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3d Early Transition Metal Complexes Supported by a New Sterically Demanding Aryloxide Ligand

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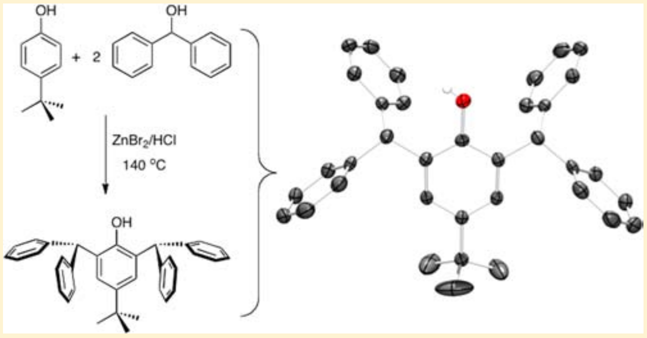
S *Supporting Information*

ABSTRACT: The bulky aryloxide 2,6-bis(diphenylmethyl)-4-*tert*-butylphenol [$HOAr^{tBu}$] (**1**) can be synthesized from 4-*tert*-butylphenol and benzhydrol in solvent-free conditions and obtained pure in 91% yield. Deprotonation of $HOAr^{tBu}$ is accomplished with $M(N(SiMe_3)_2)$ (M = Na, Li), yielding the corresponding salts of the aryloxide [$MOAr^{tBu}$] (M^+ = Na (**2**), Li(**3**)) in 83% and 73% yield, respectively. Facile salt formation of the aryloxide ligand allows for transmetalation to a variety of metal halides. Through transmetalation reactions involving two aryloxides, mononuclear complexes of the type [$M'(OAr^{tBu})_2Cl(THF)_2$] (M′ = Sc (**4**), V (**5**), Cr (**6**), Ti (**7**)) can be prepared from the corresponding metal halide precursor $MCl_3(THF)_3$. Additionally, two aryloxides can be coordinated to Ti(IV) via a protonolysis route of $Ti(NMe_2)_2Cl_2$ and 2 equiv of $HOAr^{tBu}$ to yield [$Ti(OAr^{tBu})_2Cl_2(NHMe_2)$] (**8**) in 72% isolated yield. Single-crystal X-ray diffraction studies of **1**, **2**, and the 3d metal complexes **5**−**8** clearly show the steric demand of the bulky ligand, whereas in transition metal complexes we do not observe the formation of mononuclear tris-aryloxide complexes.



■ INTRODUCTION

Sterically demanding monodentate ligands (alkoxides, amides, aryls, carbenes, silyls, etc.) have proven indispensable in stabilizing low-coordinate transition metal complexes.[1] Of these ligands, alkoxides are an attractive choice for low-coordinate early transition metal complexes because of their large degree of electronic flexibility and steric modification.[2−10] Additionally, alkoxide ligands can model the less well-defined oxide or silicon-oxide supported systems and provide mechanistic insights into various heterogeneous catalytic transformations while also modulating the coordination number and geometry.[11−16] The oxygen atom of the alkoxide can serve as a multielectron donor to the metal center through π-interactions, making these ligands suitable for electron-deficient early transition metals without detrimental side reactions such as demetalation. However, when not engaging in π-donations, the oxygen lone pairs can also result in the undesirable oligomerization[17−24] of low-coordinate complexes, rendering them susceptible to radical-based decomposition or disproportionation reactions.[25−27] As a result, sufficient steric bulk is crucial in synthesizing low-coordinate monomeric complexes, which are usually more reactive than their oligomeric counterpart.[28,29] These highly modular steric parameters can be readily incorporated to the central phenol ring of an aryloxide ligand through electrophilic aromatic substitution reactions. By installing bulky and chemically robust groups, the ligand would experience increased chemical and thermal stability preventing degradation pathways such as cyclometalation, which are common to commercially available aryloxides possessing isopropyl, phenyl, or *tert*-butyl substituents in the *ortho* positions.[30−35] For these reasons, we were attracted to the diphenylmethyl substituent that has been recently employed in the synthesis of a bulky *N*-heterocyclic carbene, [1,3(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazo-2-ylidene],[36] and several nitrogen-based ligands, [(2,6-bis(diphenylmethyl)-4-methylphenyl)(R)amine] (R = $SiMe_3$, $SiMePh_2$, $SiPh_3$, Ph, Mes).[37−39] By incorporating the aforementioned diphenylmethyl groups, we envisioned the design of a bulky and chemically robust aryloxide ligand. Although the triarylmethane unit could be a source of reactivity in an oxidizing environment, through the formation of a stable radical akin to the well-known triphenylmethyl radical discovered by Gomberg,[40−42] cyclometalation involving a phenyl group from the diphenylmethyl substituent would be disfavored given the formation of a seven-membered ring. Here, we report the general synthesis of a new and exceptionally bulky aryloxide ligand, 2,6-bis(diphenylmethyl)-4-*tert*-butylphenol [$HOAr^{tBu}$] (**1**), the deprotonation of **1** to yield the sodium and lithium derivatives ([$NaOAr^{tBu}$] (**2**) and [$LiOAr^{tBu}(Et_2O)$] (**3**)), and the facile coordination of this aryloxide to a variety of early 3d-metals through either transmetalation or protonolysis reactions. In all cases, coordination of three aryloxides to one single metal ion has proven elusive due to the large steric demands of the ligand.

■ RESULTS AND DISCUSSION

The bulky aryloxide, 2,6-bis(diphenylmethyl)-4-*tert*-butylphenol [$HOAr^{tBu}$] (**1**), was synthesized by modification of a previously reported synthesis of an aniline derivative.[36] A close analogue,

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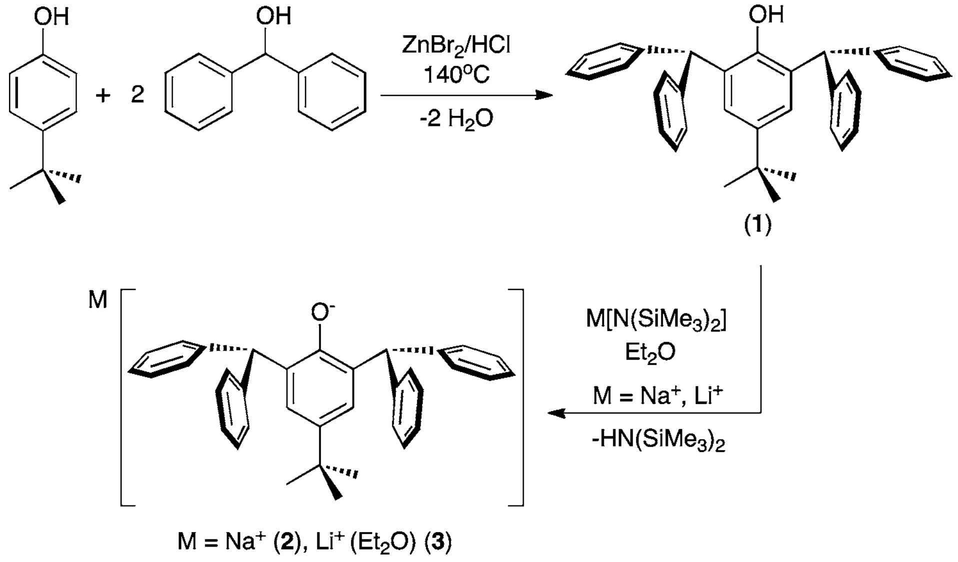
Scheme 1. Synthesis of Compounds [HOAr^{tBu}] (1), [Na(OAr^{tBu})] (2), and [Li(OAr^{tBu})(Et$_2$O)] (3)



2,6-bis(diphenylmethyl)-4-methylphenol, was also recently reported by Mindiola and Meyer, and its coordination chemistry was explored with U(III) and U(V), therefore suggesting this scaffold to be resistant under reducing conditions.[43] The reaction of 4-*tert*-butylphenol and benzhydrol, in solvent-free conditions at 140 °C for 2.5 h, with the addition of stoichiometric amounts of HCl (12 M) and ZnBr$_2$, resulted in double electrophilic aromatic substitution of the phenol (Scheme 1). Upon extracting the resulting solid into dichloromethane and subsequent washing with brine, compound **1** was isolated as a white solid in 91% yield. The ^{1}H NMR spectrum of **1** in C$_6$D$_6$ displays diagnostic chemical shifts for the *tert*-butyl substituent at 0.97 ppm (9H) as well as the methine and hydroxyl protons at 5.61 (2H) and 4.32 ppm (1H), respectively. The chemical shift for the *meta* protons of the phenol ring can be identified as a singlet at 6.65 ppm (2H), while the aromatic protons of the diphenylmethyl substituents are well resolved and can be identified as the *ortho*, *meta*, and *para* protons centered at 7.04 (8H), 7.21 (8H), and 7.14 ppm (4H), respectively.

To understand potential intermolecular interactions of the ligand in the solid state, X-ray diffraction studies of **1** were performed on a clear single crystal grown from layering a concentrated toluene solution with pentane. Complex **1** crystallizes in the monoclinic space group $P2_1/n$ (Figure 1 and Table 1), and selected bond lengths and angles are listed in Table 2. The smallest dihedral angles containing the ipso-carbon of the phenol ring and a single substituent of the diphenymethyl group are represented by C2−C3−C4−H41 (47.33°) and C2−C20−C21−H211 (46.62°). These angles are significantly skewed from being coplanar with the central phenol ring. This distortion is attributed to both intermolecular hydrogen bonding of the hydroxyl proton, which was located in the Fourier map, and π-interactions of adjacent diphenylmethyl substituents that can be observed in a view of the unit cell. Comparing the solid-state structure of **1** to 2,6-diphenyl-phenol shows a distinct difference in that the later experiences intramolecular hydrogen bonding of the hydroxyl proton with the *ortho* phenyl ring, preventing dimerization through hydrogen bonding of the hydroxyl proton.[44] In contrast, 2,6-diisopropyl-phenol experiences intermolecular hydrogen bonding between the hydroxyl proton and an intermolecular oxygen atom resulting in tetrameric aggregates in the solid state.[45] The steric bulk of the diphenylmethyl substituents of **1** as

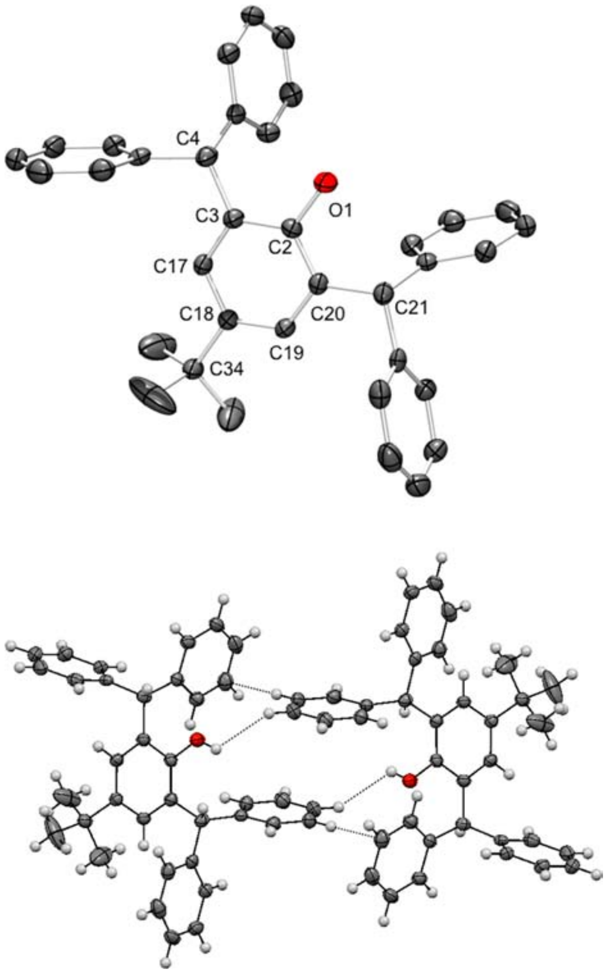


Figure 1. (Top) ORTEP drawing of the non-hydrogen atoms of [HOAr^{tBu}] (**1**), showing selected atom labeling with ellipsoids at the 50% probability level. (Bottom) A portion of the unit cell depicting the intermolecular hydrogen bonding and π-interactions.

Table 1. Crystal Data and Structure Refinement

	1	2	5	6	8
molecular formula	$C_{36}H_{34}O_1$	$C_{80}H_{82}Na_2O_4$	$C_{92}H_{106}ClO_7V$	$C_{94}H_{98}ClCrO_4$	$C_{74}H_{73}Cl_2NO_2Ti$
formula weight	482.66	1153.51	1410.24	1379.26	1127.20
temp (K)	150	150	150	100	100
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$
cell constants					
a (Å)	5.7469(2)	10.3211(17)	23.298(2)	18.4411(6)	10.9681(18)
b (Å)	19.1069(8)	12.777(2)	15.8883(14)	16.1932(6)	27.621(5)
c (Å)	24.8188(9)	13.069(2)	23.727(2)	26.2278(9)	21.003(4)
α (deg)	90	80.374(3)	90	90	90
β (deg)	92.146(2)	76.077(3)	115.921(2)	105.8380(10)	90.070(4)
γ (deg)	90	80.536(4)	90	90	90
Z	4	1	4	4	4
V (Å^3)	2723.33(18)	1635.4(5)	7899.1(12)	7534.8(5)	6362.8(19)
abs coeff (mm^{-1})	0.0690	0.082	0.0214	0.240	0.264
calcd density (g/cm^3)	1.177	1.171	1.186	1.216	1.177
F(000)	1032	616	3016	2940	2384
crystal dimensions (mm)	0.08 × 0.15 × 0.22	0.10 × 0.20 × 0.41	0.40 × 0.25 × 0.22	0.005 × 0.034 × 0.035	0.004 × 0.006 × 0.015
wavelength (Å)	0.71071	0.71071	0.71071	0.41328	0.41328
h,k,l ranges collected	$-6 \le h \le 6$, $-22 \le k \le 22$, $-29 \le l \le 27$	$-14 \le h \le 14$, $-16 \le k \le 17$, $-12 \le l \le 18$	$-28 \le h \le 30$, $-18 \le k \le 20$, $-26 \le l \le 30$	$-29 \le h \le 29$, $-17 \le k \le 25$, $-40 \le l \le 41$	$-13 \le h \le 12$, $0 \le k \le 32$, $0 \le l \le 25$
θ range for data collection (deg)	1.35–25.17	1.630–30.079	1.02–27.57	0.869–19.228	1.026–14.276
number of reflns collected	18 051	31 025	62 328	163 228	10 881
number of unique reflns	4833	9499	17 889	31 710	17 690
number of parameters	334	425	1039	973	722
data to parameter ratio	4833/334	9499/425	17 889/1039	31 710/973	17 690/722
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
R_1[a]	0.0475	0.0542	0.0580	0.0571	0.0947
wR_2[b]	0.1327	0.1386	0.1607	0.1280	0.2228

[a] $R_1 = (|F_o| - |F_c|)/|F_o|$. [b] $wR_2 = [[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Compounds **1**, **2** **5**, **6**, and **8**

$[\mathrm{HOAr}^{t\mathrm{Bu}}]$ (**1**)		$[\mathrm{NaOAr}^{t\mathrm{Bu}}(\mathrm{THF})]$ (**2**)		$[\mathrm{V}(\mathrm{OAr}^{t\mathrm{Bu}})_2\mathrm{Cl}(\mathrm{THF})_2]$ (**5**)	
O1−C2	1.383(2)	O1−Na1	2.2165(12)	V1−Cl1	2.2798(8)
C2−C3	1.389(2)	O2−Na1	2.2472(14)	V1−O1	1.8590(15)
C3−C4	1.532(2)	O1′-Na1	2.2229(12)	V1−O2	1.8590(16)
C3−C17	1.389(3)	Na1−arene$_{(\eta\text{-3 cent})}$	2.714	V1−O3	2.065(4)
C17−C18	1.398(2)	O1−Na1−O1′	93.41(4)	V1−O4	2.084(11)
C18−C19	1.388(2)	O1−Na1−O2	102.49(5)	Cl1−V1−O1	118.58(5)
C19−C20	1.389(2)	O1′−Na1−O2	120.85(5)	Cl1−V1−O2	116.07(5)
C20−C21	1.525(2)	Na1−O1−Na1′	86.59(4)	O1−V1−O2	125.35(7)
C20−C2	1.393(2)	arene$_{(\eta\text{-3 cent})}$−Na1−O1	138.21	O3−V1−O4	179(2)
C18−C34	1.534(3)	arene$_{(\eta\text{-3 cent})}$−Na1−O2	115.61	O3−V1−Cl1	88.12(13)
C2−C3−C4−H4	46.62[a]	arene$_{(\eta\text{-3 cent})}$−Na1−O1′	83.04	O3−V1−O1	93.9(2)
C2−C20−C21−H21	47.33[a]			O3−V1−O2	87.4(2)

$[\mathrm{Cr}(\mathrm{OAr}^{t\mathrm{Bu}})_2\mathrm{Cl}(\mathrm{THF})_2]$ (**6**)		$[\mathrm{Ti}(\mathrm{OAr}^{t\mathrm{Bu}})_2\mathrm{Cl}_2(\mathrm{NHMe}_2)]$ (**8**)	
Cr1−Cl1	2.2400(4)	Ti1−Cl1	2.277(3)
Cr1−O1	1.8694(10)	Ti1−Cl2	2.296(3)
Cr1−O2	1.8730(11)	Ti1−O1	1.804(5)
Cr1−O3	2.0151(11)	Ti1−O2	1.777(5)
Cr1−O4	2.0045(11)	Ti1−N1	2.243(7)
Cl1−Cr1−O1	109.77(4)	Cl1−Ti1−Cl2	136.30(10)
Cl1−Cr1−O2	105.09(3)	Cl1−Ti1−O2	111.15(19)
O1−Cr1−O2	145.14(5)	Cl2−Ti1−O2	109.0(2)
O3−Cr1−O4	168.95(5)	O1−Ti1−N1	165.2(2)
O3−Cr1−Cl1	95.46(4)	O1−Ti1−O2	105.2(2)
O3−Cr1−O1	85.26(5)	O1−Ti1−Cl1	96.28(19)
O3−Cr1−O2	91.38(5)	O1−Ti1−Cl2	89.32(18)

[a] Becasue of the nature of the crystal, all hydrogen atoms were assigned to geometric positions about the parent atoms.

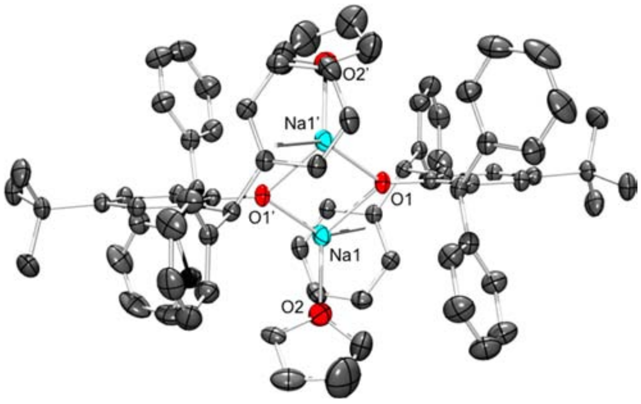


Figure 2. ORTEP drawing of the non-hydrogen atoms of $[\mathrm{NaOAr}^{t\mathrm{Bu}}(\mathrm{THF})]$ (**2**), showing selected atom labeling with ellipsoids at the 50% probability level.

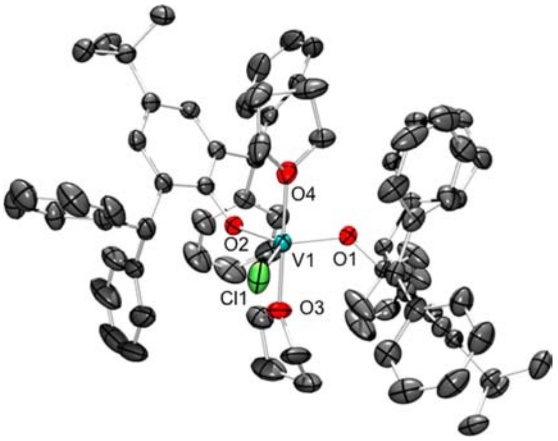


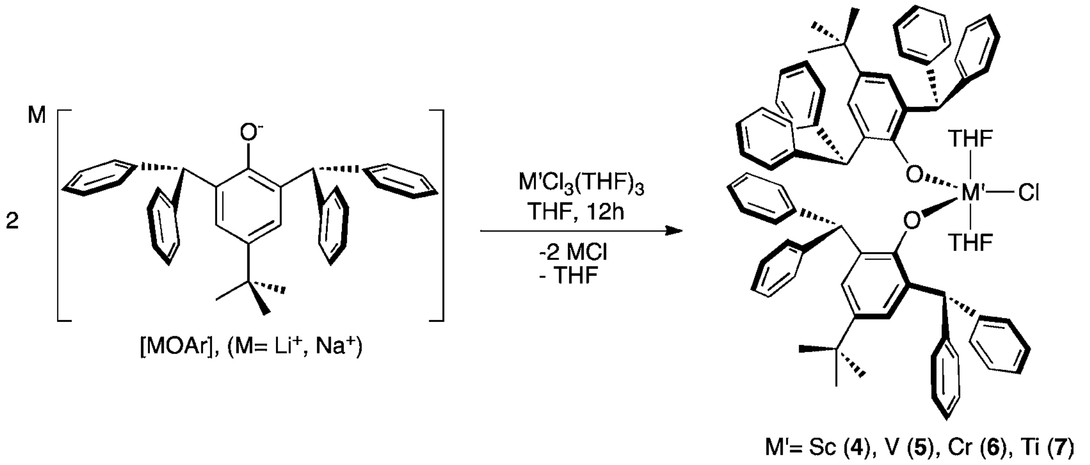
Figure 3. ORTEP drawing of the non-hydrogen atoms of $[\mathrm{V}(\mathrm{OAr}^{t\mathrm{Bu}})_2\mathrm{Cl}(\mathrm{THF})_2]$ (**5**), showing selected atom labeling with the ellipsoids at the 50% probability level. All noninteracting solvent molecules have been omitted for clarity.

well as stabilizing intermolecular π-interactions prevent the higher degree of aggregation in the solid state.

Addition of 1 equiv of $\mathrm{M}[\mathrm{N}(\mathrm{SiMe}_3)_2]$ (M = Li, Na) to a white suspension of **1** in diethyl ether resulted in a homogeneous yellow solution, resulting from the deprotonation of the alcohol. Upon concentration of the solution a suspension forms, and filtration and subsequent washing of the solid with pentane results in isolation of the corresponding salts $[\mathrm{NaOAr}^{t\mathrm{Bu}}]$ (**2**) and $[\mathrm{LiOAr}^{t\mathrm{Bu}}(\mathrm{Et}_2\mathrm{O})]$ (**3**) in 83% and 78% yield, respectively (Scheme 1). The ^{1}H NMR spectra of both **2** and **3** in $\mathrm{C}_6\mathrm{D}_6$ are slightly altered from that of **1**, and the number of chemical shifts are indicative of the hydroxyl proton being absent, as expected. Unlike **2**, complex **3** exhibits additional resonances centered at 3.07 and 0.98 ppm, in accord with a retained diethyl ether. Integration of these resonances in the ^{1}H NMR spectrum suggests that diethyl ether binds in a 1:1 ratio with $\mathrm{LiOAr}^{t\mathrm{Bu}}$. Exposure to vacuum for the duration of 24 h does not result in loss of diethyl ether.

Interested in the effect of Na^+ on the aggregation of compound **2**, X-ray diffraction studies were performed on a brown plate, grown by cooling a concentrated THF solution to −37 °C. Compound **2** crystallizes in the triclinic space group $P\overline{1}$ (Figure 2 and Table 1), and selected bond lengths and angles are listed in Table 2. Compound **2** exists as a centrosymmetric dimer, comprised of two aryloxide ligands, where O1 and O1′ are bridged through Na1 and Na1′. In addition to aryloxide coordination, each Na^+ interacts in an η^3-coordination mode with a single arene of the diphenylmethyl substituent and an

Scheme 2. General Synthesis of Complexes [Sc(OAr^{tBu})$_2$Cl(THF)$_2$] (4), [V(OAr^{tBu})$_2$Cl(THF)$_2$] (5), [Cr(OAr^{tBu})$_2$Cl(THF)$_2$] (6), and [Ti(OAr^{tBu})$_2$Cl(THF)$_2$] (7)



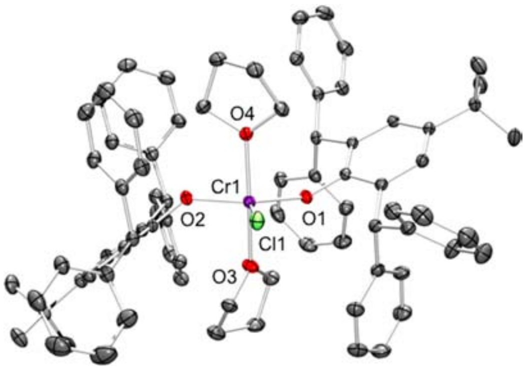


Figure 4. ORTEP drawing of the non-hydrogen atoms of [Cr(OAr^{tBu})$_2$Cl(THF)$_2$] (6), showing selected atom labeling with the ellipsoids at the 50% probability level. All noninteracting solvent molecules have been omitted for clarity.

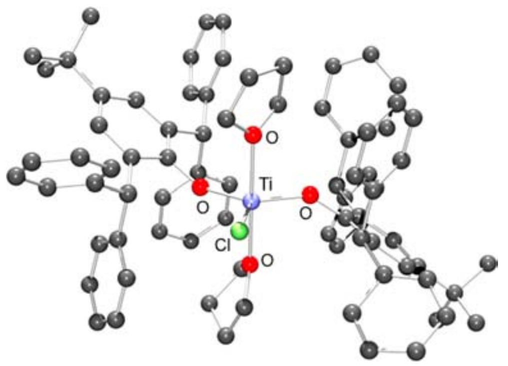


Figure 5. Ball-and-stick representation of [Ti(OAr^{tBu})$_2$Cl(THF)$_2$] (7).

oxygen atom of a THF molecule. This type of arene interaction has also been observed in other aryloxides incorporating similar (1-methyl-1-phenyl)ethyl and phenylmethyl substituents.[46,47] Although the solid-state structure of **2** shows incorporation of one THF molecule per Na$^+$, solvation by ethers can be removed from the complex upon exposure to vacuum.

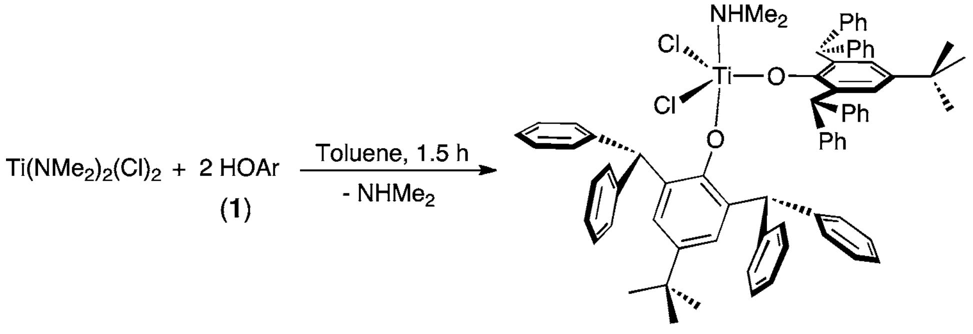
Transmetalation involving 2 equiv of either **2** or **3** with several trivalent metal halides, including but not limited to $ScCl_3(THF)_3$, $TiCl_3(THF)_3$, $VCl_3(THF)_3$, and $CrCl_3(THF)_3$, resulted in the formation of the complexes [M′(OAr^{tBu})$_2$Cl(THF)$_2$] (M′ = Sc (**4**), V (**5**), Cr (**6**), and Ti(**7**)) (Scheme 2). Adding a cooled (−37 °C) THF solution containing 2 equiv of either **2** or **3** to an equally cooled THF solution of M′$Cl_3(THF)_3$ resulted in ligation of the aryloxide ligand to the metal after allowing the reaction to proceed for 12 h. Removal of the volatiles under reduced pressure, followed by extraction of the crude material into toluene and recrystallization, resulted in complexes **4**−**6** being isolated in yields between 65% and 85%. For the synthesis of complexes **4** and **5**, compound **2** was more convenient to use, while complex **6** formed cleaner when the lithio derivative **3** was applied.

As expected for a d^0 system, the white solid [Sc(OAr^{tBu})$_2$Cl(THF)$_2$] (**4**) is diamagnetic, and the ^{1}H NMR spectrum, recorded in C_6D_6, is fully consistent with the coordination of two aryloxides and two THF molecules. The THF ligands of **4** are represented by two broadened signals centered at 3.40 and 0.92 ppm. Additionally, a singlet centered at 1.10 ppm represents the *tert*-butyl substituents of two chemically equivalent aryloxide ligands. The methine and aromatic protons of the aryloxide ligands are all well resolved spanning the range of 7.45−6.70 ppm. While attempts to grow single crystals of this complex have proven unsuccessful, all NMR spectroscopic data are fully consistent with a molecule possessing C_2 symmetry in solution, and combustion analysis further corroborates the chemical formula. Although there are reports of Sc(OAr)$_3$ complexes (OAr = 2,6-bis-*tert*-butyl-4-methylphenoxide, 2,6-diphenyl-phenoxide),[48,49] incorporation of an additional aryloxide to **4** through transmetalation has proven unsuccessful.

Complex **5**, [V(OAr^{tBu})$_2$Cl(THF)$_2$], is a green solid that was isolated in 86% yield. The room-temperature Evans magnetic measurements of **5** performed in C_6D_6 at 298 K reveal a μ_{eff} value of 2.87 μ_B, which is consistent with the calculated spin-only value of 2.83 μ_B for an $S = 1$ system. In accord with the paramagnetic nature of **5**, the ^{1}H NMR spectrum in C_6D_6 is represented by several broadened chemical shifts ranging from 26.25 to 1.11 ppm. X-ray diffraction studies performed on a green single crystal of **5** grown from a saturated diethyl ether solution cooled to −37 °C reveal a V(III) ion adopting a strictly trigonal bypiramidal structure ($\tau = 0.90$).[50] Complex **5** crystallizes in the monoclinic space group $P2_1/n$ (Figure 3 and Table 1), and selected bond lengths and angles are listed in Table 2.

The solid-state molecular structure of **5** indicates the two coordinated THF molecules to occupy the axial positions

Scheme 3. Synthesis of $[Ti(OAr^{tBu})_2Cl_2(NHMe_2)]$ (8)



(8)

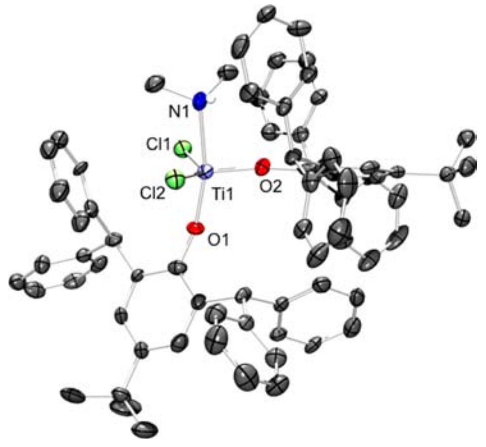


Figure 6. ORTEP drawing of $[Ti(OAr^{tBu})_2Cl_2(NHMe_2)]$ (8), showing selected atom labeling with the ellipsoids at the 50% probability level. All hydrogen atoms have been omitted except for those coordinated to nitrogen. All noninteracting solvent molecules have been omitted for clarity.

(O3−V1−O4, 179(2)°), rendering the chloride and both aryloxide ligands in the equatorial plane ($\sum_{eq}$ = 360.00°). Surprisingly, the O1−V1−O2 angle is increased only slightly (5.35°) from idealized trigonal bypiramidal. However, to accommodate the large steric demands of the ligand, the $V1-O_{OAr}-C_{ipso}$ angles (130.77(13)° and 129.90(15)°) of these ligands adopt a very bent geometry positioning their steric bulk in opposite directions, which generates an idealized C_2 axis containing the chloride and V(III) ion.

Considering the molecular structure of **5** is similar to other V(III) complexes, supported by two mesityl-phenoxide, ($[V(OMes)_2Cl(THF)_2]$ (OMes = 2,4,6-trimethyl-phenoxide)),[51] or two 2,6-diisopropyl-phenoxide ligands, ($[V(ODipp)_2Cl(THF)_2]$ (ODipp = 2,6-diisopropyl-phenoxide)),[52] similar trigonal bypiramidal structures with τ-values of 1.00 and 0.84, respectively, are observed. However, in the former complex, it is possible to coordinate a third mesityl-phenoxide ligand to the V(III) ion yielding the $[V(OMes)_3(THF)_2]$ complex, where all three mesityl-phenoxides occupy the equatorial plane of a trigonal bypiramidal structure.[51] Additional tris-aryloxide complexes of V(III) can be found in the literature when using 2,6-dimethyl-phenoxide[53] and 2-*tert*-butyl-phenoxide.[51] In our case, and akin to complex **4**, attempts to coordinate three of our bulky −OAr ligands to V(III) have proven unsuccessful, which we again attribute to the large steric demands of our aryloxide ligand.

Using the starting materials $CrCl_3(THF)_3$ and 2 equiv of the alkoxide salt, complex **6**, $[Cr(OAr^{tBu})_2Cl(THF)_2]$, was isolated as a purple-red solid in 82% yield. The ^1H NMR spectrum of **6** obtained in C_6D_6 displays paramagnetically broadened chemical shifts spanning from 31.73 to 1.47 ppm. The Evans magnetic measurements of **6** performed in C_6D_6 at 298 K provided a μ_{eff} value of 3.82 μ_B, which is consistent with the calculated spin-only value of 3.87 μ_B in accord with an $S = 3/2$ system. In anticipation of a geometric change when moving to the smaller ionic radius of Cr(III) as compared to V(III), we conducted X-ray diffraction studies on a single plate of **6** grown from a toluene−pentane mixture cooled to −37 °C (Figure 4).

Accordingly, complex **6** crystallizes in the monoclinic $P2_1/n$ space group (Table 1) and adopts a geometry between square pyramidal and trigonal bypiramidal (τ = 0.40).[50] Selected bond lengths and angles are listed in Table 2. The primary coordination sphere of **6** is similar to that of **5**, with the exception of the O1−Cr1−O2 angle increasing to 145.14(5)° when compared to the more acute O1−V1−O2 angle of 125.35(7)° observed for complex **5**. The larger angle between the aryloxide ligands of complex **6** is attributed to the smaller covalent radius of chromium, 1.39 Å, when compared to vanadium, 1.53 Å.[54,55] By increasing the $^{tBu}ArO-Cr-OAr^{tBu}$ angle in **6**, steric clashing of the aryloxide ligands is likely minimized. The $Cr1-O_{Ar}-C_{ipso}$ angles (145.02(9)° and 138.14(10)°) distort in a manner similar to that described for **5**, further minimizing the steric congestion of the ligands. To the best of our knowledge, no structures of a mononuclear Cr(III) supported by two monodentate aryloxide ligands have been reported in the literature.

Attempts to incorporate 2 equiv of either **2** or **3** onto $TiCl_3(THF)_3$ via a transmetalation reaction resulted in complicated mixtures of products from which a small amount of $[Ti(OAr^{tBu})_2Cl(THF)_2]$ (**7**) was isolated, but in impure form. Likewise, this complex is highly unstable and decomposes in solution. However, we have confirmed that this complex is formed in the mixture albeit in very low isolated yield via a single-crystal X-ray diffraction study (Figure 5). In addition, the Evans magnetic measurement of a small fraction of crystals of **7** at 298 K provided a μ_{eff} value of 1.92 μ_B, consistent with an $S = 1/2$ system. Although the structure is of poor quality and we cannot comment on metrical parameters, the incorporation of two aryloxides and two axial THF ligands is clearly evident.[56] From the overall gross structure of **7**, a τ = 0.82[50] suggests this system to more closely resemble the vanadium derivative **5**. Low isolated yields of **7** and the presence of other side products have prevented bulk analysis or complete characterization of the complex.

To circumvent the low yield of complex **7**, we explored instead Ti(IV) as a starting material. It was found that the aryloxide ligand can be readily incorporated to a Ti(IV) ion through the protonolysis of $[\mathrm{Ti(NMe_2)_2Cl_2}]$[57] with 2 equiv of **1** in toluene. After removal of volatiles under reduced pressure and washing the crude solid with cold pentane, a red-orange solid, complex $[\mathrm{Ti(OAr^{tBu})_2Cl_2(NHMe_2)}]$ (**8**), was isolated in 72% yield (Scheme 3). We have established the identity of diamagnetic **8** using both ^{1}H NMR spectroscopy as well as single-crystal X-ray diffraction studies. Accordingly, the ^{1}H NMR spectrum of **8**, recorded in C_6D_6, displays a single resonance at 1.07 ppm for two *tert*-butyl groups of chemically equivalent aryloxide ligands. Additionally, resonances in the aromatic region spanning 7.20−6.88 ppm support the assignment of a complex possessing 2-fold symmetry in solution. Centered at 1.58 ppm is a broad resonance integrating to 1H and a singlet centered at 1.47 ppm integrating to 6H, which are assigned to the neutral ligand $\mathrm{NH(Me)_2}$.

X-ray diffraction studies on red-orange blocks grown from cooling a concentrated pentane solution to −37 °C reveal the Ti(IV) ion of complex **8** to adopt a geometry confined between trigonal bipyramidal and square pyramidal ($\tau = 0.48$) (Figure 6).[50] One of the aryloxides and the coordinated dimethylamine occupy the axial ligand positions (O1−Ti1−N1, 165.2(2)), rendering the two chlorides and the second aryloxide equatorial ($\sum_{\mathrm{eq}} = 356.45°$). Surprisingly, the two aryloxides are ligated in a *cis*-coordination environment (O1−Ti1−O2, 105.2(2)°) to the Ti(IV) ion. The Ti1−O1−C1 angle (159.5(5)°) deviates from linearity found in the Ti1−O2−C37 angle (170.1(5)°), which might be the result of steric clashing of the bulky aryloxide ligands. Although the solid-state structure is of idealized C_s symmetry, solution-state NMR studies at room temperature suggest the geometry of **8** to be fluxional on the NMR time scale. It is evident that the steric demands of our bulky aryloxide prevent dimerization of the Ti(IV) ion, which is common of other *ortho*-substituted polyaryloxide ligands possessing methyl,[58,59] phenyl,[60,61] and *tert*-butyl[58,62] substituents. Unfortunately, we have been unable to produce **7** via one-electron reduction of **8**.

■ CONCLUSIONS

In this work, we have described the synthesis of a new bulky aryloxide framework by incorporation of diphenylmethyl substituents in the 2,6-aryl positions. The synthesis of this arylalcohol is facile and can be obtained in high yields and purity without need of solvent. Furthermore, we have demonstrated the incorporation of the aryloxide ($^{-}\mathrm{OAr^{tBu}}$) ligand to a variety of 3d metals, through both protonolysis and trasmetalation reactions. The steric demand of the ligand allows for the isolation of monomeric transition metal complexes where no bridging chlorides or alkoxides are observed. We are presently exploring the chemistry of these molecules as precursors to either low-coordinate or low-valent synthons, and we have also begun investigating the chemistry of the heavy congeners for some of the complexes presented.

■ EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-drybox under an atmosphere of purified nitrogen or using high vacuum standard Schlenk techniques under a nitrogen atmosphere. Anhydrous pentane, toluene, *n*-hexane, and benzene were purchased from Aldrich in sure-sealed reservoirs (18 L) and dried by passage through two columns of activated alumina and a Q-5 column. THF and Et_2O were distilled, under nitrogen, from purple sodium benzophenone ketyl and stored over sodium metal. Distilled THF and Et_2O were transferred under vacuum into thick walled reaction vessels before being carried into a drybox. Deuterobenzene was purchased from Cambridge Isotope Laboratory (CIL), degassed by freeze−pump−thaw cycles, and stored over 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. Complexes $\mathrm{ScCl_3(THF)_3}$, $\mathrm{VCl_3(THF)_3}$, $\mathrm{CrCl_3(THF)_3}$, $\mathrm{TiCl_3(THF)_3}$, and $\mathrm{Ti(NMe_2)_2Cl_2}$ were prepared following literature procedures.[57,63−67] All other chemicals were purchased from commercial sources and used as received. ^{1}H and ^{13}C NMR spectra were recorded on Varian 500 and 400 MHz NMR spectrometers. ^{1}H and ^{13}C NMR are reported with reference to residual ^{1}H solvent resonances of C_6D_6 at 7.16 and 128.06 ppm, respectively. Elemental analyses were performed at Indiana University and Robertson Microlit Laboratories.

*[HO-2,6-^{i}Ph$_2$C$_6$H$_2$-4-^{t}Bu] (HOAr^{tBu}) (**1**).* In air, to a 250 mL round-bottom flask were charged 4-*tert*-butylphenol (11.0 g, 73.2 mmol), benzhydrol (27.0 g, 146.5 mmol), and a large stirring bar. The reaction flask was heated to 140 °C to produce a melt followed by the addition of a solution of HCl (12 M)/$ZnBr_2$ (2.22 mL, 73.2 mmol of HCl; 37 mmol of $ZnBr_2$ (8.2 g) or $ZnCl_2$ (5.2 g)) dropwise via a glass pipet. After being stirred for 0.5 h, the reaction mixture solidified into a solid. The solid was allowed to heat for an additional 2 h to ensure completion. The reaction flask was cooled to room temperature, and the crude solids were extracted into CH_2Cl_2 and washed once with water and twice with brine. All volatiles were removed by a rotary evaporator, and cold MeOH (50 mL) was added to precipitate clean white solid of the product. Single crystals were grown from layering a concentrated toluene solution with pentane. Yield = 91% (32.0 g, 66.3 mmol). ^{1}H NMR (25 °C, 400.11 MHz, C_6D_6): δ 7.21 (t, J_{HH} = 7.24 Hz, 8H, Ar−H_{meta}), 7.14 (t, J_{HH} = 7.23 Hz, 4H, Ar−H_{para}), 7.04 (d, J_{HH} = 7.90 Hz, 8H, Ar−H_{ortho}), 6.65 (s, 2H, Ar−H_{meta}), 5.61 (s, 2H, −C*H*(Ph)$_2$), 4.32 (s, 1H, −O*H*), 0.97 (s, 9H, −C(C*H*$_3$)$_3$). ^{13}C NMR (25 °C, 100.61 MHz, C_6D_6): δ 150.05 (−C_{Ar}), 143.42 (−C_{Ar}), 142.91 (−C_{Ar}), 130.85 (−C_{Ar}), 129.83 (−$\mathrm{CH_{Ar}}$), 128.77 (−$\mathrm{CH_{Ar}}$), 126.86 (−$\mathrm{CH_{Ar}}$), 126.39 (−$\mathrm{CH_{Ar}}$), 52.09 (−CH(Ph)$_2$), 34.37 (−C(CH$_3$)$_3$), 31.57(−C(CH$_3$)$_3$). Anal. Calcd for $C_{36}H_{34}O$: C, 89.58; H, 7.10. Found: C, 89.90; H, 6.95.

*[NaO(2,6-^{i}Ph$_2$C$_6$H$_2$-4-^{t}Bu)] (NaOAr^{tBu}) (**2**).* To a white suspension of HO-2,6-^{i}Ph$_2$C$_6$H$_2$-4-^{t}Bu (14.968 g, 31.04 mmol) in diethyl ether (200 mL) at room temperature were added solid portions of $\mathrm{Na[N(SiMe_3)_2]}$ (6.260 g, 34.14 mmol) over 15 min to produce a homogeneous yellow solution. The mixture was allowed to proceed for another hour, and reduction of the solvent volume to 50 mL induced precipitation of a white crystalline solid. Subsequently, the white solid was collected by vacuum filtration, washed with cold pentane (20 mL), and dried under reduced pressure. Single crystals of **2** were grown from cooling a saturated THF solution to −37 °C. Yield = 83% (13.0 g, 25.7 mmol). ^{1}H NMR (25 °C, 400.11 MHz, C_6D_6): δ 7.25 (d, J_{HH} = 7.39 Hz, 8H, Ar−H_{ortho}), 7.05 (t, J_{HH} = 7.59 Hz, 8H, Ar−H_{meta}), 6.93 (s, 2H, Ar−H_{meta}), 6.90 (t, J_{HH} = 7.33 Hz, 4H, Ar−-H_{para}), 5.58 (s, 2H, −C*H*(Ph)$_2$), 1.25 (s, 9H, −C(C*H*$_3$)$_3$). ^{13}C NMR (25 °C, 100.61 MHz, C_6D_6): δ 162.77 (−C_{Ar}), 146.90 (−C_{Ar}), 132.17 (−C_{Ar}), 130.71 (−C_{Ar}), 129.63 (−$\mathrm{CH_{Ar}}$), 128.46 (−$\mathrm{CH_{Ar}}$), 126.00 (−$\mathrm{CH_{Ar}}$), 125.59 (−$\mathrm{CH_{Ar}}$), 54.50 (−CH(Ph)$_2$), 34.16 (−C(CH$_3$)$_3$), 32.31 (−C(CH$_3$)$_3$).

*[LiO-2,6-^{i}Ph$_2$C$_6$H$_2$-4-tBu][Et$_2$O] (LiOAr^{tBu}) (**3**).* To a white suspension of HO-2,6-^{i}Ph$_2$-C$_6$H$_2$-4-^{t}Bu (4.864 g, 10.08 mmol) in diethyl ether (200 mL) at room temperature were added solid portions of $\mathrm{Li[N(SiMe_3)_2]}$ (1.903 g, 11.37 mmol) over 15 min to produce a homogeneous yellow solution. The mixture was allowed to proceed for another hour, and reduction of the solvent volume to 50 mL induced precipitation of a white crystalline solid. Subsequently, the white solid was collected by vacuum filtration, washed with cold pentane (20 mL), and dried under reduced pressure. Yield = 78% (4.44 g, 7.89 mmol). ^{1}H NMR (25 °C, 499.80 MHz, C_6D_6): δ 7.22 (d, J_{HH} = 7.49 Hz, 8H, Ar−H_{ortho}), 7.08 (t, J_{HH} = 7.58 Hz, 8H, Ar−H_{meta}) 7.02 (s, 2H, Ar−H_{meta}), 6.96 (t, J_{HH} = 7.30 Hz, 4H, Ar−H_{para}), 5.88 (s, 2H, −C*H*(Ph)$_2$), 3.08 (q, J_{HH} = 6.89 Hz, 4H, −C*H*$_2$−), 1.18 (s, 9H, −C(C*H*$_3$)$_3$), 0.98 (t, J_{HH} = 6.97 Hz, 6H, −C*H*$_3$). ^{13}C NMR (25 °C, 125.68 MHz, C_6D_6): δ 159.79 (−C_{Ar}),

146.14 ($-C_{Ar}$), 135.49 ($-C_{Ar}$), 131.13 ($-C_{Ar}$), 129.65 ($-CH_{Ar}$), 128.73 ($-CH_{Ar}$), 126.40 ($-CH_{Ar}$), 125.86 ($-CH_{Ar}$), 66.05 ($-O(CH_2CH_3)_2$), 52.34 ($-CH(Ph)_2$), 34.15 ($-C(CH_3)_3$), 32.02 ($-C(CH_3)_3$), 15.22 ($-O(CH_2CH_3)_2$).

[Sc(OAr^{tBu})$_2$Cl(THF)$_2$] **(4).** At −37 °C, to a 100 mL round-bottom flask containing a 15 mL THF slurry of $ScCl_3(THF)_3$ (197.4 mg, 0.54 mmol) was added a 15 mL THF solution of NaOAr^{tBu} (542.0 mg, 1.07 mmol) via a glass pipet. After addition, the reaction mixture became cloudy and was stirred for 12 h at room temperature. All volatiles were removed under reduced pressure, and the resulting solid was extracted into 10 mL of toluene and filtered through a small medium porosity frit containing Celite. All volatiles were removed from the resulting filtrate, and the white product was transferred to a medium porosity frit and rinsed with cold hexanes (10 mL). Yield = 65% (417 mg, 0.35 mmol). ^{1}H NMR (25 °C, 400.11 MHz, C_6D_6): δ 7.38 (d, J_{HH} = 7.50 Hz, 16H, Ar−H_{ortho}), 7.23 (s, 4H, Ar−H_{meta}), 7.10 (t, J_{HH} = 7.50 Hz, 16H, Ar−H_{meta}), 6.99 (t, J_{HH} = 7.22 Hz, 8H, Ar−H_{para}), 6.77 (s, 4H, $-CH(Ph)_2$), 3.40 (m, 8H, THF), 1.10 (s, 18H, $-C(CH_3)_3$), 0.92 (m, 8H, THF). ^{13}C NMR (25 °C, 100.67 MHz, C_6D_6): δ 157.22 ($-C_{Ar}$), 146.07 ($-C_{Ar}$), 140.11 ($-C_{Ar}$), 131.62 ($-C_{Ar}$), 130.44 ($-CH_{Ar}$), 128.35 ($-CH_{Ar}$), 126.78 ($-CH_{Ar}$), 126.17 ($-CH_{Ar}$), 71.84 ($-THF_{alpha}$), 50.24 ($-CH(Ph)_2$), 34.28 ($-C(CH_3)_3$), 31.65 ($-C(CH_3)_3$), 25.05 ($-THF_{beta}$). Anal. Calcd for $C_{80}H_{82}O_4ScCl$: C, 80.89; H, 6.96. Found: C, 81.25; H, 6.88.

[V(OAr^{tBu})$_2$Cl(THF)$_2$] **(5).** At −37 °C, to a 250 mL round-bottom flask containing a 50 mL THF solution of $VCl_3(THF)_3$ (740 mg, 1.98 mmol) was added dropwise a 20 mL THF solution of NaOAr^{tBu} (2.00 g, 3.96 mmol) via a glass pipet. The reaction mixture initially turned yellow-brown and finally to dark green upon completed addition of ligands. The reaction mixture was stirred for 12 h at room temperature. All volatiles were removed under reduced pressure, and the solid was triturated with hexanes and dried again under vacuum. The crude product was extracted into toluene and filtered through a medium porosity frit containing Celite, and all remaining volatiles were removed under reduced pressure. Addition of hexanes led to a suspension, and the product was collected via a medium porosity frit and dried under reduced pressure. The filtrate was reduced in volume and recrystallized at −37 °C to yield additional product. Green single crystals were grown from cooling a saturated diethylether solution to −37 °C. Yield = 85.6% (2.02 g, 1.69 mmol) from two batches. ^{1}H NMR (25 °C, 400.11 MHz, C_6D_6): δ 26.25 ($\Delta\nu_{1/2}$ = 2568 Hz), 7.01 ($\Delta\nu_{1/2}$ = 96 Hz), 5.85 ($\Delta\nu_{1/2}$ = 156 Hz), 5.15 ($\Delta\nu_{1/2}$ = 172 Hz), 3.28 ($\Delta\nu_{1/2}$ = 332 Hz), 1.11 ($\Delta\nu_{1/2}$ = 44 Hz). μ_{eff} = 2.87 μ_B (C_6D_6, 298 K, Evan's method). Anal. Calcd for $C_{80}H_{82}O_4VCl$: C, 80.48; H, 6.92. Found: C, 80.60; H, 7.12.

[Cr(OAr^{tBu})$_2$Cl(THF)$_2$] **(6).** To a 250 mL round-bottom flask containing a purple slurry of $CrCl_3(THF)_3$ (506 mg, 1.35 mmol) in 40 mL THF solution was added dropwise a 40 mL THF solution of LiOAr^{tBu} (1.50 g, 2.67 mmol) via a glass pipet. Upon addition, the reaction mixture turned to a dark purple-red color. The reaction mixture was stirred for 12 h at room temperature, and all volatiles were removed under reduced pressure. To the resulting dark purple-red solid was added with pentane and concentrated to dryness. The crude product was extracted into 40 mL of toluene and filtered through a medium porosity frit containing Celite. To the dark purple-red solution (the filtrate) was added 160 mL of pentane, and the solution was cooled to −35 °C, which precipitated a purple crystalline solid. The solid was isolated by filtration and washed with cold pentane (20 mL). The filtrate was reduced in volume and recrystallized at −35 °C to afford a second crop of product, which was isolated by filtration and washed with cold pentane (20 mL). Yield = 82% (1.318 g, 1.10 mmol) from two crops. ^{1}H NMR (25 °C, 400.11 MHz, C_6D_6): δ 31.73 ($\Delta\nu_{1/2}$ = 528 Hz), 7.11 ($\Delta\nu_{1/2}$ = 192 Hz), 1.47 ($\Delta\nu_{1/2}$ = 64 Hz). μ_{eff} = 3.82 μ_B (C_6D_6, 298 K, Evan's method). Anal. Calcd for $C_{80}H_{82}O_4CrCl$: C, 80.41; H, 6.92. Found: C, 80.15; H, 6.80.

[Ti(OAr^{tBu})$_2$Cl(THF)$_2$] **(7).** To a 20 mL scintillation vial containing a 15 mL THF solution of $TiCl_3(THF)_3$ (100 mg, 0.27 mmol) was added a 5 mL THF solution of NaOAr^{tBu} (272 mg, 0.54 mmol) via a glass pipet at −37 °C. The light blue reaction gradually darkens, and after 48 h, the reaction mixture was dark purple. All volatiles were removed, and the crude product was triturated with pentane and reduced to dryness. The crude product was extracted into Et_2O (10 mL) and filtered through a glass pipet containing Celite and stored at −37 °C. Decantation of the mother liquor provided a collection of trace amounts of light purple crystals as well as other unidentified products. μ_{eff} = 1.92 μ_B (C_6D_6, 298 K, Evans' method). Multiple attempts to obtain crystalline material in larger amounts have been unsuccessful given the unstable nature of this compound.

[Ti(OAr^{tBu})$_2$Cl$_2$(NHMe$_2$)] **(8).** To a 20 mL scintillation vial containing a 10 mL yellow-orange toluene solution of $TiCl_2(NMe_2)_2$ (51 mg, 0.25 mmol) was added dropwise a 5 mL toluene solution of HOAr^{tBu} (237 mg, 0.49 mmol) via a glass pipet. Through the duration of ligand addition, the solution gradually darkens, resulting in a dark red solution. After mixing for 2 h, all volatiles were removed under reduced pressure, and the resulting dark red solid was transferred to a medium porosity frit and rinsed with cold pentane (15 mL). Yield = 72% (200 mg, 0.18 mmol). Red-orange single crystals were grown from cooling a saturated pentane solution to −37 °C. ^{1}H NMR (25 °C, 400.11 MHz, C_6D_6): δ 7.20 (d, J_{HH} = 7.37 Hz, 16H, Ar−H_{ortho}), 7.14 (s, 4H, Ar−H_{meta}), 7.01 (t, J_{HH} = 7.30 Hz, 16H, Ar−H_{meta}), 6.95 (t, J_{HH} = 7.24 Hz, 8H, Ar−H_{para}), 6.91 (s, 4H, $-CH(Ph)_2$), 1.58 (br m, 1H, $-NH(CH_3)_2$), 1.47 (br m, 6H, $-NH(CH_3)_2$), 1.07 (s, 18H, $-C(CH_3)_3$). ^{13}C NMR (25 °C, 100.67 MHz, C_6D_6): δ 165.57 ($-C_{Ar}$), 146.09 ($-C_{Ar}$), 144.67 ($-C_{Ar}$), 133.98 ($-C_{Ar}$), 130.48 ($-CH_{Ar}$), 128.51 ($-CH_{Ar}$), 127.07 ($-CH_{Ar}$), 126.46 ($-CH_{Ar}$), 50.70 ($-CH(Ph)_2$), 40.08 ($-NH(CH_3)_2$), 34.68 ($-C(CH_3)_3$), 31.35 ($-C(CH_3)_3$).

X-ray Crystallography. Suitable crystals for analysis of **1**, **2**, and **5** were placed onto the tip of MiTeGen loop coated in NVH oil and mounted on an Apex Kappa Duo diffractometer. The data collection was carried out at 150 K using Mo Kα radiation (graphite monochromator). A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 0.50° steps in ω and ϕ scans. Data collection for **6** and **8** was collected at 100 K at the Advanced Photon Source in Argonne National Laboratory using synchrotron radiation (λ = 0.41328, silicon 111 and 311 monochromators, and two mirrors to exclude higher harmonics). Final cell constants were calculated from the *xyz* centroids of a particular number of strong reflections for each crystal from the actual data collection after integration (SAINT).[68] The intensity data were corrected for absorption (SADABS).[69] The space groups were determined on the basis of intensity statistics and systematic absences. The structures were solved using SIR-92[70] and refined (full-matrix-least-squares) using either SHELXL-97[71] or Oxford University Crystals for Windows system.[72] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic information (CIF) and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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