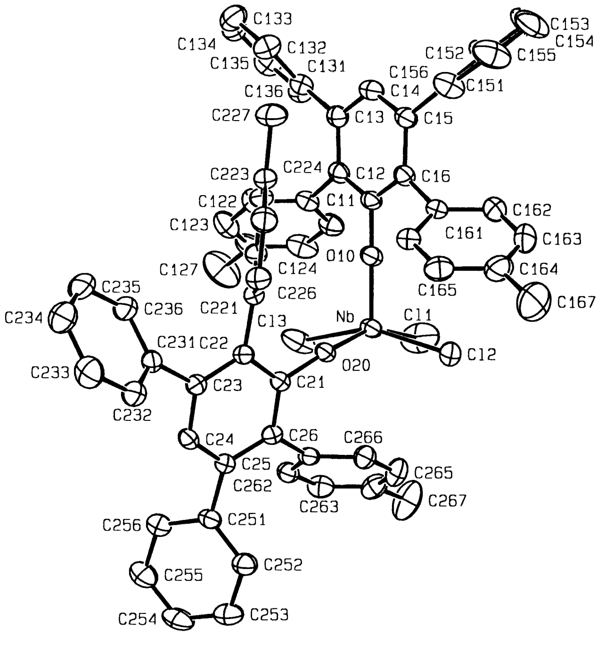
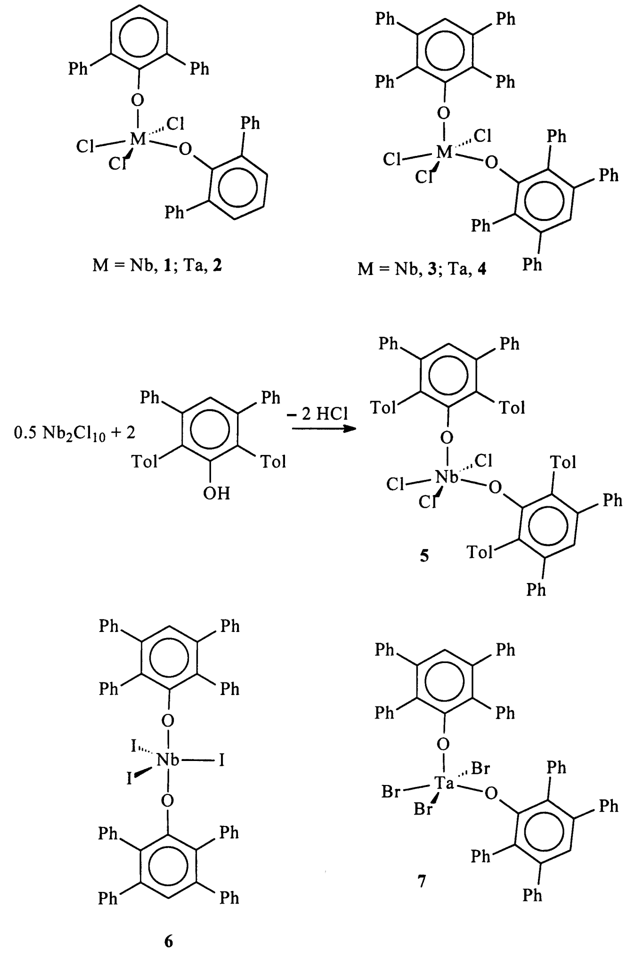


Fig. 1 Molecular structure of $[Nb(OC_6H(OC_6H_4Me\text{-}4)_2\text{-}2,6\text{-}Ph_2\text{-}3,5)_2Cl_3]$ **5**.



Scheme 1

corresponding chlorides. The switch from square based pyramid to trigonal bipyramid on moving from the bromide to the iodide possibly reflects a steric effect, with the bulkier iodine atoms being separated by larger angles in the latter geometry.

Table 2 Selected bond distances (Å) and angles (°) for $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2I_3]$ **6**

Nb–O	1.879(4)	Nb–I(2)	2.601(8)
Nb–I(3)	2.710(1)		
O(1)–Nb–O(1′)	174.2(3)	O(1)–Nb–I(2)	93.21(14)
O(1)–Nb–I(2′)	90.45(14)	O(1)–Nb–I(3)	87.09(16)
O(1′)–Nb–I(2)	90.45(14)	O(1′)–Nb–I(2′)	93.21(14)
O(1′)–Nb–I(3)	87.09(16)	I(2)–Nb–I(2′)	101.80(4)
I(2)–Nb–I(3)	129.10(2)	I(2′)–Nb–I(3)	129.10(2)
Nb–O(1)–C(11)	178.9(5)		

Table 3 Selected bond distances (Å) and angles (°) for $[Ta(OC_6HPh_4\text{-}2,3,5,6)_2Br_3]$ **7**

Ta–O(1)	1.865(3)	Ta–O(2)	1.825(3)
Ta–Br(1)	2.5037(6)	Ta–Br(2)	2.4679(5)
Ta–Br(3)	2.4995(2)		
O(1)–Ta–O(2)	104.30(14)	O(1)–Ta–Br(1)	85.61(10)
O(1)–Ta–Br(2)	90.45(10)	O(1)–Ta–Br(3)	154.38(10)
O(2)–Ta–Br(1)	102.46(10)	O(2)–Ta–Br(2)	103.21(10)
O(2)–Ta–Br(3)	101.11(10)	Br(1)–Ta–Br(2)	154.21(2)
Br(2)–Ta–Br(3)	86.97(2)	Br(3)–Ta–Br(1)	85.73(2)
C(11)–O(1)–Ta	152.9(3)	C(21)–O(2)–Ta	162.2(3)

The Nb–OAr distances in compounds **5–7** are identical with those found for other five-coordinate aryloxides of Nb(v) or Ta(v)[1] and appear to be insensitive to the nature of the ancillary halide atoms. The M–halide distances increase by ~0.15 Å and ~0.20 Å on moving from chloride to bromide to iodide. This elongation is as expected on the basis of interatomic distances in simple molecules such as H–Cl (1.274 Å), H–Br (1.408 Å) and H–I (1.608 Å).[7] The M–Cl and M–Br distances are similar to those reported for other Nb(Ta) chlorides and bromides; *cf.* Nb–Br = 2.50 Å (av.) in $[PPh_4][NbBr_6]$.[8] However, analysis of the Cambridge Structural Database[9] shows that the Nb–I distances of 2.601(8) Å and 2.710(1) Å in **6** are the shortest so far reported. This simply reflects the fact that **6** represents the first structurally characterized iodide of either Nb(v) or Ta(v). Previously reported iodides appear to be either electron rich or lower valent derivatives; *cf.* M–I distances of 2.945(3) Å in $[Nb(I)(CO)_2(CNBu^t)_4]$[10] and 2.8840(7) Å in $[Cp_2Ta(I)(=CHMe)]$.[11] The shortest Ta–I distance previously reported appears to be 2.819(2) Å in $[Ta(I)(dmpe)(CO)_4]$.[12]

Alkylation studies

The exhaustive alkylation (complete substitution of chloride ligands) of a variety of tantalum trichlorides $[Ta(OAr)_2Cl_3]$ has been carried out. This work showed that the products obtained were strongly dependent on the nature (bulk) of the aryloxide ligands. With relatively small ligands the tris-alkyls $[Ta(OAr)_2R_3]$ (R = Me, CH_2Ph, CH_2SiMe_3, Ph) can be obtained.[13] Mixed alkyl, alkylidene compounds $[Ta(OAr)(=CHR)(CH_2R)]$ (R = H, Ph, $SiMe_3$) are generated either thermally with bulky aryloxides, or photochemically from the tris-alkyl precursor. With 2,6-di-*tert*-butylphenoxide or 2,6-diphenylphenoxides, facile cyclometallation of the aryloxides is a typical reaction leading to six-membered oxa-metallacycles.[14] In the case of the 2,6-diphenylphenoxides the rate of cyclometallation can be controlled by the introduction of *meta*-substituents.[13a] All of the monomeric, structurally characterized chlorides $[Ta(OAr)_2Cl_3]$ adopt a square pyramidal geometry with an axial aryloxide whereas all tris-alkyls adopt a trigonal bipyramidal structure with *trans*, axial aryloxides. In order to determine at which point of alkylation the geometry switches from sp to tbp, we have isolated and characterized a number of mono- and bis-alkyl intermediates. We have also investigated in detail the alkylation of the niobium precursor **3**. This reaction was found to produce strikingly different results than the corresponding tantalum compound.

Reaction of substrates **2–4** with one equivalent of Grignard reagents $PhCH_2MgCl$ or Me_3SiCH_2MgCl leads to the mono-alkyls **8–10** (Scheme 2). Structural studies show all three

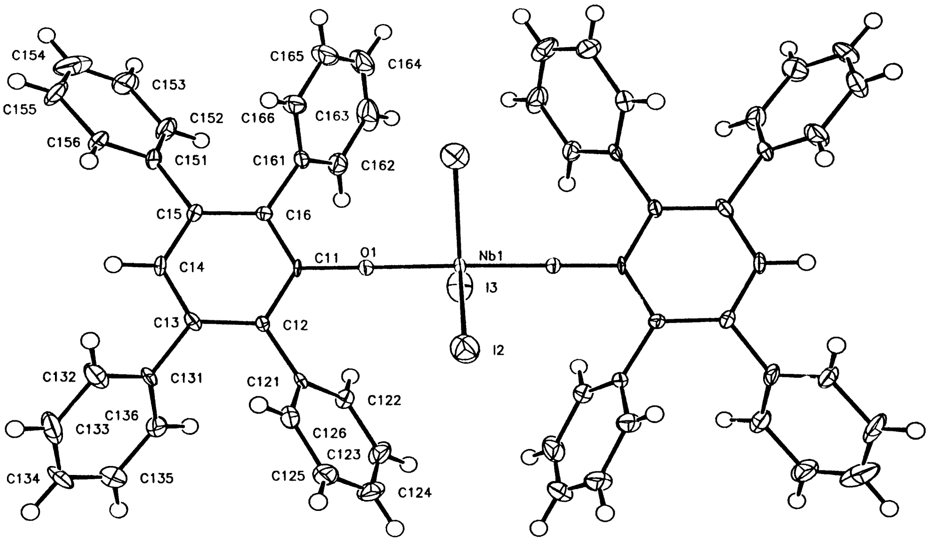


Fig. 2 Molecular structure of $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2I_3]$ **6**.

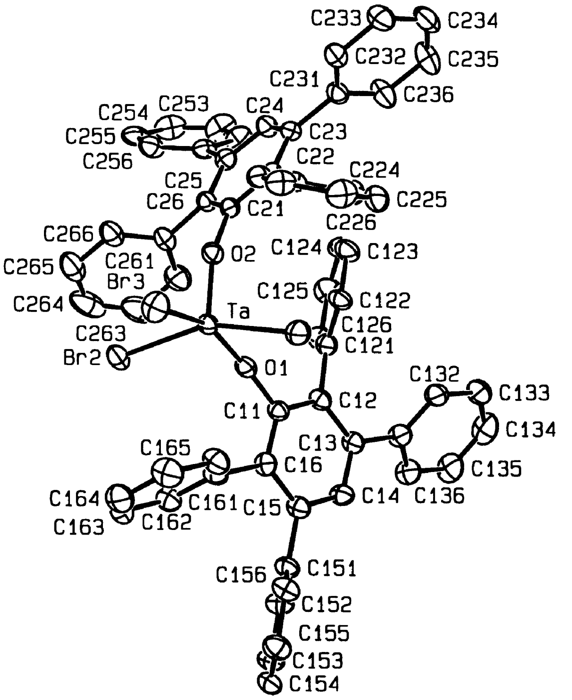
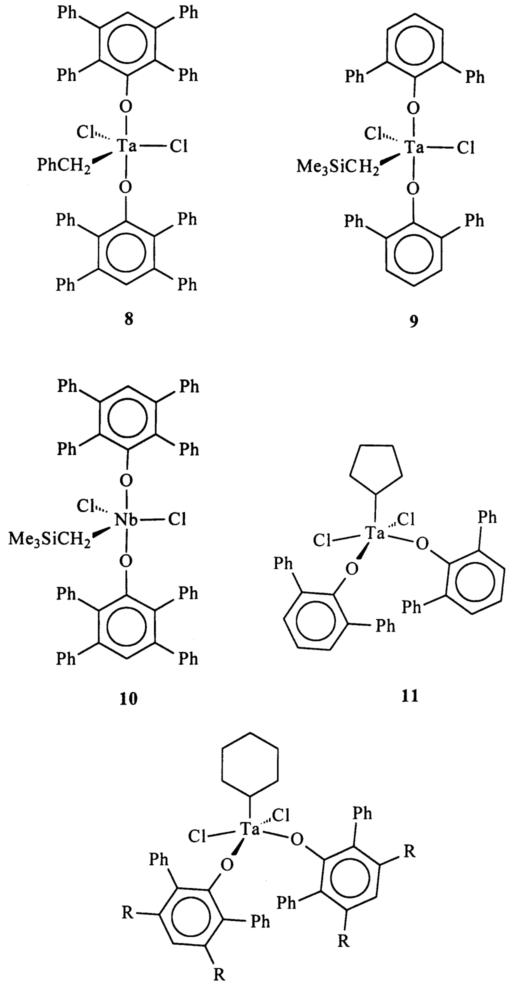


Fig. 3 Molecular structure of $[Ta(OC_6HPh_4\text{-}2,3,5,6)_2Br_3]$ **7**.

Table 4 Selected bond distances (Å) and angles (°) for $[Ta(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(CH_2Ph)]$ **8**

Ta–O(10)	1.900(3)	Ta–O(20)	1.885(3)
Ta–Cl(1)	2.3051(15)	Ta–Cl(2)	2.3429(13)
Ta–C(30)	2.223(4)		
O(20)–Ta–O(10)	170.25(13)	O(20)–Ta–C(30)	91.32(14)
O(10)–Ta–C(30)	91.62(14)	O(20)–Ta–Cl(1)	93.31(11)
O(10)–Ta–Cl(1)	93.74(10)	C(30)–Ta–Cl(1)	116.11(12)
O(20)–Ta–Cl(2)	86.11(11)	O(10)–Ta–Cl(2)	84.37(10)
C(30)–Ta–Cl(2)	120.27(12)	Cl(1)–Ta–Cl(2)	123.62(6)
C(11)–O(10)–Ta	155.8(3)	C(21)–O(20)–Ta	166.7(3)
C(31)–C(30)–Ta	93.6(3)	C(31)–C(30)–Ta	93.6(3)



8 **9** **10** **11**

R = H, **12**; Ph, **13**

Scheme 2

compounds to adopt a structure best described as tbp with axial aryloxides (*e.g.* Fig. 4, Tables 4–6). In all three cases the O–M–O angles are very close to 170°. Within the equatorial plane, the Cl–M–Cl angle is consistently larger than the two Cl–M–C(alkyl) angles for all three compounds. The mono-benzyl derivative **8** contains a sharp Ta–CH_2–Ph angle of 93.6(3)° (Table 4). Sharp angles are a common feature of structurally characterized high-valent early d-block metal benzyl compounds. However, care must be taken in over-interpreting the importance/strength of any η^n-interaction from solid state studies alone.

In contrast the alkylation of **2** with either cyclopentyl- or cyclohexyl-Grignard was found to lead to the corresponding mono-alkyls **11** and **12** shown by X-ray diffration to adopt square pyramidal geometries with an axial carbon atom (Scheme 2, Figs. 5 and 6, Tables 7 and 8). The 2,3,5,6-

Table 5 Selected bond distances (Å) and angles (°) for [Ta($OC_6H_3Ph_2$-2,6)$_2Cl_2(CH_2SiMe_3)$] **9**

Ta–O(2)	1.874(2)	Ta–O(1)	1.904(2)
Ta–C(1)	2.090(3)	Ta–Cl(1)	2.2952(8)
Ta–Cl(2)	2.3529(8)		
O(2)–Ta–O(1)	169.71(9)	O(2)–Ta–C(1)	92.52(11)
O(2)–Ta–Cl(1)	92.49(7)	O(2)–Ta–Cl(2)	86.77(7)
O(1)–Ta–C(1)	95.38(11)	O(1)–Ta–Cl(1)	91.10(7)
O(1)–Ta–Cl(2)	84.06(7)	C(1)–Ta–Cl(1)	109.37(9)
C(1)–Ta–Cl(2)	113.30(9)	Cl(1)–Ta–Cl(2)	137.31(3)
C(21)–O(2)–Ta	175.6(2)	C(11)–O(1)–Ta	143.7(2)
Si(1)–C(1)–Ta	122.8(2)		

Table 6 Selected bond distances (Å) and angles (°) for [Nb(OC_6HPh_4-2,3,5,6)$_2Cl_2(CH_2SiMe_3)$] **10**

Nb–O(4)	1.880(3)	Nb–O(5)	1.892(3)
Nb–Cl(1)	2.3580(12)	Nb–Cl(2)	2.3080(11)
Nb–C(30)	2.068(4)		
O(4)–Nb–O(5)	170.89(12)	C(30)–Nb–Cl(1)	116.02(12)
Cl(1)–Nb–Cl(2)	134.60(5)	Cl(2)–Nb–C(30)	109.37(12)
O(4)–Nb–C(30)	93.60(14)	O(4)–Nb–Cl(1)	86.20(9)
O(4)–Nb–Cl(2)	91.35(9)	O(5)–Nb–C(30)	91.15(15)
O(5)–Nb–Cl(1)	84.73(9)	O(5)–Nb–Cl(2)	94.40(8)
C(41)–O(4)–Nb	171.6(3)	C(51)–O(5)–Nb	159.9(3)
Si(31)–C(30)–Nb	123.2(2)		

Table 7 Selected bond distances (Å) and angles (°) for [Ta($OC_6H_3Ph_2$-2,6)$_2Cl_2$(c-C_5H_9)] **11**

Ta–O(1)	1.907(4)	Ta–O(2)	1.854(4)
Ta–Cl(1)	2.3605(14)	Ta–Cl(2)	2.3434(14)
Ta–C(1)	2.108(5)		
O(1)–Ta–O(2)	91.97(15)	O(2)–Ta–C(1)	103.18(18)
O(1)–Ta–C(1)	99.01(18)	O(2)–Ta–Cl(2)	152.62(12)
O(1)–Ta–C(2)	84.11(11)	C(1)–Ta–Cl(2)	104.20(15)
O(2)–Ta–Cl(1)	91.53(12)	O(1)–Ta–Cl(1)	166.66(11)
C(1)–Ta–Cl(1)	92.71(15)	Cl(2)–Ta–Cl(1)	86.87(6)
C(11)–O(1)–Ta	143.7(3)	C(21)–O(2)–Ta	163.7(3)
C(5)–C(1)–Ta	116.7(4)	C(2)–C(1)–Ta	113.8(3)
C(5)–C(1)–C(2)	104.2(4)		

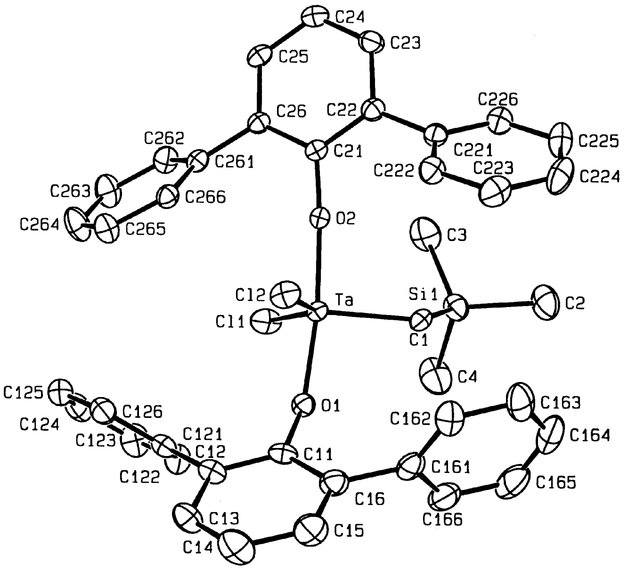


Fig. 4 Molecular structure of [Ta($OC_6H_3Ph_2$-2,6)$_2Cl_2(CH_2SiMe_3)$] **9**.

Table 8 Selected bond distances (Å) and angles (°) for [Ta($OC_6H_3Ph_2$-2,6)$_2Cl_2$(c-C_6H_{11})] **12**

Ta–O(2)	1.850(3)	Ta–O(3)	1.911(3)
Ta–Cl(4)	2.3575(11)	Ta–Cl(5)	2.3466(10)
Ta–C(1)	2.139(4)		
O(2)–Ta–O(3)	92.93(12)	O(2)–Ta–C(1)	100.82(15)
O(2)–Ta–Cl(5)	92.94(9)	O(2)–Ta–Cl(4)	148.91(9)
O(3)–Ta–C(1)	96.53(14)	O(3)–Ta–Cl(5)	168.88(9)
O(3)–Ta–Cl(4)	84.26(9)	C(1)–Ta–Cl(5)	91.6(1)
C(1)–Ta–Cl(4)	110.3(1)	Cl(5)–Ta–Cl(4)	85.83(4)
C(31)–O(3)–Ta	145.2(3)	C(21)–O(2)–Ta	162.6(3)
C(6)–C(1)–Ta	112.8(3)	C(2)–C(1)–Ta	113.5(3)
C(6)–C(1)–C(2)	110.4(4)		

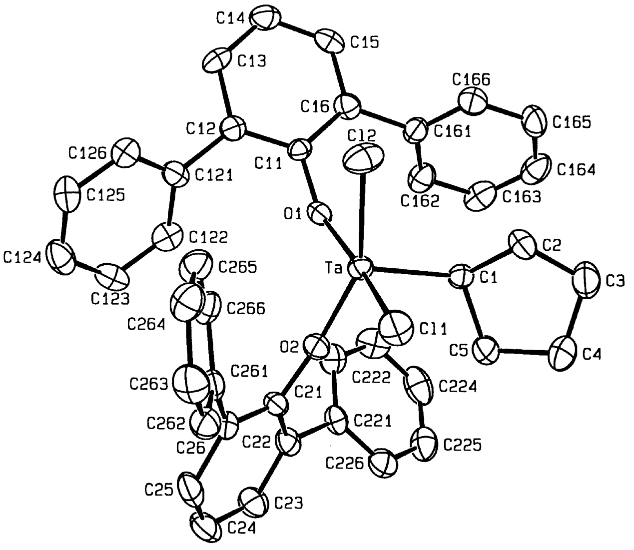


Fig. 5 Molecular structure of [Ta($OC_6H_3Ph_2$-2,6)$_2Cl_2$(c-C_5H_9)] **11**.

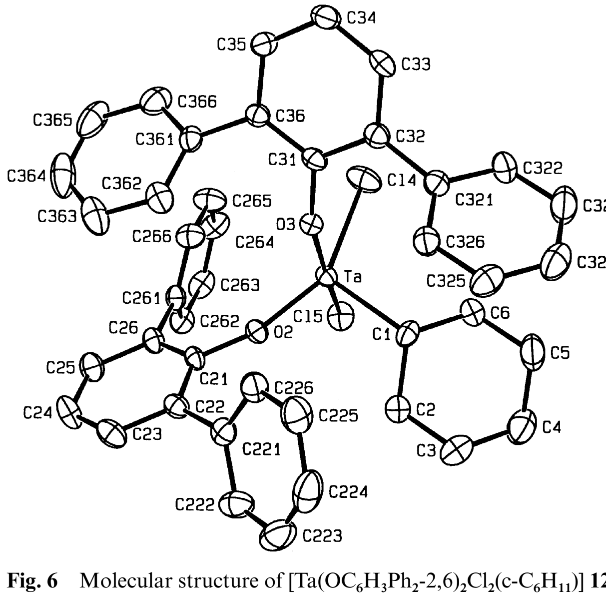


Fig. 6 Molecular structure of [Ta($OC_6H_3Ph_2$-2,6)$_2Cl_2$(c-C_6H_{11})] **12**.

tetraphenylphenoxide **13** was also synthesized from **4** (Scheme 2). The basal aryloxide oxygen atoms in **11** and **12** are clearly mutually *cis*, with O–Ta–O angles of 92° and 93° respectively. This contrasts with the trimethylsilylmethyl derivative **9** (same aryloxide ligands) where the O–Ta–O angle is *ca.* 170°. The tantalum atom can be seen to occupy the equatorial site of the cyclohexyl ring and pseudo-equatorial site of the cyclopentyl derivative. We have no hypothesis as to why there is such a dramatic structural change on replacing CH_2SiMe_3 by a cyclopentyl or cyclohexyl group. Despite the presence of β-hydrogens within the alkyl groups, compounds **11–13** appeared to be indefinitely stable at ambient temperatures both in the solid state and C_6D_6 solution (as monitored by ^1H NMR spectroscopy). It is interesting to note that although many have been synthesized, there are relatively few transition metal cyclohexyl structures reported, and only one previous example

Table 9 Selected bond distances (Å) and angles (°) for $[Ta(OC_6H_3Ph_2\text{-}2,6)_2Cl(CH_2SiMe_3)_2]$ **14**

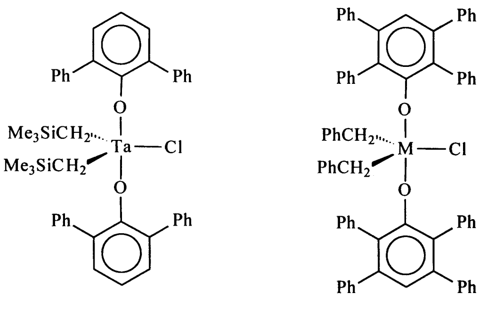
Ta–O(1)	1.903(12)	Ta–O(2)	1.933(12)
Ta–C(41)	2.088(6)	Ta–C(31)	2.104(6)
Ta–Cl	2.3996(18)		
O(1)–Ta–O(2)	176.0(6)	O(1)–Ta–C(41)	92.5(4)
O(2)–Ta–C(41)	88.5(4)	O(1)–Ta–C(31)	91.0(3)
O(2)–Ta–C(31)	92.1(4)	C(41)–Ta–C(31)	115.3(3)
O(1)–Ta–Cl	88.4(3)	O(2)–Ta–Cl	87.7(3)
C(41)–Ta–Cl	117.0(2)	C(31)–Ta–Cl	127.7(2)
Ta–O(1)–C(11)	155.7(11)	Ta–O(2)–C(21)	157.6(11)
Ta–C(31)–Si(3)	122.1(4)	Ta–C(41)–Si(4)	118.7(4)

Table 10 Selected bond distances (Å) and angles (°) for $[Ta(OC_6HPh_4\text{-}2,3,5,6)_2Cl(CH_2Ph)_2]$ **16**

Ta–O(1)	1.894(4)	Ta–O(2)	1.894(4)
Ta–Cl	2.354(2)	Ta–C(3)	2.137(6)
Ta–C(4)	2.203(5)		
O(1)–Ta–O(2)	176.3(2)	O(2)–Ta–C(3)	90.4(2)
O(1)–Ta–C(3)	90.5(2)	O(2)–Ta–C(4)	91.5(2)
O(1)–Ta–C(4)	91.3(2)	C(3)–Ta–C(4)	119.8(2)
O(2)–Ta–Cl	88.6(1)	O(1)–Ta–Cl	87.9(1)
C(3)–Ta–Cl	121.3(2)	C(4)–Ta–Cl	118.9(1)
C(11)–O(1)–Ta	176.0(4)	C(21)–O(2)–Ta	177.0(4)
C(31)–C(3)–Ta	106.1(4)	C(41)–C(4)–Ta	125.5(4)

of a cyclopentyl compound appears to have been structurally characterized. The cyclohexyl compounds include the homoleptic derivatives $[M(C_6H_{11})_4]$ (M = Cr, Ru, Os);[15] dinuclear $[Mn_2(C_6H_{11})_4(dmpe)]$;[16] $[CpIr(PMe_3)(C_6H_{11})(H)]$;[17] $[(\eta^6\text{-}C_6Me_6)Ir(CO)(C_6H_{11})]$;[18] $[\{N(CH_2CH_2NSiMe_3)_3\}Mo(C_6H_{11})]$[19] and $[(dmg)Co(C_6H_{11})(benzimidazole)]$ (H_2dmg = dimethylglyoxime).[20] The cyclopentyl compound is also coordinated to the cobalt–dimethylglyoximato nucleus, $[(dmg)Co(C_5H_9)(OH_2)]$.[21] The molybdenum cyclopentyl and cyclohexyl compounds $[\{N(CH_2CH_2NSiMe_3)_3\}Mo(C_nH_{2n+2})]$ (n = 5,6) studied by Schrock *et al.* were shown to undergo facile, reversible α-hydrogen abstraction many orders of magnitude faster than β-hydrogen abstraction.[19]

Further treatment of **11–13** with cyclopentyl- or cyclohexyl-Grignard did not lead to tractable products. The alkylation of the tantalum chlorides **2** or **4** with up to three equivalents of $PhCH_2MgCl$ or Me_3SiCH_2MgCl proceeds smoothly *via* the bis(alkyl) intermediates **14** and **16** (Scheme 3) to produce the previously reported tris(benzyl) or tris(trimethylsilyl) derivatives. The bis(alkyls) **14** (previously synthesized) and **16** were subjected to a single crystal X-ray diffraction analysis and found to both contain tbp structures with *trans* axial aryloxides (Figs. 7 and 8, Tables 9 and 10).



14 M = Nb, **15**; Ta, **16**

Scheme 3

In contrast, the reaction of the niobium chloride **3** with greater than one equivalent of $PhCH_2MgCl$ or Me_3SiCH_2MgCl was found to produce a complex mixture of products. In the case of the benzyl Grignard, spectroscopic evidence was obtained for the presence of at least one benzylidene species. From one reaction mixture it was found possible to isolate a few crystals of the bis(benzyl) compound **15** (Scheme 3) shown to be isomorphous with the tantalum compound **16** (Table 11). We have spent considerable effort at trying to completely characterize the reaction mixtures obtained by addition of two or three equivalents of Me_3SiCH_2MgCl to **3**. Spectroscopic analysis by ^{29}Si and ^1H NMR (Table 12) indicated the presence of a number of diamagnetic compounds while ESR showed the presence of paramagnetic species. Generating any of these components in high yield proved difficult. From the reaction with two equivalents, the bis(alkyl) **17** (Scheme 4) was identified spectroscopically along with a small amount of an alkylidene compound. The latter compound contained a sharp singlet at δ 11.79 in the ^1H NMR spectrum which we assign to the Ta=C*H*SiMe$_3$ proton signal. When this reaction mixture was heated in C_6D_6 the alkylidene species began to build up at the expense of the bis(alkyl) along with other unidentified compounds. Hence, on the basis of the spectroscopic data (Table 12) it seems reasonable to formulate the alkylidene compound as $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl({=}CHSiMe_3)]$ **18**. The treatment of **3** with three equivalents of Me_3SiCH_2MgCl also produced a mixture of products. From the dark red/brown reaction mixture a few crystals of the tris(alkyl) **19** (Scheme 4) were isolated and structurally characterized (Fig. 9, Table 13). The structure is very similar to previously reported tantalum compounds $[Ta(OAr)_2(CH_2SiMe_3)_3]$ with *trans*-axial aryloxides. The remaining supernatant was found to contain at least two components. The first was identified spectroscopically as the alkyl, alkylidene $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2({=}CHSiMe_3)(CH_2SiMe_3)]$ **20**. Alkylidene **20** was also produced cleanly when a C_6D_6 solution of **19** was heated at 100 °C for a few hours. A variety of analogous trimethylsilylmethylidenes of tantalum have previously been

Table 11 Selected bond distances (Å) and angles (°) for $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl(CH_2C_6H_5)_2]$ **15**

Nb–O(1)	1.908(2)	Nb–O(2)	1.903(2)
Nb–Cl	2.3567(9)	Nb–C(3)	2.210(3)
Nb–C(4)	2.162(3)		
O(1)–Nb–O(2)	176.87(9)	O(2)–Nb–C(3)	91.18(10)
O(1)–Nb–C(3)	91.22(10)	O(2)–Nb–C(4)	90.39(11)
O(1)–Nb–C(4)	90.01(11)	C(3)–Nb–C(4)	122.6(1)
O(2)–Nb–Cl	88.88(7)	O(1)–Nb–Cl	88.24(7)
C(4)–Nb–Cl	120.4(1)	C(3)–Nb–Cl	117.00(8)
C(11)–O(1)–Nb	174.6(2)	C(21)–O(2)–Nb	177.0(2)
C(31)–C(3)–Nb	124.1(2)	C(41)–C(4)–Nb	103.2(2)

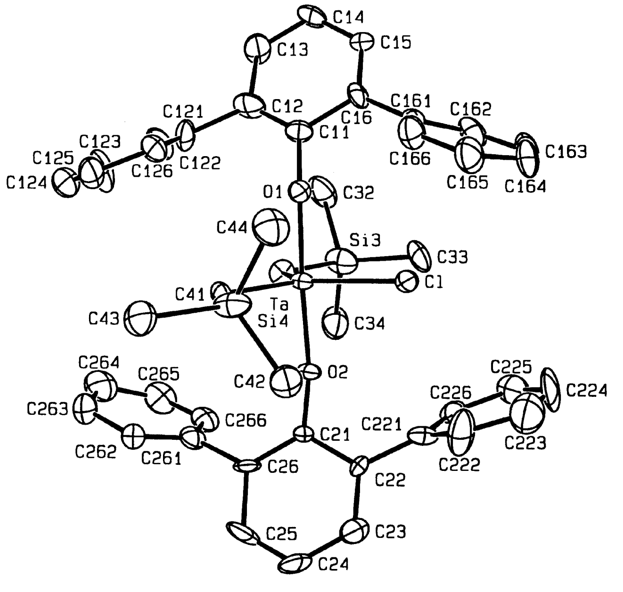


Fig. 7 Molecular structure of $[Ta(OC_6H_3Ph_2\text{-}2,6)_2Cl(CH_2SiMe_3)_2]$ **14**.

Table 12 Selected NMR properties of products from the reaction of **3** with Me_3SiCH_2MgCl[a]

Compound	^{29}Si NMR		^{1}H NMR	
$[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(CH_2SiMe_3)]$ **10**	1.21	$(CH_2\mathit{Si}Me_3)$	1.46	$(C\mathit{H}_2SiMe_3)$
			−0.15	$(CH_2Si\mathit{Me}_3)$
$[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl(CH_2SiMe_3)_2]$ **17**	0.89	$(CH_2\mathit{Si}Me_3)$	0.32	$(C\mathit{H}_2SiMe_3)$
			0.05	$(CH_2Si\mathit{Me}_3)$
$[Nb(OC_6HPh_4\text{-}2,3,5,6)_2(CH_2SiMe_3)_3]$ **19**	0.58	$(CH_2\mathit{Si}Me_3)$	0.18	$(C\mathit{H}_2SiMe_3)$
			0.09	$(CH_2Si\mathit{Me}_3)$
$[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl({=}CHSiMe_3)]$ **18**	−7.40	$(CH\mathit{Si}Me_3)$	11.79	$(C\mathit{H}SiMe_3)$
			0.04	$(CHSi\mathit{Me}_3)$
$[Nb(OC_6HPh_4\text{-}2,3,5,6)_2({=}CHSiMe_3)(CH_2SiMe_3)]$ **20**	3.07	$(CH_2\mathit{Si}Me_3)$	10.92	$(C\mathit{H}SiMe_3)$
	−9.92	$(CH\mathit{Si}Me_3)$	0.20	$(C\mathit{H}_2SiMe_3)$
			0.05	$(CH_2Si\mathit{Me}_3$ and $CHSi\mathit{Me}_3)$

[a] C_6D_6 solvent at 30 °C. Chemical shift/ppm. ^{29}Si NMR spectra were recorded with 5% $Cr(acac)_3$ added and are referenced to internal TMS.

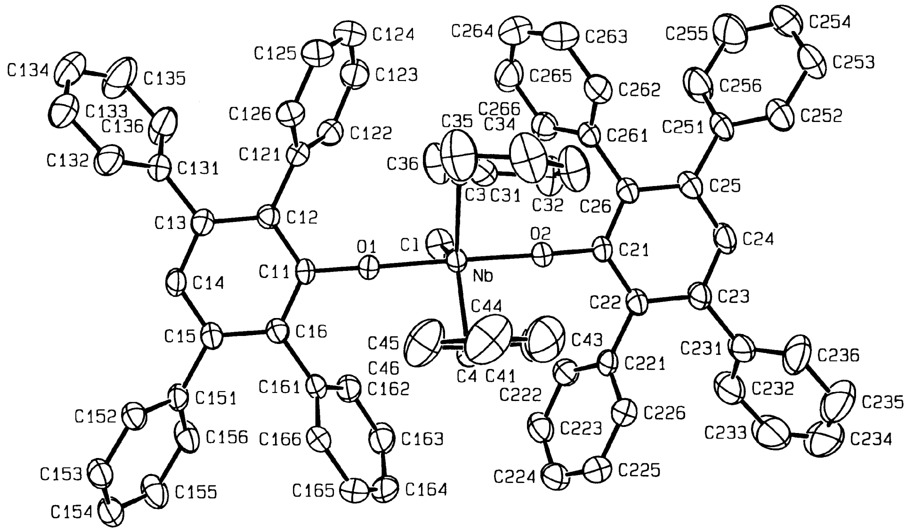


Fig. 8 Molecular structure of $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl(CH_2Ph)_2]$ **15**. The tantalum compound **16** is isomorphous and isostructural.

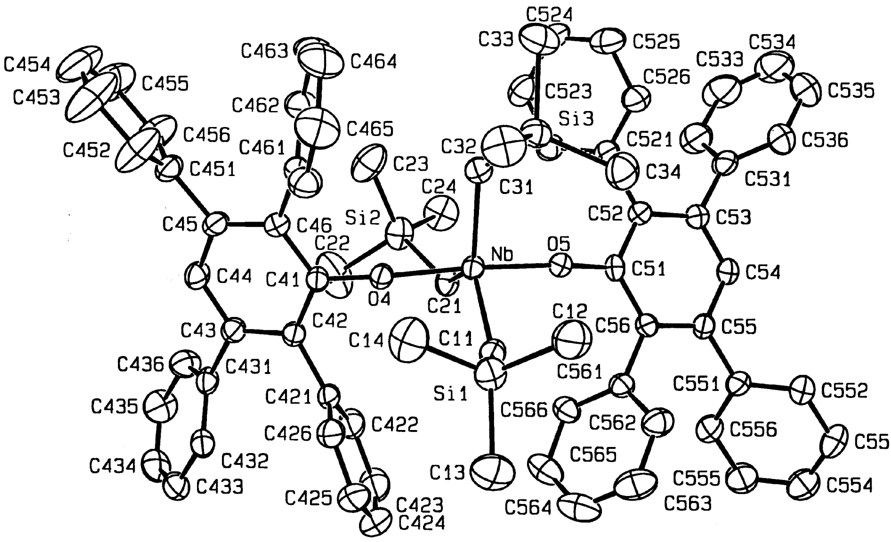
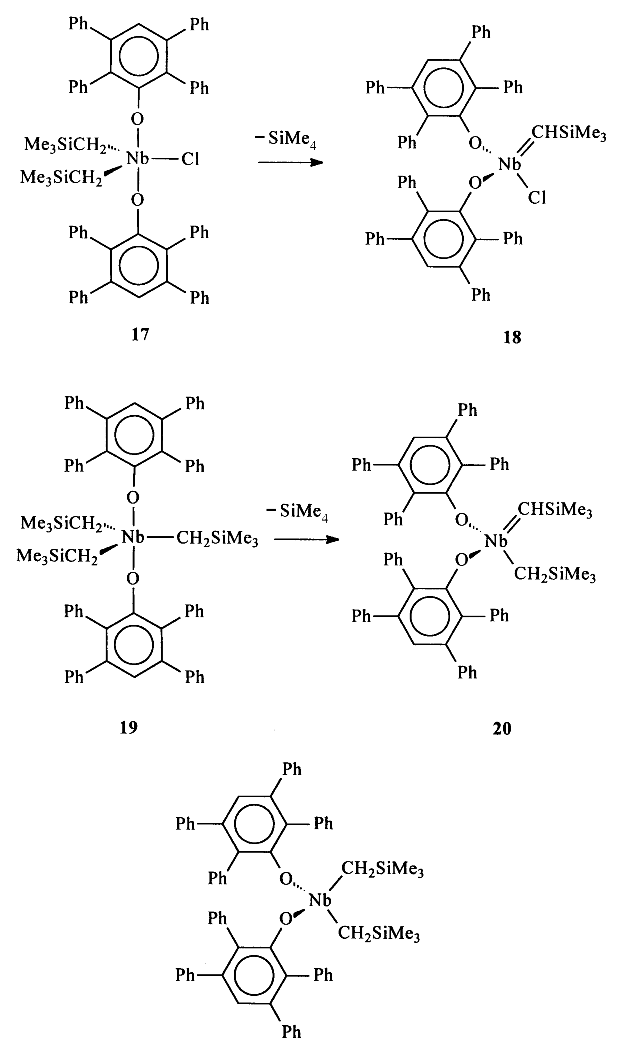


Fig. 9 Molecular structure of $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2(CH_2SiMe_3)_3]$ **19**.

reported, formed either thermally or photochemically from alkyl precursors.[6a] The reaction mixture was also found to contain a paramagnetic material by ESR spectroscopy. Recrystallization from benzene layered with pentane led to the formation of a red material that consistently contained one C_6H_6 and $\frac{1}{2}$ n-pentane per Nb. The niobium atom was consistently four-coordinate with two aryloxides and two carbon groups bound. Refinement of the tetraphenylphenoxides and one Nb–CH_2SiMe_3 unit could be achieved but the remaining Nb–C–$SiMe_3$ group proved problematic. The Nb–C distance for this group also varied from sample to sample. It was therefore concluded that the two compounds $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2({=}CHSiMe_3)(CH_2SiMe_3)]$ **20** and $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2(CH_2SiMe_3)_2]$ **21** (Scheme 4) co-crystallized. This was confirmed by NMR and ESR analysis of the crystalline samples. Eventually a few single crystals were obtained from benzene–n-hexane (this time one C_6H_6 and $\frac{1}{2}$ n-hexane per Nb) were obtained that contained no diamagnetic alkylidene component (^{1}H NMR) and the solid state structure of the d^1-dialkyl **21** could be obtained (Fig. 10, Table 14).

Table 13 Selected bond distances (Å) and angles (°) for $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2(CH_2SiMe_3)_3]$ **19**

Nb–O(4)	1.926(2)	Nb–O(5)	1.932(2)
Nb–C(11)	2.139(3)	Nb–C(21)	2.199(3)
Nb–C(31)	2.140(3)		
O(4)–Nb–O(5)	172.28(7)	C(11)–Nb–C(21)	117.5(1)
C(21)–Nb–C(31)	120.3(1)	C(31)–Nb–C(11)	122.2(1)
O(4)–Nb–C(11)	88.86(9)	O(4)–Nb–C(21)	86.31(9)
O(4)–Nb–C(31)	93.66(9)	O(5)–Nb–C(11)	92.16(9)
O(5)–Nb–C(21)	86.44(9)	O(5)–Nb–C(31)	92.27(9)
C(41)–O(4)–Nb	156.6(2)	C(51)–O(5)–Nb	169.7(2)
Nb–C(11)–Si(1)	133.3(2)	Nb–C(21)–Si(2)	128.5(1)
Nb–C(31)–Si(3)	128.9(2)		



17 18 19 20 21

Scheme 4

Table 14 Selected bond distances (Å) and angles (°) for $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2(CH_2SiMe_3)_2]$ **21**

Nb–O(2)	1.9016(16)	Nb–O(1)	1.9174(17)
Nb–C(30)	2.117(3)	Nb–C(40)	2.145(3)
O(2)–Nb–O(1)	147.15(7)	O(2)–Nb–C(30)	99.54(9)
O(2)–Nb–C(40)	99.34(9)	O(1)–Nb–C(30)	100.71(9)
O(1)–Nb–C(40)	101.21(9)	C(30)–Nb–C(40)	102.42(12)
C(21)–O(2)–Nb	159.02(16)	C(11)–O(1)–Nb	153.93(15)
Nb–C(30)–Si(30)	123.0(2)	Nb–C(40)–Si(40)	124.6(2)

Table 15 Selected bond distances (Å) and angles (°) for $[Nb(OC_6HCy_2\text{-}2,6\text{-}Ph_2\text{-}3,5)_2(H)_2(PMe_3)_2]$ **22**

Nb–H(1)	1.77(5)	Nb–O(10)	1.916(2)
Nb–P	2.586(2)		
H(1)–Nb–H(1′)	180.00(3)	H(1)–Nb–O(10)	92.0(2)
H(1′)–Nb–O(10)	88.0(2)	H(1)–Nb–P	83.0(2)
H(1′)–Nb–P	97.0(2)	O(10)–Nb–P	89.54(7)
O(10′)–Nb–P	90.46(7)	P–Nb–P′	180.00(7)
C(11)–O(10)–Nb	169.7(2)	O(10′)–Nb–P′	89.54(7)

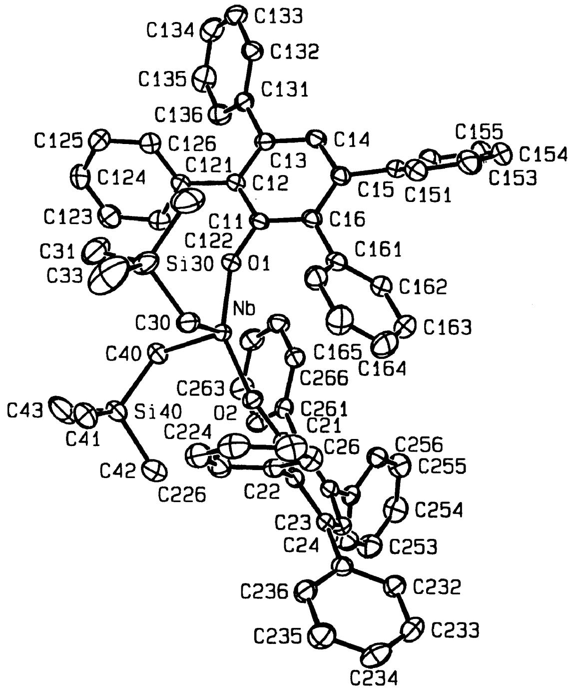
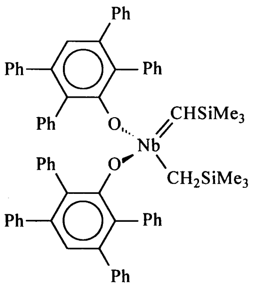


Fig. 10 Molecular structure of $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2(CH_2SiMe_3)_2]$ **21**.

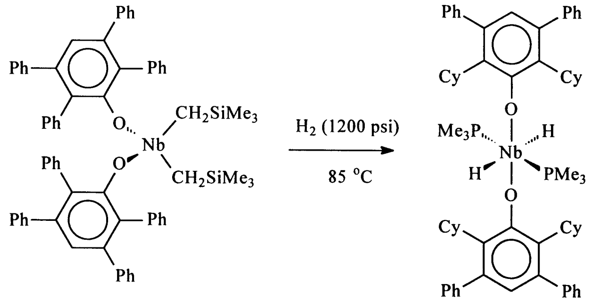
Synthesis and characterization of the d^1-hydride $[Nb(OC_6HCy_2\text{-}2,6\text{-}Ph_2\text{-}3,5)_2(H)_2(PMe_3)_2]$

The hydrogenolysis of alkyl(aryloxides) of tantalum in the presence of donor ligands has been shown to lead to the corresponding hydrido(aryloxides). Two distinct structural motifs have been identified, depending on the steric requirement of the ligands. A series of seven-coordinate bis(aryloxides) $[Ta(OAr)_2(H)_x(Cl)_{3-x}(L)_2]$ ($x = 1,2,3$; L = tertiary phosphine) have been obtained for relatively small aryloxides. These compounds adopt a pentagonal bipyramidal structure with *trans* aryloxides. With either an additional aryloxide, or bulkier substituents the six-coordinate adducts $[Ta(OAr)_3(H)_2(L)]$ or $[Ta(OAr)_2(H)_2(Cl)(L)]$ are formed. These compounds show an interesting structural distortion both in solution and the solid state in which the hydride ligands are dramatically bent towards the phosphine ligand. This distortion has been the focus of theoretical analysis.

A deep red benzene solution of a mixture of **20** and **21** and PMe_3 was heated at 85 °C under 1200 psi of H_2. Inspection of the reaction mixture after slow cooling and careful degassing showed the presence of dark emerald green crystals below a green supernatant. Analysis of the crystals by X-ray diffraction showed the compound to be the d^1-di(hydride) $[Nb(OC_6HCy_2\text{-}2,6\text{-}Ph_2\text{-}3,5)_2(H)_2(PMe_3)_2]$ **22** (Scheme 5, Fig. 11, Table 15). The compound contains a crystallographic inversion center with an all-*trans* $NbH_2O_2P_2$ core. A series of related chlorides and bromides all *trans*-$[M(OAr)_2X_2(L)_2]$ have been previously isolated and characterized. The d^1-species **22** exhibits a ten line ESR signal (^{93}Nb, $I = 9/2$) in toluene at 77 K and a single ν(Nb–H) stretching vibration at 1720 cm^{-1}. Formation of compound **22** involves not only hydrogenolysis of niobium alkyl/alkylidene bonds but also the intramolecular hydrogenation of the *ortho*-phenyl rings of the aryloxide ligands. This type of behavior has been well documented in previous studies. Analysis (NMR) of



20



21 **22**

Scheme 5

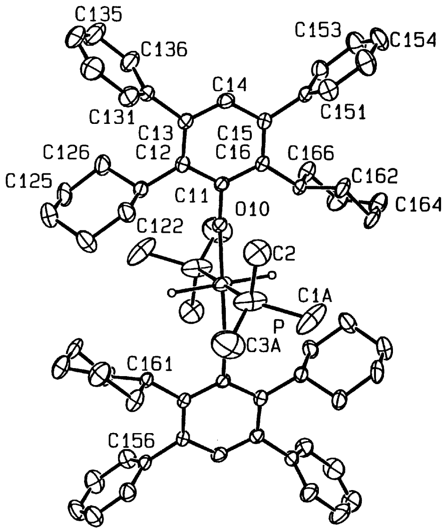


Fig. 11 Molecular structure of [Nb(OC$_6$HCy$_2$-2,6-Ph$_2$-3,5)$_2$(H)$_2$(PMe$_3$)$_2$] **22**.

the supernatant from the reaction showed it to consist of mainly cyclohexane. Experiments show that compound **22** is a catalyst(precursor) for the intermolecular hydrogenation of benzene and aryl-phosphine ligands. These results and a study of the stoichiometric reactivity of **22** will be the focus of a future publication.

Experimental

All operations were carried out under a dry nitrogen atmosphere or *in vacuo* either in a Vacuum Atmosphere Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium–benzophenone and stored under dry nitrogen. Trimethylphosphine was purchased from Strem Chemical Co. and 1,3-cyclohexadiene and styrene were purchased from Aldrich Chemical Co. All reagents were dried over 3 Å molecular sieves prior to use. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Associates Gemini 200 and an Inova 300 spectrometer and were referenced using protio impurities of commercial benzene-d_6 as an internal standard. ^{29}Si NMR spectra were recorded with 5% Cr(acac)$_3$ added and are referenced to internal TMS. Microanalytical data were obtained in-house at Purdue. A number of the compounds crystallized containing hydrocarbon molecules in the unit cell. Hence accurate microanalytical data were difficult to obtain in some cases due to partial loss of solvate during analysis. This is compounded by the fact that poly(phenylated)phenoxide ligands tend to generate low carbon analyses due to incomplete combustion. All high-pressure reactions were performed in a Parr Model 4561, 300 mL internal volume minireactor.

The X-ray diffraction studies were completed "in-house" at Purdue University.

Syntheses

[Nb{OC$_6$H(C$_6$H$_4$Me-4)$_2$-2,6-Ph$_2$-3,5}$_2$Cl$_3$] (5). A solution of [NbCl$_5$] (1.60 g, 5.92 mmol) in benzene (100 mL) was stirred under nitrogen at room temperature. To the orange suspension, 2,6-di-*p*-tolyl-3,5-diphenylphenol (5.30 g, 12.4 mmol)[22] was slowly added. The mixture was stirred for 30 min, which afforded a dark red solution. The clear red solution was dried *in vacuo*. The crude product was washed with hexane to remove any phenolic impurities. X-Ray quality crystals were grown from benzene layered with pentane. Yield = 4.99 g (80.4%). Anal. calc. for NbC$_{64}$H$_{50}$O$_2$Cl$_3$·C$_6$H$_6$: C, 74.50; H, 5.00; Calc. for NbC$_{64}$H$_{50}$O$_2$Cl$_3$: C, 73.18; H, 4.80; Found: C, 73.61; H, 4.97%. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 1.95 (s, 12 H, -C$_6$H$_4$*Me*), 6.79–7.25 (m, aromatics), 7.34 (s, 2H, -*p*-C*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 30 °C): δ 20.99 (-C$_6$H$_4$*Me*), 126.82–141.99 (aromatics), 162.71 (*ipso-C*).

[Nb(OC$_6$HPh$_4$-2,3,5,6)$_2$I$_3$] (6). To a suspension of [Nb(OC$_6$HPh$_4$-2,3,5,6)$_2$Cl$_3$] (3.0 g, 3.02 mmol) in toluene (50 mL) at 0 °C was slowly added dropwise a solution of MeMgI (9.00 mmol) in ether (3.00 mL) *via* a syringe. The reaction was stirred for 5 h, filtered to remove the salts and the solvent removed under vacuum. The resulting brown, gummy solid was taken up in a minimum of benzene and layered with pentane to afford a few brown crystals of **6**. The crystals were washed with pentane and dried under vacuum. Anal. calc. for C$_{60}$H$_{42}$O$_2$I$_3$Nb·2C$_6$H$_6$: C, 60.69; H, 3.82. Found: C, 60.31; H, 3.67%. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 6.8–7.2 (m, aromatics).

[Ta(OC$_6$HPh$_4$-2,3,5,6)$_2$Br$_3$] (7). A solid sample of 2,3,5,6-tetraphenylphenol (16.18 g, 40.6 mmol) was slowly added to a yellow solution of [TaBr$_5$] (11.68 g, 20.0 mmol) in toluene (100 mL) under a flow of nitrogen with stirring. The resulting orange solution was refluxed for five hours. Then the solution was allowed to cool overnight (approx. 16 hours) without stirring. The supernatant was decanted off the resulting precipitate, which was dried under vacuum. The crude product was purified by dissolving it in a minimum of benzene and layering the resulting solution with pentane. Yield 19.4 g (79%). Anal. calc. for C$_{60}$H$_{42}$O$_2$Br$_3$Ta·2C$_6$H$_6$: C, 63.04; H, 3.97. Found: C, 63.57; H, 4.14%. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 6.7–7.2 (m, aromatics).

[Ta(OC$_6$HPh$_4$-2,3,5,6)$_2$Cl$_2$(CH$_2$Ph)] (8). To a suspension of [Ta(OC$_6$HPh$_4$-2,3,5,6)$_2$Cl$_3$] (1.0 g, 0.9 mmol) in toluene (25 mL), was added ClMgCH$_2$Ph (0.14 g, 0.9 mmol) at −78 °C. The reaction was stirred for 24 h, after which time a fine brown precipitate of MgCl$_2$ formed. The solution was filtered to remove the salts and dried *in vacuo* to give an orange yellow solid. The solid was redissolved in a minimum amount of benzene and layered with pentane (1 mL) yielding the product as yellow crystals which were washed with pentane and dried under vacuum. Yield: 230 mg (23%). ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 6.45–7.52 (aromatic protons), 0.60 (s, C*H*$_2$Ph). ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 158.7 (s, *ipso*-C), 125.3–142.3 (aromatic carbons), 84.5 (s, *C*H$_2$Ph).

$[Ta(OC_6H_3Ph_2\text{-}2,6)_2Cl_2(CH_2SiMe_3)]$ (9). To a suspension of $[Ta(OC_6H_3Ph_2\text{-}2,6)_2Cl_3]$ (1.0 g, 1.3 mmol) in toluene (20 mL), was added $ClMgCH_2SiMe_3$ (0.20 g, 1.3 mmol) *via* syringe in a dry ice bath. The reaction was stirred for 2 h, after which time a fine brown precipitate of $MgCl_2$ formed. The solution was dried *in vacuo* and filtered to remove the salts to give an orange crackly solid. The solid was dissolved in a minimum amount of benzene and layered with pentane (1 mL) yielding the product as yellow crystals which were washed with pentane and dried under vacuum. Yield: 399 mg (37%). ^1H NMR (C_6D_6, 25 °C): δ 6.83–7.47 (aromatic protons), 0.94 (s, $C\mathit{H}_2SiMe_3$), −0.18 (s, $CH_2Si\mathit{Me}_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 156.7 (s, *ipso*-C), 121.4–140.3 (aromatic carbons), 95.3 (br, $\mathit{C}H_2SiMe_3$), 0.74 (s, $CH_2Si\mathit{Me}_3$).

$[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(CH_2SiMe_3)]$ (10). To a suspension of $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$ (1.0 g, 1.0 mmol) in benzene (20 mL), was added $ClMgCH_2SiMe_3$ (0.30 g, 2.0 mmol). The reaction was stirred for 2 h, after which time a fine brown precipitate of $MgCl_2$ formed. The solution was filtered to remove the salts and dried *in vacuo* to give an orange crackly solid. The solid was redissolved in a minimum amount of benzene and layered with pentane (1 mL) yielding the product as yellow crystals which were washed with pentane and dried under vacuum. Yield: 250 mg (24%). ^1H NMR (C_6D_6, 25 °C): δ 6.77–7.37 (aromatic protons), 1.46 (s, $C\mathit{H}_2SiMe_3$), −0.15 (s, $CH_2Si\mathit{Me}_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 158.7 (s, *ipso*-C), 126.4–142.3 (aromatic carbons), 96.0 (br, $\mathit{C}H_2SiMe_3$), 22.2 (s, $CH_2Si\mathit{Me}_3$). ^{29}Si NMR (C_6D_6, 25 °C): δ 1.21 (s, $CH_2\mathit{Si}Me_3$).

$[Ta(OC_6H_3Ph_2\text{-}2,6)_2Cl_2(c\text{-}C_5H_9)]$ (11). To a solution of $[Ta(OC_6H_3Ph_2\text{-}2,6)_2Cl_3]$ (0.80 g, 1.00 mmol) in benzene (20 mL), was added $ClMgC_6H_{11}$ (0.130 g, 1.00 mmol, 1.0 equiv.) *via* syringe under an N_2 flush using Schlenk techniques. The reaction was stirred for 4 h, filtered to remove the salts and dried *in vacuo* to give a yellow solid. Recrystallization from benzene–pentane afforded large yellow crystals (250 mg, 30.8% yield) which were washed with pentane and dried under vacuum. Anal. calc. for $C_{41}H_{35}Cl_2O_2Ta$: C, 60.68; H, 4.35. Found: C, 60.77; H, 4.35%. ^1H NMR (C_6D_6, 25 °C): δ 6.7–7.6 (m, aromatics), 2.4 (br), 1.5 (br), 1.3 (br), 0.8 (br). ^{13}C NMR (C_6D_6, 25 °C): δ 157.5 (s, *ipso*-C), 124.0–140.0 (m, aromatics), 112.6 (Ta–C), 37.4 (CH_2), 28.0 (CH_2).

$[Ta(OC_6H_3Ph_2\text{-}2,6)_2Cl_2(c\text{-}C_6H_{11})]$ (12). To a solution of $[Ta(OC_6H_3Ph_2\text{-}2,6)_2Cl_3]$ (1.0 g, 1.28 mmol) in benzene (25 mL), was added $ClMgC_6H_{11}$ (0.132 g, 0.920 mmol, 0.71 equiv.) *via* syringe under an N_2 flush using Schlenk techniques. The reaction was stirred for 5 h, filtered to remove the salts and dried *in vacuo* to give a yellow solid. Recrystallization from benzene–pentane afforded yellow crystals (860 mg, 81.0% yield) which were washed with pentane and dried under vacuum. Anal. calc. for $C_{42}H_{37}Cl_2O_2Ta$: C, 61.10; H, 4.52; Cl, 8.59. Found: C, 60.93; H, 4.43; Cl, 8.51%. ^1H NMR (C_6D_6, 25 °C): δ 6.70–7.40 (m, aromatics), 2.43 (m), 1.80 (m), 1.71 (m), 1.55 (m), 1.39(m), 0.85 (m), 0.50 (m, $C_6\mathit{H}_{11}$). ^{13}C NMR (C_6D_6, 25 °C): δ 157.30 (*ipso*-C), 156.51 (*ipso*-C), 120.80–139.21 (m, aromatics), 112.54 (Ta–*C*), 37.34 (*o*-C), 31.57 (*m*-C), 25.19 (*p*-C).

$[Ta(OC_6H_3Ph_4\text{-}2,3,5,6)_2Cl_2(c\text{-}C_6H_{11})]$ (13). To a solution of $[Ta(OC_6H_3Ph_4\text{-}2,3,5,6)_2Cl_3]$ (1.0 g, 0.923 mmol) in toluene (25 mL), was added $ClMgC_6H_{11}$ (0.144 g, 0.923 mmol, 1 equiv.) *via* syringe under an N_2 flush using Schlenk techniques. The reaction was stirred for 4 h in a dry ice bath, filtered to remove the salts and dried *in vacuo* to give a yellow solid. Recrystallization from 80 : 20 benzene–pentane afforded a fine yellow powder which was isolated and subsequently washed several times with pentane and dried under vacuum (632 mg, 60.6% yield). Anal. calc. for $C_{66}H_{53}Cl_2O_2Ta$: C, 70.15; H, 4.73. Found: C, 70.22; H, 4.86%. ^1H NMR (C_6D_6, 25 °C): δ 6.85–7.40 (m, aromatics), 2.10 (m), 1.90 (m), 1.62 (m), 1.40 (m), 0.91(m), 0.58 (m, $C_6\mathit{H}_{11}$). ^{13}C NMR (C_6D_6, 25 °C): δ 157.83 (*ipso*-C), 124.71–142.64 (m, aromatics), 112.24 (Ta–*C*), 37.53 (*o*-C), 31.74 (*m*-C), 25.16 (*p*-C).

$[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl(CH_2Ph)_2]$ (15). To a suspension of $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$ (3.02 g, 3.04 mmol) in toluene (100 mL), was added $ClMgCH_2Ph$ (1.51 g, 10.3 mmol) at 0 °C. The reaction was stirred for 3 h. The solution was filtered to remove the salts and dried under vacuum to give an orange brown solid. Analysis of this crude product by ^1H NMR showed the presence of an alkylidene species, peak at δ 10.53 (br, $C\mathit{H}Ph$). The solid was dissolved in a minimum amount of benzene and layered with hexane yielding **15** as red crystals, which were washed with pentane and dried under vacuum. Yield: 1.25 g (37%). Anal. calc. for $C_{74}H_{56}ClO_2Nb{\cdot}3C_6H_6$: C, 82.47; H, 5.57; Cl, 2.65. Found: C, 82.65; H, 5.85; Cl, 2.43%. ^1H NMR (C_6D_6, 25 °C): δ 6.70–7.27 (aromatic protons), 1.53 (s, $C\mathit{H}_2Ph$).

$[Ta(OC_6HPh_4\text{-}2,3,5,6)_2Cl(CH_2Ph)_2]$ (16). To a suspension of $[Ta(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$ (1.0 g, 0.9 mmol) in toluene (20 mL), was added $ClMgCH_2Ph$ (0.28 g, 1.84 mmol) at −78 °C. The reaction was stirred for 24 h, after which time a fine brown precipitate of $MgCl_2$ formed. The solution was filtered to remove the salts and dried *in vacuo* to give an orange yellow solid. The solid was redissolved in a minimum amount of benzene and layered with pentane (1 mL) yielding the product as yellow crystals, which were washed with pentane and dried under vacuum. Yield: 557 mg (56%). ^1H NMR (C_6D_6, 25 °C): δ 6.45–7.52 (aromatic protons), 1.60 (s, $C\mathit{H}_2Ph$).

$[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl(CH_2SiMe_3)_2]$ (17) and $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl({=}CHSiMe_3)]$ (18). To a suspension of $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$ (1.0 g, 1.0 mmol) in toluene (20 mL), in a dry ice bath was added $ClMgCH_2SiMe_3$ (0.30 g, 2.0 mmol). The reaction was stirred for 2 h and then allowed to warm up to room temperature overnight. The reaction mixture was filtered to remove salts and dried under vacuum to yield a fine yellow powder. Yield: 0.22 g (18.8%) ^1H NMR (C_6D_6, 25 °C): δ 6.56–7.50 (aromatic protons), 0.315 (s, $C\mathit{H}_2SiMe_3$), 0.046 (s, $CH_2Si\mathit{Me}_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 158.66 (s, *ipso*-C), 126.28–142.68 (aromatic carbons), 83.20 (br, $\mathit{C}H_2SiMe_3$), 2.40 (s, $CH_2Si\mathit{Me}_3$). ^{29}Si NMR (C_6D_6, 25 °C): δ 0.886 (s, $CH_2\mathit{Si}Me_3$). An NMR sample of **17** in d_6-benzene was heated for several minutes in an oil bath. A slow conversion from **17** to **18** was monitored *via* ^1H and ^{29}Si NMR. ^1H NMR (C_6D_6, 25 °C): δ 11.79 (s, $C\mathit{H}SiMe_3$), 6.56–7.50 (aromatic protons), 0.044 (s, $CHSi\mathit{Me}_3$). ^{29}Si NMR (C_6D_6, 25 °C): δ −7.40 (s, $CH\mathit{Si}Me_3$).

$[Nb(OC_6HPh_4\text{-}2,3,5,6)_2(CH_2SiMe_3)_3]$ (19), $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2({=}CHSiMe_3)(CH_2SiMe_3)]$ (20) and $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2(CH_2SiMe_3)_2]$ (21). To a suspension of $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$ (1.0 g, 1.0 mmol) in benzene (20 mL) was slowly added a 1.0 M solution of $ClMgCH_2SiMe_3$ (0.60 g, 4.0 mmol) in ether *via* syringe. The reaction was stirred for several hours after which time a fine precipitate of $MgCl_2$ formed. The solution was filtered to remove the salts. The red supernatant was collected, reduced in volume under vacuum to about 5 mL, and layered with pentane at which time a yellow precipitate formed. The supernatant was decanted and **19** was isolated as a yellow powder in 33% yield (330 mg). The red supernatant was layered with an additional aliquot of pentane to yield 230 mg of a red crystalline material composed of **20** and **21** and shown by crystallography to contain one benzene and $\frac{1}{2}$ n-pentane per Nb. A sample of **21** was obtained from benzene–n-hexane mixtures and shown by NMR to contain no diamagnetic component. For **19**: Anal. calc. for $C_{72}H_{75}O_2Si_3Nb{\cdot}0.5C_6H_6$: C, 75.79; H, 6.61. Calc. for $C_{72}H_{75}O_2Si_3Nb$: C, 75.23; H, 6.58. Found: C, 74.89; H, 6.18. Repeat: C, 74.95; H, 6.66%. ^1H NMR (C_6D_6, 25 °C): δ 6.83–7.34 (aromatic protons), 0.40 (s, $C\mathit{H}_2SiMe_3$), 0.18 (s, $CH_2Si\mathit{Me}_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 158.5 (s, *ipso*-C),

Table 16 Crystal data and data collection parameters

	5	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**14**	**15**	**16**	**19**	**21**	**22**
Formula	$C_{64}H_{50}Cl_3$-$NbO_2{\cdot}C_6H_6$	$C_{60}H_{42}I_3$-$NbO_2{\cdot}2C_6H_6$	$C_{60}H_{42}Br_3$-$TaO_2{\cdot}2C_6H_6$	$C_{67}H_{49}Cl_2$-$TaO_2{\cdot}C_6H_6$	$C_{40}H_{37}Cl_2$-O_2SiTa	$C_{64}H_{54}Cl_2$-O_2SiNb	$C_{41}H_{35}Cl_2$-O_2Ta	$C_{42}H_{37}Cl_2$-O_2Ta	$C_{44}H_{48}$-ClO_2Si_2Ta	$C_{74}H_{56}$-$ClO_2Nb{\cdot}3C_6H_6$	$C_{74}H_{56}ClO_2$-$Ta{\cdot}3C_6H_6$	$C_{72}H_{75}O_2$-$Si_3Nb{\cdot}1/2C_6H_6$	$C_{68}H_{64}O_2Si_2$-$Nb{\cdot}C_6H_6{\cdot}1/2C_6H_{14}$	$C_{66}H_{86}O_2$-P_2Nb
M	1128.49	1424.85	1371.91	1216.11	829.68	1046.03	811.59	825.62	881.45	1339.97	1428.02	1188.62	1183.55	1066.27
Space group	$P2_1/n$ (No. 14)	$C2$ (No. 5)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 1)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a/Å	11.3325(2)	25.7491(8)	12.5985(7)	10.6577(4)	15.3362(3)	9.9783(4)	9.9773(6)	11.1243(5)	10.0085(2)	13.3332(4)	13.3027(8)	12.7620(3)	23.6191(5)	11.473(2)
b/Å	21.2903(3)	7.9562(3)	13.8730(8)	14.7497(5)	12.7656(2)	12.5003(6)	11.4412(6)	12.5130(6)	10.8522(2)	15.3768(5)	15.3219(9)	18.0027(4)	10.9492(2)	11.980(2)
c/Å	23.9340(4)	19.5543(6)	17.8161(6)	19.1650(7)	18.5286(3)	22.6124(13)	16.3041(9)	14.9163(5)	11.2929(2)	19.2026(5)	19.1817(10)	28.8284(7)	27.7450(6)	12.491(3)
α/°			87.288(3)	96.494(2)		97.143(3)	101.983(3)	99.192(3)	63.9019(8)	109.4762(15)	109.364(3)			106.08(2)
β/°	96.2926(9)	125.8090(16)	73.317(3)	93.782(2)	95.3177(11)	91.442(3)	94.502(2)	104.620(3)	87.6411(7)	97.3407(17)	97.258(4)	95.5229(14)	114.967(8)	97.68(2)
γ/°			76.722(2)	106.265(2)		108.890(3)	110.754(3)	114.392(2)	68.9612(8)	102.6676(13)	102.355(3)			111.58(1)
V/Å^3	5739.8(3)	3248.7(4)	2902.5(4)	2858.5(4)	3611.84(19)	2641.4(5)	1678.8(4)	1745.7(3)	1018.06(4)	3533.9(4)	3519.5(8)	6592.6(5)	6504.6(4)	1479.8(1)
Z	4	2	2	2	4	2	2	2	1	2	2	4	4	1
ρ_{calc}/g cm^{-3}	1.306	1.456	1.570	1.413	1.526	1.315	1.605	1.571	1.438	1.259	1.347	1.197	1.209	1.196
Temperature/K	203(1)	203(1)	193(1)	173(1)	150(1)	193(1)	193(1)	193(1)	150(1)	203(1)	173(1)	203(1)	163(1)	203(1)
R^a	0.049	0.051	0.043	0.045	0.031	0.066	0.043	0.034	0.042	0.059	0.057	0.049	0.048	0.043
$R_w{}^b$	0.119	0.139	0.098	0.113	0.073	0.116	0.097	0.081	0.108	0.131	0.108	0.110	0.121	0.117
μ/mm^{-1}	3.84	1.63	3.96	2.04	0.38	3.22	3.43	3.30	2.82	0.25	1.63	0.27	0.26	0.29
Reflections collected	46609	14265	22999	23365	34144	24738	13777	134988	11150	37974	28890	40016	42658	4869
Independent reflections	15178 (R_{int} = 0.051)	5623 (R_{int} = 0.049)	12171 (R_{int} = 0.060)	12058 (R_{int} = 0.069)	8132 (R_{int} = 0.047)	9225 (R_{int} = 0.137)	7063 (R_{int} = 0.064)	7340 (R_{int} = 0.045)	7777 (R_{int} = 0.027)	14354 (R_{int} = 0.077)	14779 (R_{int} = 0.156)	13250 (R_{int} = 0.066)	15330 (R_{int} = 0.043)	4629 (R_{int} = 0.030)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o{}^2 > 2\Sigma(F_o{}^2)$. [b] $R_w = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w|F_o{}^2|^2]^{1/2}$.

126.4–143.1 (aromatic carbons), 66.1 (br, CH_2SiMe_3), 12.7 (s, CH_2SiMe_3). ^{29}Si NMR (C_6D_6, 25 °C): δ 0.583 (s, CH_2SiMe_3). For **20**: ^{1}H NMR (C_6D_6, 25 °C): δ 10.92 (s, $CHSiMe_3$), 6.99–7.36 (aromatic protons), 0.196 (s, CH_2SiMe_3), 0.044 (s, Me_3). ^{13}C NMR (C_6D_6, 25 °C): δ 262.4 (br, $CHSiMe_3$), 158.3 (s, *ipso*-C), 126.5–141.9 (aromatic carbons), 71.3 (br, CH_2SiMe_3), 2.03 (s, $CHSiMe_3$), 1.92 (s, CH_2SiMe_3). ^{29}Si NMR (C_6D_6, 25 °C): δ 3.07 (s, CH_2SiMe_3), −9.92 (s, $CHSiMe_3$). For **21**: Anal. calc. for $C_{68}H_{64}O_2Si_2Nb\cdot C_6H_6\cdot 0.5C_6H_{14}$: C, 77.62; H, 6.77. Found: C, 77.21; H, 6.37%. ESR (C_6D_6, 25 °C): *g*-value 1.96.

[Nb(OC_6HCy_2-2,6-Ph_2-3,5)$_2$(H)$_2$(PMe_3)$_2$] (22). In a 50 mL round bottom flask, **20**/**21** (510 mg, 0.481 mmol, 1 equiv.) was dissolved in benzene (15 mL). Trimethylphosphine (PMe_3) (2.4 mmol, 5 equiv.) was condensed from a calibrated gas manifold into the red solution with no observable color change. In a dry lab, the 50 mL round bottom flask containing the mixture was placed into the mini-reactor, which was sealed, removed from the dry box and pressurized to 1200 psi with H_2. The mini-reactor was heated to 85 °C for 24 hours, while being stirred only for the first hour of reaction time. The mini-reactor was cooled slowly before being de-pressurized and taken back into the dry box to be opened. The red brown supernatant was decanted from the green crystals that had formed. The crystals were washed with pentane and dried under vacuum. Yield: 0.25 g (49%). Anal. calc. for $NbC_{66}H_{86}O_2P_2$: C, 74.35; H, 8.13; P, 5.81. Found: C, 73.83; H, 8.26; P, 5.60%. IR (Nujol mull) ν(Nb–H) 1720 cm^{-1}.

X-Ray data collection and reduction

Crystal data and data collection parameters are contained in Table 16. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) on a Nonius Kappa-CCD. Lorentz and polarization corrections were applied to the data.[23] An empirical absorption correction using SCALEPACK was applied.[24] Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.[25] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded, except in the case of **22** where the metal-hydride ligands were located in a difference map and refined. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ and the weight w is defined as $w = 1/[\Sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$ where $P = (F_o^2 + 2F_c^2)/3$. Scattering factors were taken from the International Tables for Crystallography.[26] Refinement was performed on a AlphaServer 2100 using SHELX-97.[27] Crystallographic drawings were done using the program ORTEP.[28]

CCDC reference numbers 159022 and 164008–164020.

See http://www.rsc.org/suppdata/dt/b1/b101722p/ for crystallographic data in CIF or other electronic format.

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