

A Room-Temperature Stable Y(II) Aryloxy: Using Steric Saturation to Kinetically Stabilize Y(II) Complexes

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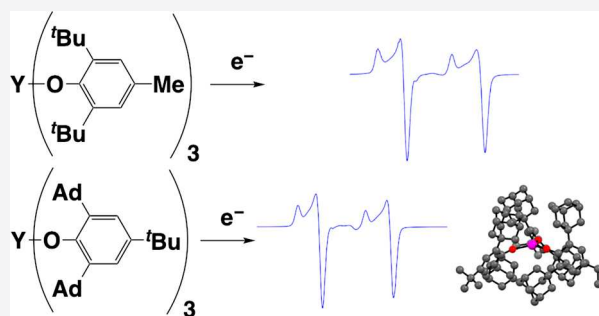


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ABSTRACT: The utility of the bulky aryloxy ligands 2,6-Ad₂-4-Me-C₆H₂O[−] (Ad,Ad,MeArO[−]) and 2,6-Ad₂-4-*t*-Bu-C₆H₂O[−] (Ad,Ad,*t*-BuArO[−]; Ad = 1-adamantyl) for stabilizing the Y(II) ion is reported and compared with the results with 2,6-*t*-Bu₂-4-Me-C₆H₂O[−] (Ar'O[−]). In contrast to the reduction product obtained from reducing Y(OAr')₃ with potassium graphite, which is only stable in solution for 60 s at room temperature, K₂C₈ reduction of Y(OAr^{Ad,Ad,t-Bu})₃ in THF in the presence of 2.2.2-cryptand (crypt) produces the room-temperature stable, crystallographically characterizable Y(II) aryloxy [K(crypt)]-[Y(OAr^{Ad,Ad,t-Bu})₃]. The X-band EPR spectrum at 77 K shows an axial pattern with resonances centered at $g_{\perp} = 1.97$ and $g_{\parallel} = 2.00$ and hyperfine coupling constants of $A_{\perp} = 156.5$ G and $A_{\parallel} = 147.8$ G and at room temperature shows an isotropic pattern with $g_{\text{iso}} = 1.98$ and $A_{\text{iso}} = 153.3$ G, which is consistent with an $S = 1/2$ spin system with nuclear spin $I = 1/2$ for the ⁸⁹Y isotope (100% natural abundance).



INTRODUCTION

Rare-earth reductive chemistry has undergone a transformation through the discovery that all of the lanthanide metals (except radioactive promethium) as well as yttrium can form crystalline molecular species containing ions in the formal +2 oxidation state.^{1–8} For years, it was thought that only Eu, Yb, Sm, Tm, Dy, and Nd would form such species, and these had 4fⁿ⁺¹ electron configurations formed by the reduction of 4fⁿ Ln(III) precursors. The isolation of the first Y(II) complex² and the first Ln(II) complexes of La,¹ Ce,¹ Pr,⁴ Gd,⁴ Tb,⁴ Ho,³ Er,³ and Lu⁴ involved the silylcyclopentadienyl ligands C₅H₃(SiMe₃)₂[−] (Cp[−]) and C₅H₄SiMe₃[−] (Cp[−]) in complexes of formulas [Cp[−]₃Ln][−] and [Cp[−]₃Ln][−]. In these coordination environments, the new lanthanide ions had nontraditional 4fⁿ5d¹ electron configurations instead of the traditional 4fⁿ⁺¹ found earlier. Since the discovery of the Cp[−] and Cp[−] complexes, the number of ligand systems that have been shown to support the “new” 4fⁿ5d¹ Ln(II) ions has grown substantially to include C₅Me₄H[−],⁹ C₅H₄Me[−],¹⁰ C₅H₄-*t*-Bu[−],¹¹ C₅-*i*-Pr₅[−],¹² (Ad,MeArO)₃mes^{3−},^{13,14} (*t*-BuO)₃SiO[−],¹⁵ and (Me₃Si)₂N[−].¹⁶

Although the chelating tris(aryloxy)mesitylene ligand, (Ad,MeArO)₃mes^{3−}, can support Ln(II) complexes,^{13,14} monodentate aryloxy ligands did not readily yield examples of new Ln(II) ions despite the fact that aryloxides have been common ligands in rare-earth chemistry for decades.^{17,18} The only exception to this statement was the isolation of the Sc(II) complex, [K(crypt)][Sc(OAr')₃] (Ar'O[−] = 2,6-*t*-Bu₂-4-Me-

C₆H₂O[−], crypt = 2.2.2-cryptand) formed by potassium graphite reduction of Sc(OAr')₃.¹⁹ The Sc(II) compound is stable for 40 min at room temperature and could be characterized by optical and EPR spectroscopy as well as X-ray crystallography. In contrast, reduction of the congeneric Y(III) complex Y(OAr')₃ formed a dark blue solution that decomposes at room temperature within 1 min. The EPR and UV–visible spectra of the dark solution were consistent with the presence of an Y(II) analog of the Sc(II) species, i.e., “[Y(OAr')₃][−],” but crystallographic confirmation has been elusive.

It seemed possible that the yttrium complex was kinetically unstable due to the larger ionic radius of Y(III) (0.90 Å for six coordination) compared to Sc(III) (0.745 Å for six coordination),²⁰ which made the yttrium complex less sterically saturated.¹⁹ Since steric saturation is a critical component in the isolation of 4fⁿ Ln(III) rare-earth complexes,^{19,21} this condition could also apply for Ln(II) complexes. However, the range of lanthanides that yielded crystalline Ln(II) complexes for a given ligand did not show a clear dependence on steric saturation, Table 1.

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Table 1. Crystallographically-Characterized Nontraditional Ln(II) Complexes As a Function of Ligand

ligand	La	Ce	Pr	Nd	Gd	Tb	Dy	Ho	Y	Er	Lu	Sc
(C ₅ H ₄ SiMe ₃) ^{2-4,6}	+	+	+	+	+	+	+	+	+	+	+	
[C ₅ H ₃ (SiMe ₃) ₂] ^{1,5}	+	+	+	+								
(C ₅ Me ₄ H) ⁹	+	+	+	+	+	+	+					
(C ₅ H ₄ - <i>t</i> -Bu) ¹¹		+										
(C ₅ H ₄ Me) ¹⁰						+	+	+		+		
(C ₅ - <i>i</i> -Pr) ¹²						+	+					
[(^{Ad,Me} ArO) ₃ mes ³⁻] ^{13,14}					+		+			+		
[(<i>t</i> -BuO) ₃ SiO] ¹⁵		+										
[(Me ₃ Si) ₂ N] ^{16,22,23}				+	+	+	+	+	+	+		+
(2,6- <i>t</i> -Bu ₂ -4-MeC ₆ H ₂ O) ¹⁹												+

In order to examine the importance of steric saturation for isolating Ln(II) complexes of aryloxides, an aryloxide ligand alternative to Ar'O⁻ was sought that would not appreciably differ from the electronic structure of Ln(OAr')₃ but would be more sterically demanding. 2,4,6-Tris(alkyl)aryloxides were thus considered, and it was expected that the metal-proximate 2 and 6 positions would be the most important for controlling steric saturation. Indeed, changing the substituent at the 2 and 6 positions of aryloxide ligands has been shown to change the nuclearity of rare-earth(III) aryloxides, *e.g.*, compare Y(OAr')₃ and [Y(μ-2,6-Me₂C₆H₃O)(2,6-Me₂C₆H₃O)₂(THF)₂]₂.^{18,24}

The Ar'O⁻ ligand has *tert*-butyl groups at the 2 and 6 positions, so substituents larger than *tert*-butyl were sought. Aryloxides, synthesized first by Watanabe *et al.* with 1-adamantyl groups at the 2 and 6 positions, *i.e.*, ^{Ad,Ad,Me}ArO⁻ and ^{Ad,Ad,*t*-Bu}ArO⁻ (^{Ad,Ad,Me}ArO⁻ = 2,6-Ad₂-4-Me-C₆H₂O⁻; ^{Ad,Ad,*t*-Bu}ArO⁻ = 2,6-Ad₂-4-*t*-Bu-C₆H₂O⁻; Ad = 1-adamantyl), have been used to stabilize Zr(IV) aryloxide-alkyls against C–H activation²⁵ and to synthesize two-coordinate Fe(II) aryloxides.²⁶ Furthermore, to a first approximation, 1-adamantyl is electronically similar to *tert*-butyl in that it is bonded to the aryloxide ring by a tertiary carbon. However, 1-adamantyl is sterically larger than *tert*-butyl in that 1-adamantyl is nearly equivalent to adding a cyclohexyl moiety to *tert*-butyl, Figure 1. Previously, the ^{Ad,Ad,Me}ArO⁻ ligand has also been used

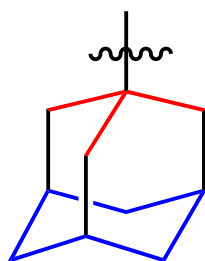


Figure 1. An illustration of the analogy between *tert*-butyl and 1-adamantyl. The wavy line through a single bond designates a bond to an aryloxide ring carbon atom. The red portion of the drawn 1-adamantyl group is the portion similar to *tert*-butyl, and the blue portion is the part similar to cyclohexyl.

to synthesize U(OAr^{Ad,Ad,Me})₃, a complex of the reducing U(III) ion.²⁷ In this work, these (adamantyl)aryloxides are assessed for their utility in stabilizing an Y(II) aryloxide complex.

RESULTS

Y(OAr^{Ad,Ad,Me})₃, 1-Y. U(OAr^{Ad,Ad,Me})₃ had previously been synthesized by salt metathesis of UI₃(dioxane)_{1.5} with 3 equiv

of KOAr^{Ad,Ad,Me}·1.5 DME (DME = 1,2-dimethoxyethane) in benzene, and this synthesis was used as a guide.²⁷ In contrast, salt metathesis of YX₃ compounds (X = Cl, I, OTf) in THF with 3 equiv of KOAr^{Ad,Ad,Me}·1.5 DME both at room temperature and at 65 °C did not yield Y(OAr^{Ad,Ad,Me})₃ as the major product in useful quantities in our hands. However, protonolysis of 1.2 equiv of Y(NR₂)₃ (R = SiMe₃) with 3 equiv of ^{Ad,Ad,Me}ArOH in toluene for 48 h at 100 °C gave Y(OAr^{Ad,Ad,Me})₃, 1-Y, but the samples also contained ^{Ad,Ad,Me}ArOH. Since 1-Y and ^{Ad,Ad,Me}ArOH have similar solubilities, it was not possible to separate them by extraction. Complex 1-Y was only sparingly soluble in arenes (benzene, toluene, mesitylene), and X-ray quality crystals were not isolated.

Y(OAr^{Ad,Ad,*t*-Bu})₃, 2-Y. In an effort to increase the solubility of the Y(III) aryloxide complex, as well as to effect a greater differential solubility between the phenol and the Y(III) aryloxide, the *tert*-butyl derivative of ^{Ad,Ad,Me}ArO⁻, namely, 2,6-Ad₂-4-*t*-Bu-C₆H₂O⁻ (^{Ad,Ad,*t*-Bu}ArO⁻), was investigated to see the effect of replacing the 4-methyl substituent with 4-*tert*-butyl. Protonolysis of 1.2 equiv of Y(NR₂)₃ with 3 equiv of ^{Ad,Ad,*t*-Bu}ArOH in toluene for 48 h at 100 °C gave Y(OAr^{Ad,Ad,*t*-Bu})₃, 2-Y, which was still contaminated with ^{Ad,Ad,*t*-Bu}ArOH (by ¹H NMR spectroscopy). Complex 2-Y was dissolved in boiling *n*-hexane and cooled to room temperature to yield colorless crystals that showed an IR spectrum that only contained a weak signal for the characteristically sharp O–H stretch of ^{Ad,Ad,*t*-Bu}ArOH at 3628 cm⁻¹. Since the ¹H NMR spectrum of this sample still showed ~15% of ^{Ad,Ad,*t*-Bu}ArOH, the ^{Ad,Ad,*t*-Bu}ArOH may be formed from 2-Y in the course of preparing the NMR sample. 2-Y was identified by ¹H NMR spectroscopy and single-crystal X-ray diffraction, Figure 2. 2-Y is sparingly soluble in benzene, toluene, and THF. Unlike Y(OAr')₃, 2-Y will not sublime even at 300 °C and 10⁻⁵ Torr, although it does not decompose under these conditions.

Y(OAr^{Ad,Ad,*t*-Bu})₃, 2-Y, crystallizes in the P2₁/n space group with two equivalents of hexane in the lattice. The complex is pseudo-C₃ symmetric. Selected metrical parameters are detailed in Table 2 alongside those of Y(OAr')₃ (OAr' = 2,6-*t*-Bu₂-4-Me-C₆H₂O).¹⁹

The six Ad groups in 2-Y point toward the yttrium center in two orientations. Two of the groups have an edge of the adamantyl framework oriented toward the metal such that one CH₂ group points toward yttrium [C(38) and C(82)]. Four of the Ad groups have the open six-membered ring pointed toward the Y [groups involving C(8), C(29), C(58), and C(79)]. The ^{Ad,Ad,*t*-Bu}ArO⁻ ligands confer greater steric saturation on the Y(III) center than Ar'O⁻, as shown by the 92% G parameter of 2-Y compared to the 81–82% of Y(OAr')₃. Despite this difference in G parameter, the average

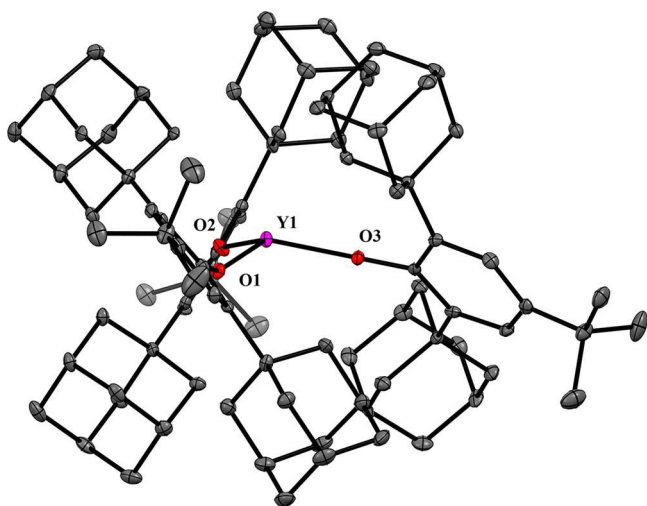


Figure 2. Molecular representation of $Y(OAr^{Ad,Ad,t-Bu})_3$ in crystals of $2-Y \cdot 2C_6H_{16}$. Hydrogen atoms and lattice *n*-hexane molecules are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Atoms and bonds in the foreground are more darkly shaded than those in the background.

Table 2. Selected Metrical Parameters of $Y(OAr^{Ad,Ad,t-Bu})_3$, 2-Y, and $Y(OAr')_3$ (Which Has Five Molecules of $Y(OAr')_3$ in Its Unit Cell)^{19a}

	$Y(OAr^{Ad,Ad,t-Bu})_3$, 2-Y	$Y(OAr')_3$
Y–O	2.038(2)–2.069(1)	2.032(2)–2.053(2)
Average Y–O	2.049(3)	2.045(7)
OAr _{cent} –C _{ipso} –O angle	175–177	176–180
Y–O–C _{ipso} angle	150.0(2)	156.5(2)–171.5(2)
	155.3 (2)	
	155.7(2)	
OAr _{cent} –C _{para} –C _{exo} angle	177–178	178–180
δ	0.431	0.009–0.479
Θ	51–60	39–78
γ	0.001(4)–0.058(4)	0.000(4)–0.027(4)
G	92	81–82

^aDistances are in Ångströms; angles are in degrees, Centroids OAr_{cent} are for the aryloxy C₆ ring. C_{exo} is the carbon atom bonded to the 4 position of the aryloxy, i.e., the 4-Me carbon on Ar'O[−] and the tertiary carbon of the 4-*tert*-butyl on $^{Ad,Ad,t-Bu}ArO^-$. δ is the displacement of Y from the O₃ plane. Θ is the angle between the O₃ plane and the plane of the aryloxy ligand. γ is the displacement of C₆ aryloxy ring carbon atoms from the plane of the aryloxy ring; error is taken from the C–C bond distance error of the C₆ aryloxy rings since the C₆ plane is a calculated average and not a measured quantity. G is the Guzei G parameter and is listed in percent.²⁸

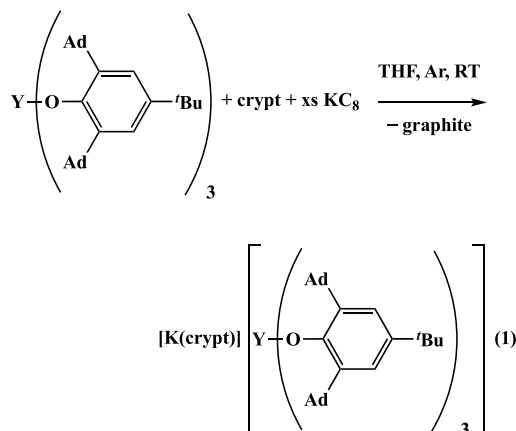
Y–O distances are the same for $Y(OAr')_3$ and 2-Y within error and the distance of the yttrium metal center out of the plane of the three oxygen donor atoms (the pyramidalization δ) in 2-Y is similar to the value of the most-pyramidal $Y(OAr')_3$ in the unit cell. The Y–O–C_{ipso} angles in 2-Y are 150.0(2), 155.3(2), and 155.7(2) compared to 156–172° in $Y(OAr')_3$.

There is a slightly increased distortion from planarity of aryloxy ligands in 2-Y vs $Y(OAr')_3$ as shown by the greater deviation of the C₆ aryloxy ring carbon atoms from the C₆ aryloxy ring plane (γ value) and slightly less linear OAr_{cent}–C_{ipso}–O and OAr_{cent}–C_{para}–C_{exo} angles. This is not accompanied by a significant deviation in C–C bond lengths in the C₆ ring of the aryloxy ligands, however. It appears that this

deviation of the C₆ ring from planarity is a common feature of aryloxy complexes with the 2,6-Ad₂ substitution pattern: for example, $U(OAr^{Ad,Ad,Me})_3$ has γ = 0.000(5)–0.064(5) Å,²⁷ $ZrCl_2(OAr^{Ad,Ad,Me})_2$ has γ = 0.001(5)–0.085(5) Å, and $Zr(CH_2Ph)_2(OAr^{Ad,Ad,Me})_2$ has γ = 0.015(6)–0.067(6) Å.²⁵ The two-coordinate Fe(II) aryloxides $Fe(OAr^{Ad,Ad,Me})_2$ [γ = 0.001(8)–0.009(8) Å] and $Fe(2,6-Ad_2-4-i-Pr-C_6H_2O)_2$ [γ = 0.001(6)–0.019(6) Å]²⁶ display significantly less distortion of the C₆ ring, despite having a smaller ionic radius than Y(III) and U(III).²⁰

The ¹H and ¹³C{¹H} NMR of 2-Y are unremarkable, as expected for a complex of diamagnetic Y(III), except that the resonance for the *ipso*-carbon of the $^{Ad,Ad,t-Bu}ArO^-$ ring is split into two equal-intensity signals in C₆D₆ (*J* = 4.0 Hz) and in toluene-*d*₈ (room temperature and 3 °C, *J* = 4.0 and 4.3 Hz, respectively). A characteristic change in the resonances of the 1-adamantyl-CH₂ protons in the ¹H NMR spectrum of $^{Ad,Ad,t-Bu}ArOH$ compared to 2-Y clearly indicates binding of the $^{Ad,Ad,t-Bu}ArO^-$ ligand.

[K(crypt)][Y(OAr^{Ad,Ad,t-Bu})₃], 3-Y. The addition of K₂C₈ to a stirred room-temperature mixture of 2-Y and crypt in THF, under an atmosphere of either Ar or N₂, results in the development of a dark blue color that intensifies as the mixture is allowed to stir, eq 1. The resulting blue material is more



soluble in THF than 2-Y. Removing the dark blue solids from the blue solution by filtration and distilling off the solvent *in vacuo* from the deep-blue solution yields dark blue solids, but no crystalline material suitable for X-ray crystallography. Spectroscopic characterization of the blue solids is described below. If the reaction is run in diethyl ether instead of THF and chilled to −35 °C, dark blue crystals of $[K(crypt)][Y(OAr^{Ad,Ad,t-Bu})_3]$, 3-Y, form, and these were identified by single-crystal X-ray diffraction.

3-Y crystallizes in *P*1̄ with two equivalents of diethyl ether in the lattice, Figure 3. The complex is pseudo-C₃ symmetric like 2-Y. Selected metrical parameters are listed in Table 3 alongside those of 2-Y, Sc(OAr')₃, and $[K(crypt)][Sc(OAr')_3]$.^{17,19} Unlike 2-Y, all of the 1-adamantyl groups in 3-Y have a six-membered ring pointed toward the Y ion.

The Ln–O average distance in 3-Y is 0.06 Å larger than that in 2-Y. In comparison, the average Sc–O distance in $[Sc(OAr')_3]$ –^{17,19} is 0.09 Å larger than that in $Sc(OAr')_3$.¹⁷ In yttrium complexes, the metal-ring centroid distance in $[Cp^*3Y]^{-2}$ is 0.03 Å larger than that in Cp^*3Y , and the Y–N average distance in $[Y(NR_2)_3]^{-22}$ is 0.07 Å larger than that in $Y(NR_2)_3$.²⁹ The Y(II) ion in 3-Y deviates less from the O₃

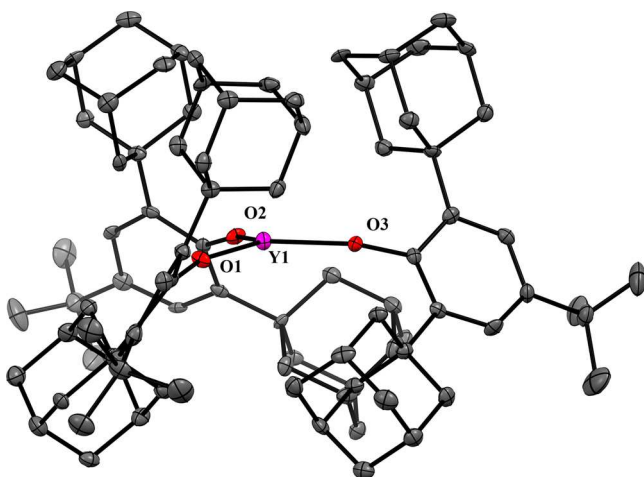


Figure 3. Molecular representation of anionic $[Y(OAr^{Ad,Ad,t-Bu})_3]^-$ in crystals of $3-Y \cdot 2OEt_2$. Hydrogen atoms, the $[K(crypt)]^+$ counter-cation, and lattice diethyl ether molecules are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Atoms and bonds in the foreground are more darkly shaded than those in the background.

Table 3. Selected Metrical Parameters of $[K(crypt)][Y(OAr^{Ad,Ad,t-Bu})_3]$ (3-Y), $Y(OAr^{Ad,Ad,t-Bu})_3$ (2-Y), $[K(crypt)][Sc(OAr')_3]$,¹⁹ and $Sc(OAr')_3$.^{17a}

	3-Y	2-Y	$[Sc(OAr')_3]^-$	$Sc(OAr')_3$
Ln–O	2.106(2)– 2.118(4)	2.038(2)– 2.069(1)	1.960(2)– 1.964(2)	1.853– 1.889
average Ln–O	2.111(6)	2.049(3)	1.962(3)	1.869
OAr _{cent} –C _{ipso} – O angle	171–172	175–177	179–180	178–179
Ln–O–C _{ipso} angle	158.2(3)	150.0(2)	175.6(1)	163.8
	160.2(3)	155.3 (2)	178.4(1)	168.3
	164.8(3)	155.7(2)	179.1(1)	173.2
OAr _{cent} –C _{para} – C _{exo} angle	175–177	177–178	178–179	178
δ	0.125	0.431	0.027	0.133
Θ	55–61	51–60	61–64	41–72
γ	0.018(8)– 0.088(8)	0.001(4)– 0.058(4)	0.000(4)– 0.004(4)	0.000– 0.028
G	90	92	83	90

^aDistances are in Ångströms, angles in degrees. Centroids OAr_{cent} are for the aryloxide C₆ ring. C_{exo} is the carbon atom bonded to the 4 position of the aryloxide, i.e., the 4-Me carbon on OAr' and the tertiary carbon of the 4-*tert*-butyl on ^{Ad,Ad,t-Bu}ArO[−]. δ is the displacement of Ln from the O₃ plane. Θ is the angle between the O₃ plane and the plane of the aryloxide ligand. γ is the displacement of C₆ aryloxide ring carbon atoms from the plane of the aryloxide ring; error is taken from the C–C bond distance error of the C₆ aryloxide ring since the C₆ plane is a calculated average and not a measured quantity. G is the Guzei G parameter and is listed in percent.²⁸

plane than in 2-Y. The value of γ does not change (within error) between 2-Y and 3-Y although the OAr_{cent}–C_{ipso}–O angle does deviate more from linearity in 3-Y.

The optical spectrum of 3-Y recorded in THF at room temperature is shown in Figure 4. There is a strong, broad absorption band centered at $\lambda_{\max} = 629$ nm with an extinction coefficient ϵ of $8100 \text{ M}^{-1}\text{cm}^{-1}$, which is consistent with other Y(II) compounds.^{2,29} In THF, 3-Y keeps its dark blue color for ~48 h at room temperature, contrary to the putative $[Y(OAr')_3]^-$, characterized by EPR spectroscopy, which decomposes in 60 s at room temperature in THF. Since

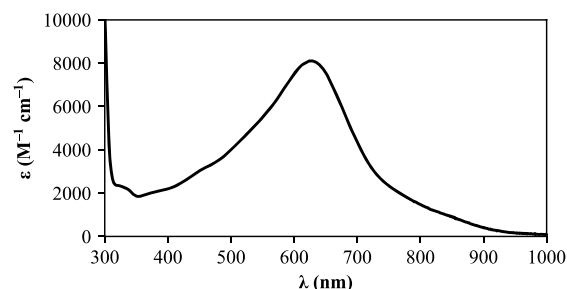


Figure 4. Optical spectrum of 3-Y at room temperature in THF.

$[Y(OAr')_3]^-$ is thermally unstable, UV–visible spectroscopy could only be performed at -78°C .¹⁹ The UV–visible spectrum of 3-Y at -78°C was thus also collected in order to compare it with $[Y(OAr')_3]^-$, Figure 5. At -78°C , 3-Y has

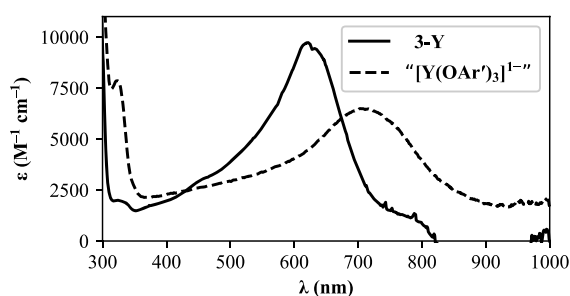


Figure 5. Optical spectra of 3-Y and $[Y(OAr')_3]^-$ obtained from reduction of $Y(OAr')_3$,¹⁹ recorded in THF at -78°C [isopropanol/ $\text{CO}_2(\text{s})$ cold bath] with a film of isopropanol around the cuvette from the cold bath.

its strongest feature at $\lambda_{\max} = 622$ nm, with $\epsilon = 9700 \text{ M}^{-1}\text{cm}^{-1}$, blue-shifted from $[Y(OAr')_3]^-$ with its strongest feature at $\lambda_{\max} = 704$ nm and $\epsilon = 6500 \text{ M}^{-1}\text{cm}^{-1}$.

The X-band EPR spectrum of 3-Y, recorded at 77 K in frozen THF, Figure 6, contains an axial signal with g values $g_{\perp}$

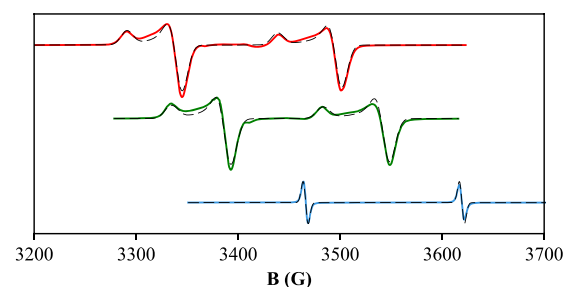


Figure 6. X-band EPR spectra of 3-Y, recorded at 77 K in THF (red, top), $[Y(OAr')_3]^-$ in THF at 77 K (green, middle), and 3-Y in THF at room temperature (blue, bottom) with associated simulated spectra in black dashed lines.

$= 1.97$ and $g_{\parallel} = 2.0$, and hyperfine coupling constants $A_{\perp} = 156.5$ G and $A_{\parallel} = 147.8$ G. At room temperature, the spectrum shows an isotropic doublet signal with $g_{\text{iso}} = 1.98$ and $A_{\text{iso}} = 153.3$ G. The EPR spectra are consistent with a single unpaired electron interacting with a single ^{89}Y nucleus ($I = 1/2$, 100% natural abundance). The axiality seen in the 77 K spectrum is also consistent with the pseudo- C_3 geometry of 3-Y. The EPR spectrum for the putative complex $[Y(OAr')_3]^-$ formed by

reduction of $Y(OAr')_3$ has similar EPR parameters at 77 K: $g_{\perp} = 1.97$, $g_{\parallel} = 2.00$, $A_{\perp} = 155.4$ G, and $A_{\parallel} = 148.7$ G.¹⁹

DISCUSSION

$Y(OAr^{Ad,Ad,t-Bu})_3$, 2-Y, vs $Y(OAr^{Ad,Ad,Me})_3$, 1-Y. The substitution of the 4-Me position with 4-*tert*-butyl in the 2,6- Ad_2 -4-R- $C_6H_2O^-$ ligand had a profound effect on the synthesis and handling of the yttrium tris(aryloxide). It was less difficult to synthesize and purify the *tert*-butyl-substituted complex, $Y(OAr^{Ad,Ad,t-Bu})_3$, 2-Y, compared to the methyl-substituted derivative, $Y(OAr^{Ad,Ad,Me})_3$, 1-Y. This change also made it possible for 2-Y to be characterized by single-crystal X-ray crystallography. Good-quality single crystals of 1-Y were not obtainable.

$Y(OAr^{Ad,Ad,t-Bu})_3$, 2-Y, vs $Y(OAr')_3$. The structure of 2-Y with 1-adamantyl substituents in the 2 and 6 positions bears striking resemblance to that of $Y(OAr')_3$ with *tert*-butyl groups in the 2 and 6 positions. The Y–O bond lengths are the same within error, and the complexes have similar deviations of the Y(III) ion out of the O_3 plane, Table 2. The biggest differences are seen in the degree of steric saturation of the two complexes and the deviation of C_6 ring carbons from the C_6 plane. $Y(OAr')_3$ has a *G* parameter of 81–82%, while 2-Y has a *G* parameter of 92%. Alteration of the 2 and 6 substituents from *tert*-butyl to 1-adamantyl effected minimal change to the primary coordination sphere (*i.e.*, the Y–O distances) but conferred much greater steric saturation.

$[K(crypt)][Y(OAr^{Ad,Ad,t-Bu})_3]$, 3-Y, vs $[Y(OAr')_3]^-$. The reduction of 2-Y in THF with crypt and KC_8 , a well-established protocol for making Ln(II) complexes,^{2,9,11,16,19} produced the dark-colored complex $[K(crypt)][Y(OAr^{Ad,Ad,t-Bu})_3]$, 3-Y, which was identified by single crystal X-ray diffraction. The EPR spectrum of 3-Y is almost indistinguishable from that of the dark product of reduction of $Y(OAr')_3$, which is likely to be $[Y(OAr')_3]^-$. The axial doublet pattern agrees with the assignment of 3-Y as a complex possessing a $4d^1$ electronic ground state configuration, with the single unpaired electron interacting with a single ^{89}Y nucleus in a trigonal axial ligand environment. This is also consistent with the theoretical prediction of the geometry and identity of $[Y(OAr')_3]^-$, which was not crystallographically characterized.¹⁹ The optical spectra of 3-Y and $[Y(OAr')_3]^-$, recorded at -78 °C, also have similar features, which suggests that the ligand change from $Ar'O^-$ to $^{Ad,Ad,t-Bu}ArO^-$ is a minor perturbation to the electronic structure of these tris(aryloxide) Y(II) compounds.

The main difference between $[K(crypt)][Y(OAr^{Ad,Ad,t-Bu})_3]$, 3-Y, and $[Y(OAr')_3]^-$ is the thermal stability. The room temperature stability of 3-Y makes it the most stable Y(II) complex known to date, whereas $[Y(OAr')_3]^-$ has not been isolable. This is likely due to steric saturation since the 90% *G* parameter of 3-Y is much greater than the estimated 77% of $[Y(OAr')_3]^-$. Since the electronic structure and donor characteristics have not changed appreciably, this shows the significant influence of optimizing steric saturation for synthesizing thermally stable Y(II) compounds.

Steric Saturation in Other Ligand Sets. It should be noted that simple maximization of the *G* parameter is not on its own a sufficient strategy for isolating Ln(II) complexes. For example, it was shown that, for the $[Cp'_3Ln]^-$ complexes, the most kinetically stable complex, $[K(crypt)][Cp'_3Pr]$, was neither the most sterically saturated nor least sterically saturated complex in the series.¹⁹ Hence, there appears to be

an optimum value, and deviation from that value, either more or less sterically saturated, leads to decreased room-temperature stability. Furthermore, the Y(II) complex $[K(crypt)][Cp''_2Y(C_5H_5)]$ has a *G* parameter of 90–91% but is less thermally stable than $[K(crypt)][Cp'_3Y]$ with its *G* parameter of 86%.³⁰ It is likely that significantly different ligand sets may have different optimum *G* parameters for stabilizing Ln(II) complexes. Furthermore, the *G* parameter does not take cation effects into account. The lower thermal stabilities of $[Cp'_3Ln]^-$ ($Ln = Y, Tb, Ho, Er$) complexes when the cation is $[K(18-crown-6)]^+$ compared to $[K(crypt)]^+$ constitute one example.⁴ Likewise, the sterically undersaturated Ln(II) complexes of the small $C_5H_4Me^-$ ligand (Cp^{Me-}) can be isolated with an inverse sandwich cation in the $[(18-crown-6)_2K_2(\mu-Cp^{Me})][Cp^{Me}_3Ln]$ complexes.¹⁰ While steric saturation is clearly not the sole determiner of thermal stability of Ln(II) complexes, it is evidently important and may allow for the isolation of Ln(II) in a broader range of sufficiently sterically saturating ligand sets.

CONCLUSION

By changing the aryloxide ligand from 2,6-*t*-Bu₂-4-Me- $C_6H_2O^-$ ($Ar'O^-$) to 2,6- Ad_2 -4-*t*-Bu- $C_6H_2O^-$ ($^{Ad,Ad,t-Bu}ArO^-$), it has been possible to synthesize, isolate, and fully characterize a crystalline Y(II) aryloxide complex, $[K(crypt)][Y(OAr^{Ad,Ad,t-Bu})_3]$, 3-Y, that is stable for 48 h at room temperature. In contrast, reduction of $Y(OAr')_3$ forms a putative $[Y(OAr')_3]^-$ that decomposes within a minute. The difference in this kinetic stability can be attributed to the increased steric saturation in 3-Y, which has a *G* parameter of 90% compared to an estimated 77% for $[Y(OAr')_3]^-$. Although steric saturation may not be so important with all ligand systems in Ln(II) complexes, it certainly appears to be critical in this aryloxide case.

EXPERIMENTAL SECTION

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over NaK alloy or Na/benzophenone, degassed by three freeze–pump–thaw cycles, and vacuum transferred before use. 1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE600 spectrometer (1H operating at 600 MHz, $^{13}C\{^1H\}$ at 151 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. Elemental analyses were conducted on a PerkinElmer 2400 Series II CHNS elemental analyzer. UV–visible spectra were collected in THF at -78 °C or room temperature in a 0.1 cm cell fitted with a Teflon stopcock using an Agilent Cary 60 UV–visible spectrophotometer. EPR spectra were collected using the X-band frequency (9.3–9.8 GHz) on a Bruker EMX spectrometer equipped with an ER4119HS-W1 microwave bridge, and the magnetic field was calibrated with DPPH ($g = 2.0036$). Infrared (IR) transmittance measurements were taken as compressed solids on an Agilent Cary 630 FTIR spectrophotometer with a diamond ATR attachment. 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, 2.2.2-cryptand (crypt, VWR) was dried under reduced pressure (10^{-3} Torr) before use. $HOAr^{Ad,Ad,Me}$, $HOAr^{Ad,Ad,t-Bu}$, $KOAr^{Ad,Ad,Me}$, 1.5(DME), $Y(NR_2)_3$ ($R = SiMe_3$), and KC_8 were synthesized using published preparations.^{25,27,31,32} EPR spectra were simulated using EasySpin.³³

$HOAr^{Ad,Ad,t-Bu}$. IR (Supporting Information, Figure S1): 3628m, 2961m sh, 2946m sh, 2900s br, 2846s, 2674w, 2654w, 1756w, 1743w, 1597w br, 1476m, 1463m sh, 1454s sh, 1443s, 1420m, 1390m,

1359m, 1342m, 1325m, 1312m, 1277m, 1262w, 1241m, 1206m, 1185m, 1170m, 1131m, 1105m, 1096m, 1078m, 1047w, 1031w, 1021w, 984m, 969m, 939m, 919w, 902w, 887w, 873m, 841w br, 820m, 803m, 779w, 786m, 740w br, 710m, 658w cm^{-1} .

$\text{Y}(\text{OAr}^{\text{Ad,Ad,t-Bu}})_3$, **2-Y**. $\text{Y}(\text{NR}_2)_3$ (1.50 g, 2.64 mmol, 1.2 equiv) and $\text{HOAr}^{\text{Ad,Ad,t-Bu}}$ (2.75 g, 6.58 mmol, 3 equiv) were combined in toluene (20 mL) in a 100 mL flask fitted with a Teflon stopcock. The pale yellow mixture was heated to 100 °C in an oil bath with stirring, and all the material was dissolved to form a golden solution. After 2 days of stirring and heating, the solvent was removed *in vacuo* to form brown-yellow solids with extensive amounts of residual toluene. The solids were suspended in 20 mL of hexane, and solvent was removed *in vacuo* once more to remove entrained toluene. The resulting solids were washed with pentane (3×20 mL) and dried *in vacuo* to give crude white solids of $\text{Y}(\text{OAr}^{\text{Ad,Ad,t-Bu}})_3$, **2-Y** (1.15 g, 39% crude yield), identified by ^1H NMR spectroscopy. Cooling a solution made in boiling *n*-hexane (80 mL) overnight at room temperature followed by washing with pentane (3×2 mL) and removal of solvent *in vacuo* yielded colorless microcrystalline solids of **2-Y** (420 mg, 14% crystalline yield). X-ray quality crystals were present after the recrystallization from boiling hexane (Supporting Information, Table S1). ^1H NMR (C_6D_6 , Supporting Information, Figure S2): δ 7.34 (s, 6H, *m*-H), 2.49 (d, $J = 11.2$ Hz, 18H, Ad-CH₂, proximal to C₆ ring), 2.35 (d, $J = 11.3$ Hz, 18H, Ad-CH₂, proximal to C₆ ring), 2.05 (s, 18H, Ad-CH), 1.75 (d, $J = 11.9$ Hz, 20H, Ad-CH₂, distal to C₆ ring, overlapping with corresponding resonance in $\text{HOAr}^{\text{Ad,Ad,t-Bu}}$), 1.66 (d, $J = 12.0$ Hz, 18H, Ad-CH₂, distal to C₆ ring), 1.43 (s, 28H, *t*-Bu, overlapping with corresponding resonance in $\text{HOAr}^{\text{Ad,Ad,t-Bu}}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , Supporting Information, Figure S3): δ 158.2 (two lines with a 4.0 Hz separation, *i*-C), 139.3 (*o*-C), 135.8 (*p*-C), 122.4 (*m*-C), 44.5 (Ad-CH₂, proximal to C₆ ring), 38.9 (quaternary C, from Ad or *t*-Bu), 37.3 (Ad-CH₂, distal to C₆ ring), 34.7 (quaternary C, from Ad or *t*-Bu), 32.1 (CMe_3), 29.8 (Ad-CH). IR (Supporting Information, Figure S4): 3086w br, 2948m sh, 1896s br, 2846s, 2678w, 2654w, 1598w, 1448m sh, 1429s, 1390m, 1359m 1342m, 1314w, 1278s, 1260s, 1243s, 1230s, 1200m, 1167w 1139m, 1100m, 1044w, 1034w, 968s, 923m, 872m, 842s, 818w, 809, 773m, 766m, 734s, 693w, 662m cm^{-1} . Anal. Calcd for $\text{C}_{90}\text{H}_{123}\text{O}_3\text{Y}$: C, 80.56; H, 9.24. Found: C, 76.27; H, 9.15. The low %C value is seen in the elemental analysis of other Ln(III) aryloxides,¹⁹ and incomplete combustion and/or difficult elemental analysis is a known problem in *f*-element chemistry generally.^{9,34–39} Results formulate as $\text{C}_{90}\text{H}_{129}$ which is close to the calculated. The results are not consistent with contamination with $\text{HOAr}^{\text{Ad,Ad,t-Bu}}$.

$[\text{K}(\text{crypt})][\text{Y}(\text{OAr}^{\text{Ad,Ad,t-Bu}})_3]$, **3-Y**. **2-Y** (150 mg, 0.11 mmol) was suspended in a THF (5 mL) solution of crypt (45 mg, 0.12 mmol). With stirring, excess KC_8 (40 mg, 0.30 mmol, 2.6 equiv) was added in two portions, and a deep blue color developed. After stirring for 10 min, the dark blue solution was filtered through Kimwipe-packed glass pipettes to remove black solids (presumably graphite and excess KC_8) to give a dark blue solution. The solids were washed with THF (10 mL), and the resulting filtrate was combined with the initial filtrate. Solvent was removed *in vacuo* to give oily dark blue solids, which were triturated with hexane (3×2 mL) and pentane (2×2 mL) to yield dark blue solids, which were dried *in vacuo* to give a free-flowing dark blue powder, $[\text{K}(\text{crypt})][\text{Y}(\text{OAr}^{\text{Ad,Ad,t-Bu}})_3]$, **3-Y** (140 mg, 72%). EPR (Figure 6; THF, 77 K): $g_{\perp} = 1.97$, $g_{\parallel} = 2.00$, $A_{\perp} = 156.5$ G, $A_{\parallel} = 147.8$ G. EPR (THF, room temperature): $g = 1.98$ and $A = 153.3$ G. UV-vis λ (ϵ ; room temperature, THF, Figure 4): 629 nm (8100 $\text{M}^{-1}\text{cm}^{-1}$). UV-vis λ (−78 °C, THF, Figure 5): 622 nm (9700 $\text{M}^{-1}\text{cm}^{-1}$). IR (Supporting Information, Figure S5): 3082w br, 2945m sh, 2888s br, 2838s, 2671w, 2648w, 1734w, 1559w, 1476w, 1444m sh, 1423s, 1388w, 1353m, 1340w, 1310w, 1276s, 1269s sh, 1239s, 1210m br, 1174w, 1131m, 1100s, 1075m, 1059m sh, 1046w, 1034w, 978m, 948m, 931m, 904w, 867m, 863m, 836s, 816m, 809m, 772m, 751w, 729m, 695w, 661w cm^{-1} . Anal. Calcd for $\text{C}_{108}\text{H}_{159}\text{KN}_2\text{O}_3\text{Y}$: C, 80.56; H, 9.24; N, 1.59. Found: C, 70.85; H, 9.15; N, 1.43. See note on the elemental analysis of **2-Y**. Results formulate as $\text{C}_{108}\text{H}_{166}\text{N}_2$ which is close to the calculated. X-ray quality crystals could be grown by using diethyl ether instead of THF (using

the same amounts of all reagents) and cooling to −35 °C overnight (Supporting Information, Table S2).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03587>.

Plots of NMR and IR spectra (PDF)

Accession Codes

CCDC 1970704–1970705 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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