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PAPER

Synthesis and reactivity of niobium complexes having a tripodal triaryloxide ligand in bidentate, tridentate, and tetradentate coordination modes†

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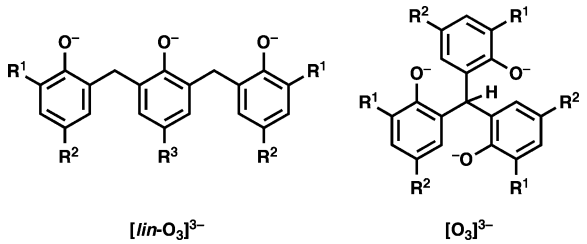
The synthesis and reactivity of niobium complexes incorporating a tripodal triphenol (tris(3,5-*tert*-butyl-2-hydroxylphenyl)methane = H_3[**O**$_3$]) have been investigated. Addition of one equivalent of $NbCl_5$ in CH_3CN to H_3[**O**$_3$] in toluene led to partial HCl elimination, giving [H(**O**$_3$)]$NbCl_3(CH_3CN)$ (**1**) with a bidendtate bis(aryloxide) ligand and a pendant phenol arm. Treatment of **1** with THF afforded [H(**O**$_3$)]$NbCl_3$(THF) (**2**). Deprotonation of **1** with NEt_3 in toluene promoted coordination of the pendant phenol group to generate (Et_3NH)[(***syn*-O**$_3$)$NbCl_3$] (**3-*syn***). Prolonged heating of **3-*syn*** resulted in clean conversion to the *anti* isomer (**3-*anti***). Attempted deprotonation of **2** with $PhCH_2MgCl$ provided [H(**O**$_3$)]$Nb(CH_2Ph)_3$ (**4**), in which alkylation took place at the metal center but the pendant phenol arm remained intact. When **3-*syn*** was treated with $PhCH_2MgCl$, [**O**$_3$**C**]$Nb(CH_2Ph)$ (**5**) was produced *via* C–H activation of the methine C–H bond. The analogous reaction with **3-*anti*** provided a benzylidene complex [***anti*-O**$_3$]Nb(CHPh)(THF) (**6**). During the course of the reaction, the *anti* ligand conformation is retained. Upon heating, **4** underwent methine C–H and phenol O–H activation, yielding the metalatrane **5**. Complexes **1**, **3-*syn***, **3-*anti***, **4**, and **5** were characterized by X-ray diffraction.

Introduction

The use of multidentate ligands in coordination chemistry and homogeneous catalysis is one of the versatile strategies in ligand design for the discovery of metal complexes with novel properties. Multidentate ligands with various combinations of donor functions and ligand structures (linear, cyclic, *etc*.) have been extensively investigated.[1–5] Aryloxides can serve as a useful scaffold for the construction of multidentate ligands owing to the availability of two substitutes at the *ortho* positions on the aryloxide ring.[6,7] This dual substitute pattern allows for the integration of aryloxide units into the multidentate ligand framework as well as the tunability of steric and electronic factors. As a result, aryloxide-based multidentate ligands have been found to support a number of catalytic and stoichiometric transformations, *e.g.*, olefin polymerization,[8–10] aerial oxidation of alcohols,[11] and activation of small molecules.[12–14]

We are interested in the coordination chemistry of aryloxide-based multidentate ligands.[15] These include triaryloxides ([***lin*-O**$_3$]$^{3-}$)[16–19] and mixed-donor ligands containing two aryloxides and one neutral donor.[20,21] In these tridentate ligands, three donor functions are linearly arranged in the ligand framework. Interested by the effect of ligand structure on chemical properties of metal complexes, we have drawn our attention to a tripodal triaryloxide, in which three aryloxide units are joined to one methine carbon ([**O**$_3$]$^{3-}$, Scheme 1). Unlike linear-type tridentate ligands adopting facial and meridional coordination modes, the tripodal triaryloxide ligand is geometrically predisposed to facial coordination. The tridentate [**O**$_3$] ligand binds to the metal in two fashions, in which the C–H bond of the bridging methine has a different orientation (*syn* and *anti* forms, Scheme 2). In addition, the [**O**$_3$] ligand could be used as a precursor for introducing a tetradentate [**O**$_3$**C**] ligand *via* C–H activation of the methine carbon.



Scheme 1 Linear and tripodal triaryloxide ligands.

Previously, we reported the synthesis and structures of titanium and zirconium complexes having [***syn*-O**$_3$]$^{3-}$, [***anti*-O**$_3$]$^{3-}$ and [**O**$_3$**C**]$^{4-}$ ligands.[22] We also employed the [***anti*-O**$_3$] ligand to prepare a diniobium hydride complex capable of cleaving dinitrogen.[23] In this report, we outline some chemistry of niobium complexes bearing the tripodal triaryloxide. The study details synthetic

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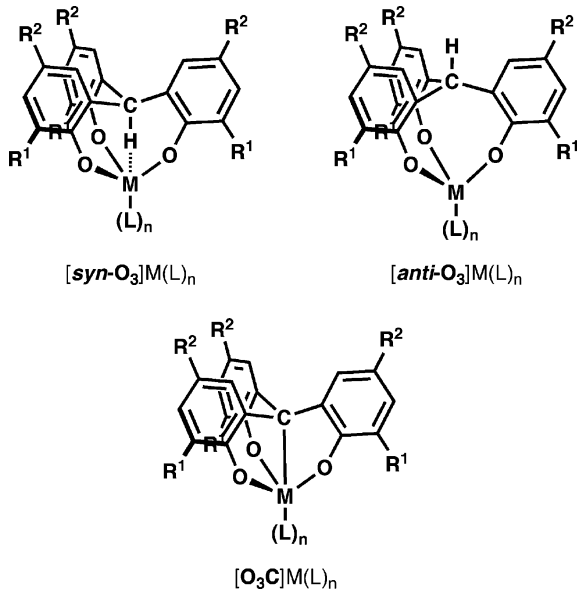


Scheme 2 Coordination modes of [$\mathbf{O_3}$] and [$\mathbf{O_3C}$] ligands.

protocols for complexes employed in studies on reactivity. Some of the results included have been previously communicated.[23]

Results and discussion

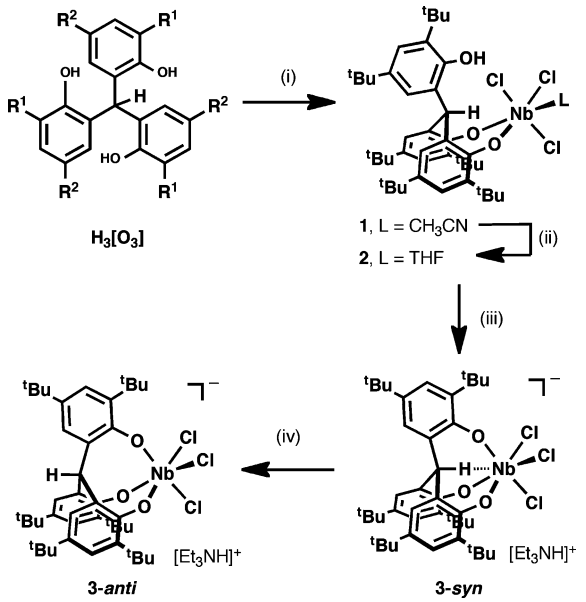
There are various synthetic routes to aryloxide complexes. The choice of the synthetic method depends on metal precursors as well as the nature of aryloxide ligands. Previously, Scott and Dinger reported that the lithium and sodium salts of $[\mathbf{O_3}]^{3-}$ reacted with metal halides such as $TiCl_4$, $NbCl_5$, and $TaCl_5$, resulting in formation of multiple and/or decomposition products.[24] Nielson *et al.* prepared a tantalum complex $[(\textit{syn}\text{-}\mathbf{O_3})TaCl_3]^-$ by the reaction of $TaCl_5$ with $H_3[\mathbf{O_3}]$ in the presence of NEt_3, but it was obtained as a small quantity of crystals.[25] These two methods appear not to be a straightforward route for installing the tripodal [$\mathbf{O_3}$] ligand on early transition metals.

Given the difficulty of isolating chloride complexes of the type $[\mathbf{O_3}]MCl_2$ in these reactions, we turned to an alternative procedure based on earlier investigations on the preparation of linear-triaryloxide [***lin*-O$_3$**] complexes. We have shown that HCl elimination reactions between MCl_5 (M = Ta, Nb) and the protio ligands are a convenient entry to linear-triaryloxide derivatives of group 5 metals.[26] A similar approach was examined with $NbCl_5$ and $H_3[\mathbf{O_3}]$ (Scheme 3). The reaction proceeded cleanly in CH_3CN to provide $[H(\mathbf{O_3})]NbCl_3(CH_3CN)$ (**1**). After evaporating the solvent and washing the residue with hexane, **1** was isolated as a brown powder in 84% yield. The ^{1}H NMR spectrum of **1** displays resonances for two types of aryl rings in a 2 : 1 ratio. The presence of a hydroxyl group and a coordinated CH_3CN molecule is characterized by two singlets at δ 5.62 and 1.23, respectively. In the IR spectrum, the ν(OH) and ν(CN) absorptions are observed at 3543 and 2290 cm^{-1}. These spectroscopic data are consistent with partial HCl elimination to generate two coordinated aryloxide groups and the remaining ligand arm dangling as the free phenol. Diagnostic spectroscopic features for [$\mathbf{O_3}$] derivatives include NMR resonances for the bridging methine, which provide a criterion for determining coordination modes of the [$\mathbf{O_3}$] ligand

Table 1 ^{1}H and ^{13}C NMR data for the bridging methine

	^{1}H (δ)	^{13}C (δ)	$^1J_{CH}$ (Hz)
1	7.83	39.0	124.5
2	7.80	38.9	—[a]
3-*syn*	7.45	36.8	91.8
3-*anti*	5.91	65.8	119.8
4	5.87	52.1	117.7
6	6.18	62.0	124.0
$H_3[\mathbf{O_3}]$	5.94	42.5	126.8

[a] The resonances for the ligand backbone are broadened due to a fluxional process in solution.



Scheme 3 Synthesis of **1**, **2**, **3-*syn*** and **3-*anti***. Reagents and conditions: (i) $NbCl_5$, CH_3CN, toluene, rt, 3 h; (ii) THF, rt; (iii) **1**, NEt_3, toluene, rt, 3 h; (iv) toluene, 80 °C, 3 d.

(Table 1).[22,24,27] The ^{1}H and ^{13}C NMR methine signals of **1** resonate at δ 7.83 and 39.0, which are shifted relative to the corresponding values for free $H_3[\mathbf{O_3}]$ (^{1}H, δ 5.94; ^{13}C, δ 42.5).

The molecular structure of **1** is presented in Fig. 1, which is closely related to that of $[H(\textit{lin}\text{-}\mathbf{O_3})]NbCl_3(CH_3CN)$.[26] Complex **1** contains a distorted octahedral Nb(v) center with a bidentate $H[\mathbf{O_3}]$ dianionic ligand, three meridionally arranged chloride ligands and a CH_3CN ligand *trans* to one of the chelating aryloxide oxygen atoms [O(1)]. The remaining phenol group is not coordinated to niobium [Nb···O(2) = 4.63 Å], while this hydroxy group could form an intramolecular hydrogen bond to one chloride ligand [Cl(3)···O(2) = 3.29 Å, Cl(3)···H(2) = 2.50 Å, Cl(3)···H(2)–O(2) = 156°].[28,29] This intramolecular hydrogen bonding might causes a slight elongation in the Nb–Cl(3) distance [2.4061(13) Å] compared to the Nb–Cl(1) and Nb–Cl(2) distances [2.376(2), 2.3495(13) Å]. The Nb–O distances (average 1.865 Å) are typical of those observed for related niobium(v) aryloxide complexes (1.82–1.92 Å).[30–34] The Nb–N distance [2.268(5) Å] is slightly longer than that of $NbCl_5(CH_3CN)$ [2.268(6) Å].[35] The molecule possesses C_1 symmetry in the solid state, while C_s symmetry is observed in solution due to dissociation/association of CH_3CN on the NMR time scale. Upon dissolution in THF, the

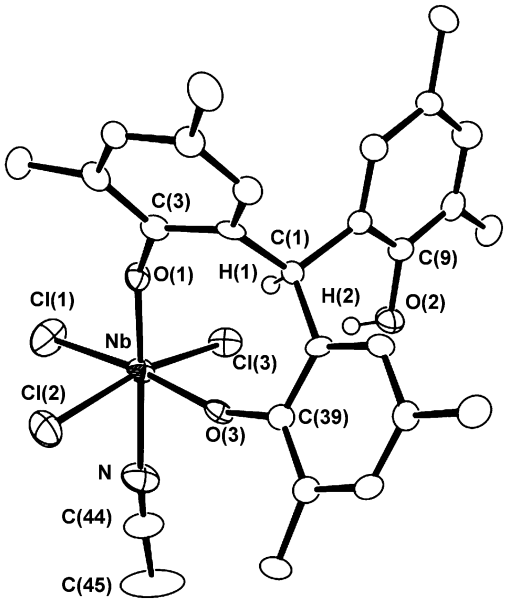


Fig. 1 Molecular structure of **1** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms and *tert*-butyl methyl groups are omitted for clarity. Selected bond distances (Å) and angles (°): Nb–Cl(1) 2.376(2), Nb–Cl(2) 2.3495(13), Nb–Cl(3) 2.4061(13), Nb–O(1) 1.852(3), Nb–O(3) 1.877(4), Nb–N 2.268(5), N–C(44) 1.136(7), Cl(1)–Nb–O(3) 171.33(10), Cl(2)–Nb–Cl(3) 164.51(6), O(1)–Nb–O(3) 96.56(14), O(1)–Nb–N 177.03(18), Nb–O(1)–C(3) 150.0(4), Nb–O(3)–C(39) 160.4(3), Nb–N–C(44) 172.2(4), N–C(44)–C(45) 176.3(7).

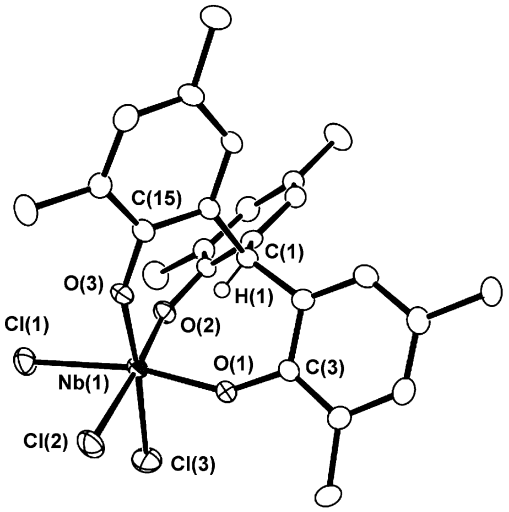


Fig. 2 Molecular structure of the anion part of **3-*syn*** with thermal ellipsoids drawn at the 50% probability level. One of the independent molecules in the asymmetric unit is presented. All hydrogen atoms and *tert*-butyl methyl groups are omitted for clarity. Selected bond distances (Å) and angles (°): Nb(1)–Cl(1) 2.4346(13), Nb(1)–Cl(2) 2.4496(12), Nb(1)–Cl(3) 2.4215(14), Nb(1)–O(1) 1.943(3), Nb(1)–O(2) 1.919(3), Nb(1)–O(3) 1.939(3), Cl(1)–Nb(1)–Cl(2) 85.02(5), Cl(1)–Nb(1)–Cl(3) 85.85(5), Cl(2)–Nb(1)–Cl(3) 88.93(5), Cl(1)–Nb(1)–O(1) 168.91(9), Cl(2)–Nb(1)–O(2) 175.60(9), Cl(3)–Nb(1)–O(3) 174.25(7), O(1)–Nb(1)–O(2) 96.86(11), O(1)–Nb(1)–O(3) 96.50(11), O(2)–Nb(1)–O(3) 94.27(11), Nb(1)–O(1)–C(3) 147.7(3), Nb(1)–O(2)–C(9) 147.6(3), Nb(1)–O(3)–C(15) 147.3(2).

labile CH_3CN ligand is readily substituted to give a THF adduct, $[H(\mathbf{O_3})]NbCl_3(THF)$ (**2**).

Although installation of the [$\mathbf{O_3}$] ligand on the metal is incomplete, clean formation of **1** and **2** prompts us to investigate deprotonation of the pendant phenol arm, resulting in a κ^3-$\mathbf{O_3}$ coordination mode. Treatment of **1** with Et_3N could effect deprotonation of the remaining hydroxyl group, giving $(Et_3NH)[(\textbf{\textit{syn}}\text{-}\mathbf{O_3})NbCl_3]$ (**3-*syn***) in 86% isolated yield. The ^{1}H NMR spectrum suggests a C_3 symmetry of the ligand backbone, possessing two *tert*-butyl singlets and two aromatic doublets. A tridentate interaction of the ancillary ligand is inferred from the loss of the hydroxyl resonance. In addition, the resonance due to the bridging methine proton at δ 7.54 is slightly shifted upfield relative to that seen for **1** (Table 1). In the gated decoupled ^{13}C NMR spectrum, the bridging methine of the [***syn*-$\mathbf{O_3}$**] ligand appears as a doublet at δ 36.8 with $^1J_{CH}$ = 91.8 Hz. This $^1J_{CH}$ coupling constant is appreciably lower than those of $H_3[\mathbf{O_3}]$ (126.8 Hz) and **1** (124.5 Hz).

Brown crystals of **3-*syn*** suitable for X-ray diffraction were obtained from a saturated toluene solution. The crystals of **3-*syn*** contain two independent molecules in the asymmetric unit. Since bond distances and angles for the two independent molecules are effectively identical, discussion will focus on only that shown in Fig. 2. The structure of **3-*syn*** closely resembles that of the related tantalum complex.[25] The anion is a distorted octahedral geometry, in which the [$\mathbf{O_3}$] ligand is bound in a facial manner [average O–Nb–O = 95.9°]. The remainder of the coordination sphere is occupied by three chloride ligands with O–Nb–Cl_{trans} and Cl–Nb–Cl angles ranging from 168.91(9) to 175.60(9)° and from 85.02(5) to 88.93(5)°, respectively. Notably, the *syn* conformation adopted by the [$\mathbf{O_3}$] ligand positions the methine H(1) proton proximal to niobium. The two atoms are only 2.15 Å apart, a distance within the range previously observed for agostic interaction.[36–40] Therefore, there may exist some transannular interaction of the methine proton with the metal center. This is in agreement with the low J_{CH} value for the methine carbon.[36–41] The Nb–O distances (average 1.934 Å) in **3-*syn*** are considerably longer than those of **1**. This elongation is presumably a consequence of some strain imposed by encapsulation of the methine proton within the [***syn*-$\mathbf{O_3}$**]Nb cage. The Nb–Cl distances of **3-*syn*** (average 2.435 Å) are longer than those of **1** (average 2.377 Å) due to the increased number of coordinated strong aryloxide donors.

We previously reported that *syn*/*anti* isomerization in $[\mathbf{O_3}]Ti(NEt_2)$ was thermally induced.[21] Likewise, upon heating a toluene solution at 80 °C for 3 days, **3-*syn*** underwent clean conversion to the *anti* isomer $(Et_3NH)[(\textbf{\textit{anti}}\text{-}\mathbf{O_3})NbCl_3]$ (**3-*anti***). The ^{1}H and ^{13}C NMR spectra are consistent with the complex **3-*anti*** retaining C_3 symmetry in solution. Isomerization of **3-*syn*** to **3-*anti*** is confirmed by an upfield shift of the methine proton at δ 5.91 along with a downfield shift of the methine carbon at δ 65.8 with the normal J_{CH} value of 119.8 Hz (Table 1). To further investigate the structure of **3-*anti***, we turned to X-ray diffraction (Fig. 3). While the coordination geometry of niobium is similar to that of **3-*syn***, a prominent difference pertains to the conformation of the triaryloxide ligand. The conformational constraint present in **3-*syn*** is relieved by adopting an *anti* from, in which the methine proton is pointed away from the metal center, leading to a shortening of the Nb–O distances in **3-*anti*** by *ca.* 0.05 Å relative to **3-*syn***. The two isomers **3-*syn*** and **3-*anti***

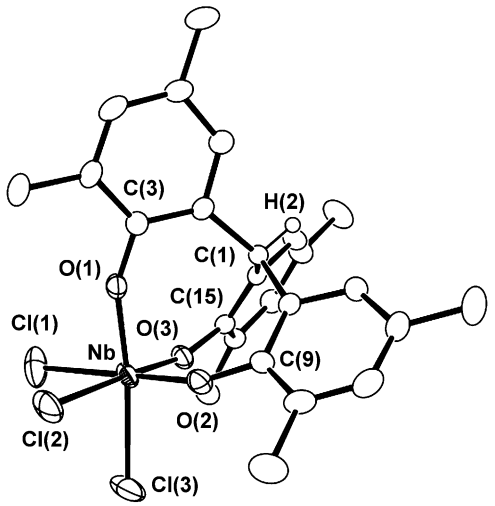
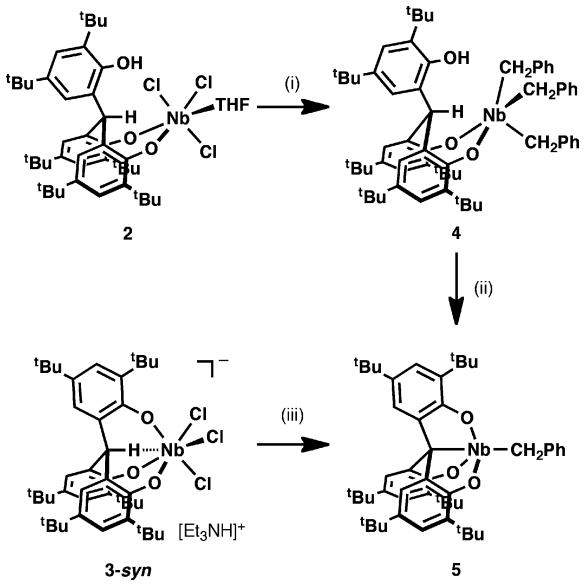


Fig. 3 Molecular structure of the anion part of **3-*anti*** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms and *tert*-butyl methyl groups are omitted for clarity. Selected bond distances (Å) and angles (°): Nb–Cl(1) 2.4571(11), Nb–Cl(2) 2.4630(10), Nb–Cl(3) 2.4200(10), Nb–O(1) 1.882(2), Nb–O(2) 1.881(2), Nb(1)–O(3) 1.883(3), Cl(1)–Nb–Cl(2) 87.64(4), Cl(1)–Nb–Cl(3) 86.20(4), Cl(2)–Nb–Cl(3) 85.77(3), Cl(1)–Nb–O(2) 177.75(7), Cl(2)–Nb–O(3) 176.85(6), Cl(3)–Nb–O(1) 173.16(6), O(1)–Nb–O(2) 89.97(9), O(1)–Nb–O(3) 94.15(9), O(2)–Nb–O(3) 90.98(9), Nb–O(1)–C(3) 155.15(17), Nb–O(2)–C(9) 150.75(19), Nb–O(3)–C(15) 155.00(18).

display approximately C_3 symmetry in the solid state, where the aryl rings of the [**O**$_3$] ligand are twisted in a propeller like fashion with average O–Nb–C(methine)–C_{ipso} torsion angles $\theta = 6.74°$ and 4.92°, respectively.

The synthesis of the desired niobium complexes having the κ^3-[**O**$_3$] ligand has been achieved by deprotonation of **1** and **2** with Et_3N, resulting in formation of **3-*syn*** and **3-*anti*** as Et_3NHCl adducts. To avoid generation of ate complexes, we examined the reaction of **2** with Grignard reagents. Attempted deprotonation of **2** with $PhCH_2MgCl$ in Et_2O led to the formation of an unexpected product [H(**O**$_3$)]Nb(CH_2Ph)$_3$ (**4**) (Scheme 4), in which alkylation at the metal center took place and the pendant phenol arm remained intact. When the amount of $PhCH_2MgCl$ was increased to three equivalents, the tribenzyl complex **4** was isolated in 77% yield. The ^{1}H NMR spectrum shows two sets of benzyl resonances in a 2 : 1 ratio as well as four *tert*-butyl resonances in a 2 : 2 : 1 : 1 ratio, suggesting a C_s-symmetric molecular structure in solution. A bidentate interaction of the ancillary ligand is further inferred on the basis of the low symmetry along with the resonance due to the hydroxyl group at δ 5.44. In the IR spectrum, the ν(OH) absorption is observed at 3448 cm^{-1}.

The X-ray structure of **4** has been determined (Fig. 4). The coordination geometry of the metal center is square pyramidal. The basal plane is comprised of two oxygen atoms of the chelating H[**O**$_3$] ligand and two benzyl ligands [C(44), C(58)], while the apical position is occupied by the benzyl ligand [C(51)]. The boat conformation of the eight-membered NbO_2C_5 chelating ring brings the methine proton to the vacant site *trans* to the apical benzyl ligand [H(1)$\cdots$Nb = 2.27 Å, C(1)–H(1)$\cdots$Nb = 149°], indicating the possibility of some agostic interaction.[36–40] However, this interaction is not retained in solution, as evidenced by a J_{CH} value of the methine carbon (117.7 Hz). The Nb–



Scheme 4 Synthesis of **4** and **5**. Reagents and conditions: (i) $PhCH_2MgCl$ (in Et_2O), toluene, –98 °C to rt, 5 h; (ii) toluene, 50 °C, 5 d; (iii) $PhCH_2MgCl$ (in Et_2O), toluene, –70 °C to rt, 2 h.

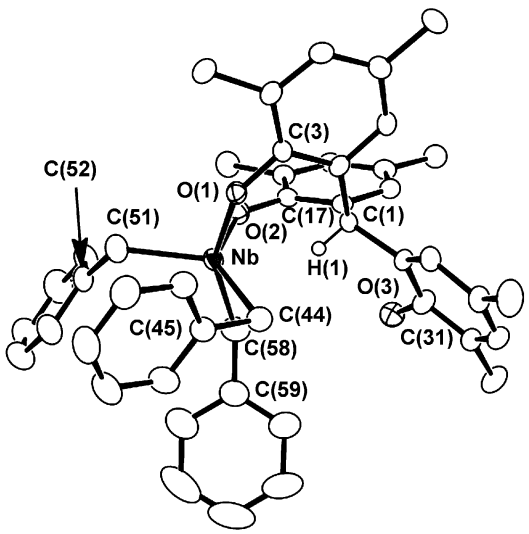


Fig. 4 Molecular structure of **4** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms and *tert*-butyl methyl groups are omitted for clarity. The pendant phenol oxygen O(3) was found to be disordered over two positions with occupancy factors of 0.70 : 0.30. Selected bond distances (Å) and angles (°): Nb–O(1) 1.915(2), Nb–O(2) 1.9449(17), Nb–C(44) 2.229(3), Nb–C(51) 2.193(3), Nb–C(58) 2.216(4), O(1)–Nb–O(2) 86.39(8), O(1)–Nb–C(51) 98.66(11), O(1)–Nb–C(58) 150.65(10), O(2)–Nb–C(44) 134.85(9), O(2)–Nb–C(51) 105.95(10), C(44)–Nb–C(58) 80.92(10), Nb–O(1)–C(3) 141.91(16), Nb–O(2)–C(17) 140.51(17), Nb–C(44)–C(45) 93.17(17), Nb–C(51)–C(52) 117.0(2), Nb–C(58)–C(59) 126.62(19).

O distances [average 1.930 Å] is elongated relative to those of the chloride complex ligand **1**, reflecting the increase in electron density at niobium arising from the presence of the alkyl groups compared with chlorides. Two of the benzyl ligands show normal η^1-bonding to niobium [Nb–C(51)–C(52) = 117.0(2)°, Nb–C(58)–C(59) = 126.62(19)°], while the third is distorted such that the Nb–C(44)–C(45) angle is acute [93.17(17)°] and the Nb–C_{ipso} carbon

[Nb–C(45) = 2.738(3) Å] is short. This η^2-benzyl bonding mode results from a weak Nb···Ph π interaction and is characteristic of electron-deficient early transition metal benzyl complexes.[7,42–45] The phenyl ring of the distorted benzyl ligand points towards the apical benzyl ligand and away from the pendant phenol arm. The apical benzyl group is slightly closer to niobium [Nb–C(51) = 2.193(3) Å] than the corresponding basal ligands [2.229(3), 2.216(4) Å]. Steric congestion around the hydroxyl group is probably ascribed as the cause of alkylation of the metal center in preference to deprotonation of the hydroxyl group. The structure of **4** is reminiscent of $[H_2(\mathbf{O_3N})]Ta(CH_2CMe_3)_4$ [$H_3(\mathbf{O_3N})$ = tris(3,5-methyl-2-hydroxylphenyl)amine], in which the $H_2[\mathbf{O_3N}]$ ligand is coordinated to the metal with one phenoxide group and two dangling phenol arms.[46]

To promote coordination of the pendant phenol arm, we carried out thermolysis of **4**. Prolonged heating of **4** in toluene at 50 °C for 5 days resulted in the formation of $[\mathbf{O_3C}]Nb(CH_2Ph)$ (**5**) in 43% isolated yield. The ^{1}H NMR spectrum of **5** reveals a pseudo C_3 symmetric species in solution with one set of resonances due to aryloxide groups. There are no resonances due to the methine proton and the hydroxyl group. The molecular structure of **5** is shown in Fig. 5. The methine C–H bond of the ligand backbone is activated along with deprotonation of the pendant phenol arm, leading to tetradentate binding of the $[\mathbf{O_3C}]$ ligand to the metal center. The O(1)–Nb–O(3) bite angle of 140.56(12)° is significantly wider than the other O–Nb–O angles [105.88(11), 100.16(11)°]. The overall geometry at niobium is best described as square pyramidal, with one aryloxide [O(2)] group of the $[\mathbf{O_3C}]$ ligand occupying the apical position. The coordination sphere is completed by a η^2-benzyl ligand [Nb–C(20)–C(21) = 83.2(3)°, Nb–C_{ipso}(21) = 2.515(4) Å], which is located *trans* to the C(1) atom and has its phenyl ring pointing toward the apical aryloxide ligand [O(2)]. The Nb–O distances fall in the range of the corresponding bonds found in **3-*syn*** and **3-*anti***.

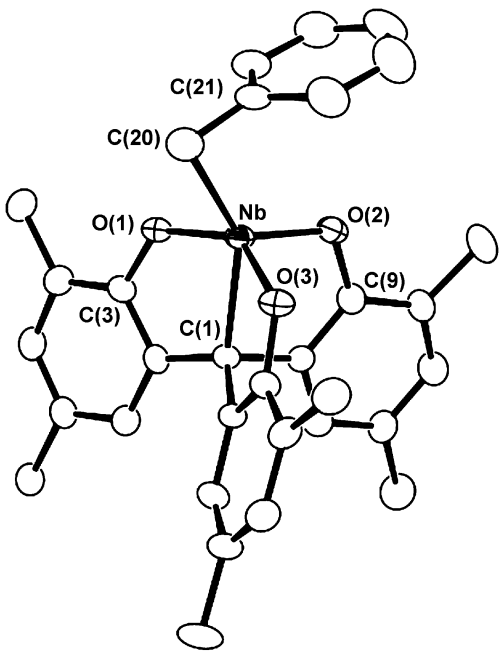
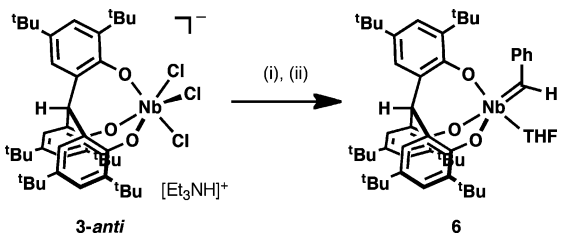


Fig. 5 Molecular structure of **5** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms and *tert*-butyl methyl groups are omitted for clarity. Selected bond distances (Å) and angles (°): Nb–O(1) 1.921(3), Nb–O(2) 1.940(3), Nb–O(3) 1.898(3), Nb–C(1) 2.243(4), Nb–C(20) 2.227(4), O(1)–Nb–O(2) 105.88(11), O(1)–Nb–O(3) 140.56(12), O(2)–Nb–O(3) 100.16(11), O(1)–Nb–C(1) 76.01(12), O(2)–Nb–C(1) 87.42(12), O(3)–Nb–C(1) 76.12(12), C(1)–Nb–C(20) 144.01(14), Nb–O(1)–C(3) 125.5(2), Nb–O(2)–C(9) 112.9(3), Nb–O(3)–C(15) 125.5(2), Nb–C(20)–C(21) 83.2(3).

The $[\mathbf{O_3C}]$ complex **5** was also prepared in 20% yield by alkylation of **3-*syn*** with four equivalents of $PhCH_2MgCl$. In contrast to thermally induced C–H activation of **4**, the reaction is found to proceed without heating the solution to elevated temperature. A possible explanation is that the Nb···H–C(methine) interaction preorganizes the reactive site and locks the metal center and the methine carbon in a confined arrangement. Cyclometalation *via* σ-bond metathesis is relatively common in early transition metal complexes with 2,6-disubstituted aryloxide ligands.[47–49] For example, thermolysis of $M(OAr')_2(CH_2Ph)$ (M = Ti, Zr; OAr′ = 2,6-di-*tert*-butylphenoxide) produced a metalated complex $M(OC_6H_3{}^tBuCMe_2CH_2)(OAr')(CH_2Ph)$ along with elimination of toluene. This type of reaction has been successfully used as a method for installation of cyclometalated **[OCO]** pincer ligands on early transition metals.[7,50–52] The $[\mathbf{syn\text{-}O_3}]$ complex could serve as a metalated $[\mathbf{O_3C}]$ precursor.

Utilization of **3-*anti*** as a starting material instead of **3-*syn*** in alkylation led to the formation of a benzylidene complex $[\mathbf{anti\text{-}O_3}]Nb(CHPh)(THF)$ (**6**) in 69% (Scheme 5). The presence of the benzylidene ligand is manifested by ^{1}H and ^{13}C NMR resonances at δ 10.25 and 245.0, respectively.[7,53,54] The ^{1}H NMR spectrum exhibits two sets of resonances due to aryloxide groups in a 2 : 1 ratio, consistent with C_s symmetry in solution on NMR time scale. In addition, the *anti* form of the $[\mathbf{O_3}]$ ligand is retained as evidenced by the methine proton (δ 6.18) and carbon resonances (δ 62.0) with $^1J_{CH}$ = 124 Hz (Table 1).



Scheme 5 Synthesis of **6**. Reagents and conditions: (i) $PhCH_2MgCl$ (in Et_2O), toluene, –98 °C to rt, 1 h; (ii) THF, rt, 3 h.

The mechanism of the formation of **5** remains unclear. However, based on literature precedents, two plausible pathways can be envisioned for alkylation of **3-*syn***.[55–61] On the assumption that a dibenzyl complex $[\mathbf{syn\text{-}O_3}]Nb(CH_2Ph)_2$ is formed in the first step, one pathway involves α-abstraction to form a benzylidene intermediate, followed by C–H activation of the ligand backbone methine to give **5**. The other pathway involves a direct σ-bond metathesis. Isolation of **6** provides support for the formation of the $[\mathbf{syn\text{-}O_3}]$ benzylidene analogue as an intermediate, while the latter pathway reminds one of conversion of $[\mathbf{syn\text{-}O_3}]Zr(CH_2Ph)$ to $[\mathbf{O_3C}]Zr(THF)_3$ *via* C–H activation.[22]

Conclusion

We have demonstrated that the triaryloxide trianion $[\mathbf{O_3}]^{3-}$ can be introduced to the niobium metal center by a two-step procedure. The first step is the partial HCl elimination between $NbCl_5$ and $H_3[\mathbf{O_3}]$, giving **1** with a bidentate bis(aryloxide) ligand and a pendant phenol arm. In the second step, deprotonation of the pendant phenol group with NEt_3 led to a tridentate (κ^3-O_3) coordination mode. The tridentate $[\mathbf{O_3}]$ ligand can coordinate to niobium in two forms, which differ mainly by the orientation of the methine C–H bond. The close proximity of the methine proton to the metal center in the *syn* form ($[\textbf{\textit{syn}}\text{-}\mathbf{O_3}]^{3-}$) facilitates C–H bond activation, resulting in a tetradentate (κ^4-O_3C) ligand $[\mathbf{O_3C}]^{4-}$. This implies that the $[\mathbf{O_3}]$ ligand in the *syn* form can provide a direct synthetic access to $[\mathbf{O_3C}]$-type metalatranes.[22] Compounds **3-*syn***, **3-*anti***, and **5** should provide excellent starting materials for investigation of the reactivity of this class of niobium complex. We expect it to demonstrate a rich chemistry.

Experimental

General experimental details

All manipulations were carried out using standard Schlenk or glovebox techniques under an argon atmosphere. Anhydrous solvents were purchased from Kanto Chemical Co. Hexane and toluene were further dried by passage through two columns of activated alumina and a Q-5 column, while THF, Et_2O, and CH_3CN were dried by passage through two columns of activated alumina. Benzene-d_6 was dried and degassed over a potassium mirror, and vacuum transferred prior to use. Chloroform-d_1 was dried and degassed over CaH_2, and vacuum transferred prior to use. $H_3[\mathbf{O_3}]$ was prepared by a literature procedure.[62] NMR spectra were recorded on JEOL LA-400 or LA-500 spectrometer. ^{1}H and ^{13}C NMR were reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, δ 7.15 and δ 128.0, residual $CHCl_3$ in $CDCl_3$, δ 7.24 and δ 77.0). Elemental analyses were measured using Yanaco MT-6 and MSU-32 microanalyzers.

Synthetic procedures

Synthesis of $[H(O_3)]NbCl_3(CH_3CN)$ (1). A solution of $NbCl_5$ (1.31 g, 4.85 mmol) in CH_3CN (40 ml) was added to a suspension of $H_3[\mathbf{O_3}]$ (3.03 g, 4.82 mmol) in toluene (70 ml) at room temperature. The mixture was stirred for 3 h to give a brown homogeneous solution. The volatiles were then removed *in vacuo*. The residue was washed with hexane to yield **1** as a brown powder in 84% (3.55 g). ^{1}H NMR δ (400 MHz, benzene-d_6, rt) ppm: 0.35 (s, 3H, C*H*$_3$CN), 1.23 (s, 18H, ^{t}Bu), 1.25 (s, 9H, ^{t}Bu), 1.52 (s, 9H, ^{t}Bu), 1.58 (br, 18H, ^{t}Bu), 5.62 (s, 1H, O*H*), 7.43 (d, 3H, J = 2.2 Hz, Ar), 7.52 (d, 1H, J = 2.2 Hz, Ar), 7.72 (d, 2H, J = 2.2 Hz, Ar), 7.83 (s, 1H, C*H*). ^{13}C δ (100 MHz, benzene-d_6, rt) ppm: 0.11 (*C*H$_3$), 30.1, 31.3, 31.9, 32.0, 34.7, 34.9, 35.4, 36.0 (^{t}Bu), 39.0 (d, $^1J_{CH}$ = 124.5 Hz, *C*H), 122.1, 123.1, 123.2, 124.2, 125.0, 140.8, 141.7, 148.4, 151.8 (Ar). Anal. Calc. for $C_{45}H_{65}O_3NCl_3Nb$: C, 62.32; H, 7.55; N, 1.62. Found: C, 62.81; H, 7.89; N, 1.57.

Synthesis of $[H(O_3)]NbCl_3(THF)$ (2). Complex **1** (1.75 g, 2.02 mmol) was dissolved in THF (15 ml), and then the volatiles were removed *in vacuo*. Washing the residue with hexane gave **2** as a brown powder in 91% (1.64 g). ^{1}H NMR δ (400 MHz, benzene-d_6, rt) ppm: 1.21 (s, 18H, ^{t}Bu), 1.22 (s, 9H, ^{t}Bu), 1.54 (br, 9H, ^{t}Bu), 1.56 (s, 18H, ^{t}Bu), 4.25 (br, 4H, C*H*$_2$O), 5.51 (br, 1H, O*H*), 7.39 (br, 1H, Ar), 7.42 (d, 2H, J = 2.2 Hz, Ar), 7.50 (d, 1H, J = 2.2 Hz, Ar), 7.67 (d, 2H, J = 2.2 Hz, Ar), 7.80 (br, 1H, C*H*). ^{13}C NMR δ (100 MHz, benzene-d_6, rt) ppm: 25.1 (thf), 30.1, 31.3, 31.8, 32.2, 34.6, 34.8, 35.4, 36.2 (^{t}Bu), 38.9 (CH), 78.4 (thf), 123.1, 123.7, 124.4, 137.9, 141.8, 151.8, 160.0 (Ar). IR (cm^{-1}): 3547 (s, ν_{OH}). Anal. Calc. for $C_{47}H_{70}O_4Cl_3Nb$: C, 62.84; H, 7.85. Found: C, 63.18; H, 8.22.

Synthesis of $[Et_3NH][(\textit{syn}\text{-}O_3)NbCl_3]$ (3-*syn*). Addition of Et_3N (0.16 mL, 1.15 mmol) to **1** (835 mg, 0.963 mmol) in toluene (50 mL) gave a red solution. The mixture was stirred for 3 h at room temperature. The solvent was evaporated and the residue was washed with hexane, giving **3-*syn*** as a brown powder in 86% (770 mg, 0.830 mmol). ^{1}H NMR δ (400 MHz, benzene-d_6, rt) ppm: 0.75 (t, 9H, J = 7.0 Hz, C*H*$_3$), 1.35 (s, 27H, ^{t}Bu), 1.74 (s, 27H, ^{t}Bu), 2.36 (q, 6 H, J = 7.0 Hz, C*H*$_2$), 7.27 (d, 3H, J = 2.5 Hz, Ar*H*), 7.54 (s, 1H, C*H*), 8.11 (d, 3H, J = 2.5 Hz, Ar*H*), 8.70 (s, 1H, N*H*). ^{13}C NMR δ (100 MHz, benzene-d_6, rt) ppm: 9.2 (*C*H$_3$), 31.5, 31.6, 34.6, 35.8 (^{t}Bu), 36.8 (d, $^1J_{CH}$ = 91.8 Hz, *C*H), 46.8 (*C*H$_2$), 122.2, 122.4, 139.6, 145.0, 148.0, 159.6 (Ar). Anal. Calc. for $C_{49}H_{77}O_3NCl_3Nb$: C, 63.46; H, 8.37; N, 1.51. Found: C, 63.44; H, 8.49; N, 1.49.

Synthesis of $[Et_3NH][(\textit{anti}\text{-}O_3)NbCl_3]$ (3-*anti*).

Method A. The mixture of **1** (2.72 g, 3.14 mmol) and Et_3N (0.55 mL, 3.95 mmol) in toluene (80 mL) was stirred for 3 days at 80 °C. After evaporation of the solvent, the residue was washed with hexane to give **3-*anti*** as a red powder in 92% (2.42 g, 2.61 mmol),

Method B. A toluene (20 mL) solution of **3-*syn*** (538 mg, 0.580 mmol) was stirred for 3 days at 80 °C. The same purification steps as in method A gave 506 mg of **3-*anti*** as a brown powder (94%).

^{1}H NMR δ (400 MHz, benzene-d_6, rt) ppm: δ 0.67 (t, 9H, J = 7.0 Hz, C*H*$_3$), 1.19 (s, 27H, ^{t}Bu), 1.79 (s, 27H, ^{t}Bu), 2.42 (dq, 6 H, J = 5.5, 7.0 Hz, C*H*$_2$), 5.91 (s, 1H, C*H*), 7.44 (d, 3H, J = 2.2 Hz, Ar*H*), 7.54 (d, 3H, J = 2.2 Hz, Ar*H*), 7.84 (br, 1H, N*H*). ^{13}C NMR δ (100 MHz, benzene-d_6, rt) ppm: δ 8.5 (*C*H$_3$), 31.6, 32.7, 34.4, 36.1 (^{t}Bu), 46.6 (*C*H$_2$), 65.8 (d, $^1J_{CH}$ = 119.8 Hz, *C*H), 124.1, 128.4, 139.4, 142.3, 144.9, 161.1 (Ar). Anal. Calc. for $C_{49}H_{77}O_3NCl_3Nb$: C, 63.46; H, 8.37; N, 1.51. Found: C, 63.52; H, 8.48; N, 1.50.

Synthesis of $[H(O_3)]Nb(CH_2Ph)_3$ (4). To a solution of **2** (957 mg, 1.06 mmol) in toluene (40 mL) was added a 1.0 M solution of $PhCH_2MgCl$ (3.3 ml, 3.3 mmol) in Et_2O dropwise at –98 °C. The mixture was warmed to room temperature and stirred for 5 h. The resulting red slurry was centrifuged to remove an insoluble material, and the supernatant solution was evaporated to dryness. Extraction of the residue with hexane followed by centrifugation gave a red solution. Concentration of the solution yielded an orange powder of **4** in 77% (813 mg). ^{1}H NMR δ (400 MHz, benzene-d_6, rt) ppm: 1.23 (s, 18H, ^{t}Bu), 1.28 (s, 9H, ^{t}Bu), 1.29 (s, 18H, ^{t}Bu), 1.66 (s, 9H, ^{t}Bu), 2.74 (s, 2H, C*H*$_2$), 3.58 (br, 4H, C*H*$_2$), 5.44 (s, 1H, O*H*), 5.87 (s, 1H, C*H*), 6.91 (t, 6H, J = 6.8 Hz, Ar), 7.03–7.13 (m, 9H, Ar), 7.38 (d, 2H, J = 2.4 Hz, Ar), 7.60 (d, 2H, J = 2.4 Hz, Ar), 7.67 (d, 1H, J = 2.4 Hz, Ar), 7.78 (d, 1H, J = 2.4 Hz, Ar). ^{13}C NMR δ (100 MHz, benzene-d_6, rt) ppm: 30.3, 30.5, 31.5, 31.9, 34.6, 34.7, 35.6, 35.7 (^{t}Bu), 52.1 (d, $^1J_{CH}$ = 117.7 Hz, *C*H),

87.2 (CH_2), 123.3, 124.0, 125.1, 125.9, 126.2, 127.2, 128.9, 129.0, 129.1, 131.6, 137.8, 137.9, 141.9, 142.9, 145.1, 152.6, 158.9 (Ar). IR (cm^{-1}): 3448 (s, ν_{OH}). Anal. Calc. for $C_{64}H_{82}O_3Nb$: C, 77.47; H, 8.33. Found: C, 77.23; H, 8.50.

Synthesis of [O_3C]Nb(CH_2Ph) (5). To a solution of **3-*syn*** (1.83 g, 1.97 mmol) in toluene (50 mL) was added a 1.0 M solution of $PhCH_2MgCl$ (6.0 mL, 6.0 mmol) in Et_2O dropwise at −70 °C. The mixture was warmed to room temperature. After stirring for 2 h, the resulting brown slurry was centrifuged to remove an insoluble material. The supernatant solution was evaporated to dryness. Extraction of the residue with hexane followed by centrifugation gave a brown solution. The solution was concentrated to yield **5** as an orange powder in 20% (316 mg, 0.391 mmol). ^{1}H NMR δ (400 MHz, benzene-d_6, rt) ppm: 1.35 (s, 27H, ^{t}Bu), 1.37 (s, 27H, ^{t}Bu), 3.12 (s, 2H, CH_2), 6.97 (t, J = 7.3 Hz, 1H, ArH), 7.18 (t, J = 7.3 Hz, 2H, ArH), 7.24 (d, J = 2.2 Hz, 3H, ArH), 7.29 (d, J = 7.3 Hz, 2H, ArH), 7.88 (d, J = 2.2 Hz, 3H, ArH). ^{13}C NMR δ (100 MHz, benzene-d_6, rt) ppm: 30.2, 31.9, 34.7, 34.9 (^{t}Bu), 68.5 (CH_2), 121.4, 125.9, 130.4, 131.1, 133.3, 134.3, 134.5, 143.8, 144.8, 162.6 (Ar). The ^{13}C NMR signal assignable to the Nb-bound carbon of the [**O_3C**] ligand was unobservable, likely because of line broadening resulting from the quadrupolar ^{93}Nb nucleus. Anal. Calc. for $C_{50}H_{67}O_3Nb$: C, 74.23; H, 8.35. Found: C, 74.29; H, 8.60.

Synthesis of [*anti*-O_3]Nb(CHPh)(THF) (6). To a toluene (30 mL) solution of **3-*anti*** (922 mg, 0.994 mmol) was added a 1.0 M solution of $PhCH_2MgCl$ (3.0 mL, 3.0 mmol) in Et_2O dropwise at −98 °C. The mixture was warmed to room temperature and was stirred for 1 h. After an insoluble material was removed by centrifugation, the resulting brown solution was evaporated to dryness. The residue was washed with cold hexane and dissolved in 20 mL of THF. After stirring for 3 h, the solvent was removed. Recrystallization from hexane afforded **5** as brown crystals in 69% (605 mg). ^{1}H NMR δ (400 MHz, benzene-d_6, rt) ppm: 1.12 (br, 22H, ^{t}Bu + THF), 1.28 (s, 9H, ^{t}Bu), 1.54 (s, 9H, ^{t}Bu), 1.58 (s, 18H, ^{t}Bu), 3.43 (br, 4H, THF), 6.18 (s, 1H, CH), 6.78 (t, J = 7.0 Hz, 1H, Ph), 7.26–7.32 (m, 5H, Ph + ArH), 7.35 (d, J = 2.4 Hz, 2H, ArH), 7.44 (d, J = 2.4 Hz, 1H, ArH), 7.47 (d, J = 2.4 Hz, 2H, ArH), 10.25 (s, 1H, CH). ^{13}C NMR δ (100 MHz, benzene-d_6, rt) ppm: 26.0 (THF), 30.4, 30.7, 31.4, 32.0, 34.3, 34.4, 35.6, 35.9 (^{t}Bu), 62.0 (d, $^1J_{CH}$ = 124 Hz, CH), 77.1 (THF), 123.2, 123.8, 125.0, 126.8, 127.1, 129.6, 129.9, 137.4, 138.2, 142.0, 143.9, 155.5, 163.4 (Ar + Ph), 245.0 (br, CH). Anal. Calc. for $C_{54}H_{75}O_4Nb$: C, 73.61; H, 8.58. Found: C, 74.05; H, 9.27.

X-Ray crystallographic studies†

Single crystals immersed in mineral oil on nylon loops and transferred to a Rigaku Mercury CCD system equipped with a Rigaku GNNP low-temperature device. Data were collected under a cold nitrogen stream at 173 K using graphite-monochromated Mo-Kα radiation (λ = 0.71070 Å). Equivalent reflections were merged, and the images were processed with the CrystalClear (Rigaku) program. Corrections for Lorentz-polarization effects and absorption were performed.

Calculations were performed with the CrystalStructure (Rigaku) software package. All structures were solved by direct methods, and the remaining heavy atoms were found in subsequent Fourier maps. The structures were refined on F^2 by the full-matrix least-squares method. For **3-*syn***, four *tert*-butyl groups and one benzene solvent molecule were disordered. For **3-*anti***, one ethyl group and a toluene solvent molecule were disordered. For **4**, one *tert*-butyl group was disordered. For **5**, two *tert*-butyl groups were disordered. These disordered carbon atoms were refined isotropically. For **4**, the pendant phenol was disordered, and its oxygen atoms were refined isotropically. The remaining non-hydrogen atoms were refined anisotropically. All hydrogen atoms were put at calculated positions, while no hydrogen atom was put on disordered carbon atoms except for ethyl groups of **3-*anti***.

Crystal data for 1. $C_{45}H_{65}O_3NCl_3Nb$, M = 867.28, monoclinic, space group $P2_1/c$ (#14), a = 12.485(5), b = 20.674(8), c = 18.359(7) Å, β = 100.406(5)°, V = 4661(3) Å^3, T = 173 K, Z = 4, μ(Mo-Kα) = 4.665 cm^{-1}, 34 400 reflections measured, 9471 independent reflections (R_{int} = 0.0983). The final R_1 values were 0.0789 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1322 (all data). The goodness of fit on F^2 was 1.116.

Crystal data for 3-*syn*. $C_{49}H_{77}O_3NCl_3Nb{\cdot}1.75(C_6H_6)$, M = 1064.12, triclinic, space group $P\bar{1}$(#2), a = 13.987(5), b = 20.447(7), c = 21.538(8) Å, α = 94.951(6), β = 99.947(5), γ = 97.388(6)°, V = 5980(4) Å^3, T = 173 K, Z = 4, μ(Mo-Kα) = 1.182 cm^{-1}, 45 362 reflections measured, 24 591 independent reflections (R_{int} = 0.045). The final R_1 values were 0.0658 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1520 (all data). The goodness of fit on F^2 was 1.078. The compound crystallized with 1.75 equivalents of benzene per Nb complex.

Crystal data for 3-*anti*. $C_{49}H_{77}O_3NCl_3Nb{\cdot}C_7H_8$, M = 1019.56, monoclinic, space group $C2/c$ (#15), a = 47.957(11), b = 13.286(3), c = 19.889(5) Å, β = 116.905(3)°, V = 11300(4) Å^3, T = 173 K, Z = 8, μ(Mo-Kα) = 3.946 cm^{-1}, 43 895 reflections measured, 12 900 independent reflections (R_{int} = 0.047). The final R_1 values were 0.0611 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1508 (all data). The goodness of fit on F^2 was 1.083. The compound crystallized with 1 equivalent of toluene per Nb complex.

Crystal data for 4. $C_{64}H_{83}O_3Nb{\cdot}C_7H_8$, M = 1085.40, monoclinic, space group $P2_1/c$ (#14), a = 22.812(6), b = 14.173(4), c = 20.084(5) Å, β = 106.140(4)°, V = 6238(3) Å^3, T = 173 K, Z = 4, μ(Mo-Kα) = 2.373 cm^{-1}, 48519 reflections measured, 14088 independent reflections (R_{int} = 0.037). The final R_1 values were 0.0604 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1521 (all data). The goodness of fit on F^2 was 1.093. The compound crystallized with 1 equivalent of toluene per Nb complex.

Crystal data for 5. $C_{50}H_{67}O_3Nb$, M = 808.98, monoclinic, space group $P2_1/c$ (#14), a = 14.679(5), b = 11.916(4), c = 27.664(9) Å, β = 110.455(4)°, V = 4534(2) Å^3, T = 173 K, Z = 4, μ(Mo-Kα) = 3.038 cm^{-1}, 35 050 reflections measured, 10 345 independent reflections (R_{int} = 0.041). The final R_1 values were 0.0684 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1779 (all data). The goodness of fit on F^2 was 1.140.

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