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Facile Synthesis of Bismuth(III) and Antimony(III) Complexes Supported by Silylated Calix[5]arenes.

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A series of bismuth(III) and antimony(III) complexes supported by silicon-containing calix[5]arene ligands were synthesized and fully characterized by NMR, X-ray, IR, mp, UV/vis, and elemental analysis. Reaction of the *para-tert*-butylcalix[5]arene [**^{t}BuC5(H)$_5$**] disodium salt, Na$_2$·**^{t}BuC5(H)$_3$**, with 1 equiv of R$_2$SiCl$_2$ (R = Me, ^{i}Pr, Ph, CH=CH$_2$) or treatment of the **^{t}BuC5(H)$_5$** lower rim monobenzyl ether [**^{t}BuC5(Bn)(H)$_4$**] in a 1:1 ratio with Me$_2$Si(NMe$_2$)$_2$ yields the **^{t}BuC5(SiRR′)(H)$_3$** (**1**−**5**) and **^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$** (**6**) ligands, respectively. The ^{1}H NMR spectra of the **^{t}BuC5(SiRR′)(H)$_3$** (**1**−**5**) ligands show three pairs of doublets and three singlets for the ^{t}Bu peaks, consistent with a C_s symmetry. In the case of the **^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$** (**6**) ligand, the presence of the monobenzyl group changes the ^{1}H NMR patterns to indicate a C_1 symmetry. Treatment of **^{t}BuC5(SiRR′)(H)$_3$** (**1**−**5**) or **^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$** (**6**) with 1 equiv of M(O^{t}Bu)$_3$ (M = Bi, Sb) or Sb(NMe$_2$)$_2$ readily yields metalated products of the type [M{**^{t}BuC5(SiRR′)**}] (**7**−**16**) and [MX{**^{t}BuC5(Bn)(SiMe$_2$)**}] (X = O^{t}Bu, (NMe$_2$)$_2$) (**17**−**19**), respectively. All monometallic complexes [M{**^{t}BuC5(SiRR′)**}] (**7**−**19**) display excellent solubility in organic solvents including pentane and hexane. The ^{1}H NMR patterns for complexes **7**−**16** are consistent with a 1,2- or 1,3-alternate conformation while complexes [MX{**^{t}BuC5(Bn)(SiMe$_2$)**}] (**17**−**19**) display patterns for a C_1 symmetry. All crystals show monomeric structures. Ligand **^{t}BuC5(SiPh$_2$)(H)$_3$** (**3**) displays a distorted cone conformation while the presence of the monobenzyl ether in **^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$** (**6**) forces a partial cone conformation. Complexes **7**−**19** all display a distorted 1,2-alternate conformation with the metal centers displaying coordination numbers of three, four or five. No Si···M interactions were observed.

Introduction

The lower and/or upper rim modification of calix[*n*]arene[1] ligands have been extensively utilized as methodologies for the complexation of specific metal centers, guest molecules, or ions.[2−4] Usually, the addition of pendant arms (aldehydes, ketones, amines, esters, etc.)[1,4−6] enhances the calixarene affinity toward certain substrates by changing the ring conformation or by decreasing the number of available hydroxide groups. Functionalized calixarenes have a wide range of applications including sensors, catalysts, drug design, biological and separation processes, enzymatic models, and others.[7−12]

In coordination chemistry, functionalized calix[*n*]arenes have been successfully employed in the synthesis of transition, main group and f-block metal complexes.[3,13,14] For instance, the use of 1,2- or 1,3-lower rim substituted calix[4]arenes allowed the preparation of monometallic main group complexes (M = Ge, Sn, Al, Mg, Bi) that were inaccessible by other methods.[15−18] Ladipo et al. have synthesized a series of titanium(IV) complexes supported by silicon-containing calix[4]arenes and discovered that they were able to catalyze alkyne cyclotrimerization or induce

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Ti−C bond formation.[19−22] Lattman et al. have reported that the use of phosphorus monosubstituted calix[5]arene ligands allowed the easy insertion of tungsten, titanium, or zirconium centers in the lower rim, and that the resulting complexes featured interesting metal−phosphorus interactions.[23,24] For the calix[*n*]arene ligands (n = 6, 8) where the large cavity usually favors the production of multinuclear complexes, the use of upper and/or lower rim substituted precursors has permitted the preparation of monometallic complexes impossible to prepare by other procedures.[13]

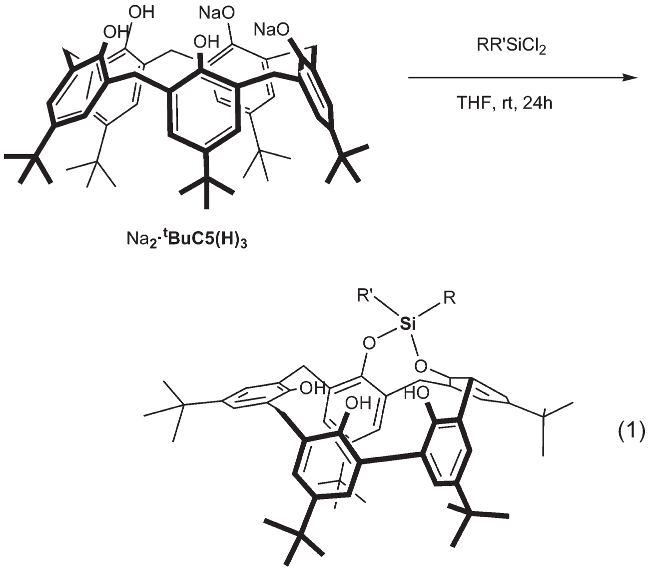
One of our research interests lies in the synthesis of bismuth(III) or antimony(III) calixarenes as precursors for heterobimetallic models of the Bi/Mo SOHIO catalyst. We have recently reported that the reaction of calix[5]arene [**RC5(H)$_5$**] trianions $M'_3\cdot$**RC5(H)$_2$** (M' = Li, Na, K)[25] with MCl_3 (M = Bi, Sb) or the reaction of parent **RC5(H)$_5$** (R = H, ^{t}Bu, Bn) with M(O^{t}Bu)$_3$[26] produced mono or bimetallic complexes containing unreacted OH groups. However, the solubility of some of these complexes is limited, decreasing their potential as building blocks.

Lattman has reported that the addition of silicon moieties (-SiR$_2$) to the lower rim of the calix[*n*]arenes (n = 4, 5) is relatively easy and that the silylated ligands feature high solubility and free OH groups that facilitate the preparation of monometallic complexes.[27−29] Also, the silyl group that aids the solubility additionally provides another site of reactivity (it could be removed with the use of fluoride ions)[30] that gives these complexes the potential for transformation into other multifunctional coordination complexes.[31] We decided to take advantage of these features by blocking the 1,2 positions of **^{t}BuC5(H)$_5$** ligands with -SiR$_2$ moieties, targeting the design of trivalent templates for the complexation of bismuth(III) and antimony(III) centers.

Herein we report the synthesis of monosilylated calix[5]arene ligands obtained by the reaction of the Na$_2\cdot$**^{t}BuC5(H)$_3$**[25] salt with 1 equiv of R$_2$SiCl$_2$ or by treatment of the monobenzyl substituted **^{t}BuC5(H)$_5$** ligand [**^{t}BuC5(Bn)(H)$_4$**] with Me$_2$Si(NMe$_2$)$_2$. The reactivity of the **^{t}BuC5(SiRR′)(H)$_3$** (**1−5**) and **^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$** (**6**) ligands with M(O^{t}Bu)$_3$ (M = Bi, Sb) or Sb(NMe$_2$)$_3$ was tested and successfully employed for the synthesis of a series of highly soluble monometallic bismuth(III) and antimony(III) complexes. We will discuss the solution and solid state features encountered upon change of substitution level in the calixarene ligands and the strength of the base used in the complex synthesis.

1. Results and Discussion

1.1. Synthesis of Silylated Calix[5]arenes ^{t}BuC5(SiRR′$_2$)(H)$_3$. To access monosilylated ligands of the type **^{t}BuC5(SiRR′$_2$)(H)$_3$**, a salt metathesis approach was employed. From the dianionic **^{t}BuC5(H)$_5$** salt precursors M$_2\cdot$**^{t}BuC5(H)$_3$** (M = Na, K, Rb, and Cs) that we have previously prepared,[25] only Na$_2\cdot$**^{t}BuC5(H)$_3$** was used, as it produces the best yields and clean reactions. The reaction of Na$_2\cdot$**^{t}BuC5(H)$_3$**[25] with 1 equiv of RR′SiCl$_2$ (R, R′ = Me, ^{i}Pr, Ph, CH=CH$_2$) in THF, produces the monosilylated **^{t}BuC5(SiRR′$_2$)(H)$_3$** ligands **1−5** as depicted in eq 1. In general, the reaction gives a mixture of the **^{t}BuC5(SiRR′$_2$)(H)$_3$** product and parent calixarene. Purification of the products is performed by slow evaporation of a concentrated pentane (or hexane) solution of the crude mixture for ligands **2−4** or by successive pentane/hexane washing cycles to remove parent calixarene in the case of **^{t}BuC5(SiMe$_2$)(H)$_3$ (1)** and **^{t}BuC5(SiMeVinyl)(H)$_3$ (5)**.



(1)

R, R' = Me	**1**
R = Me, R' = Ph	**2**
R, R' = Ph	**3**
R, R' = ^{i}Pr	**4**
R = Me, R' = C$_2$H$_3$	**5**

Lattman and co-workers have previously reported the synthesis of ligands **1** and **2** by the reaction of **^{t}BuC5(H)$_5$** and Me$_2$Si(NMe$_2$)$_2$.[29] When a 1:1 ratio was used, a mixture of mono- and disubstituted products was observed. The disubstituted products could only be avoided when the reaction ratio was changed to 1:0.35 [**^{t}BuC5(H)$_5$**:R$_2$Si(NMe$_2$)$_2$]. However, under these reaction conditions, a large amount of unreacted **^{t}BuC5(H)$_5$** had to be removed and the yields (based on calixarene) were too low. In addition, the insertion of bulkier silane groups such as -SiPh$_2$ was unsuccessful when applying this methodology.

On the other hand, by utilizing our **^{t}BuC5(H)$_3\cdot$Na$_2$** precursor, we were able to isolate the ligands **1**, **2**, and **3** in good yields (74−85%, based on calixarene) after an easy

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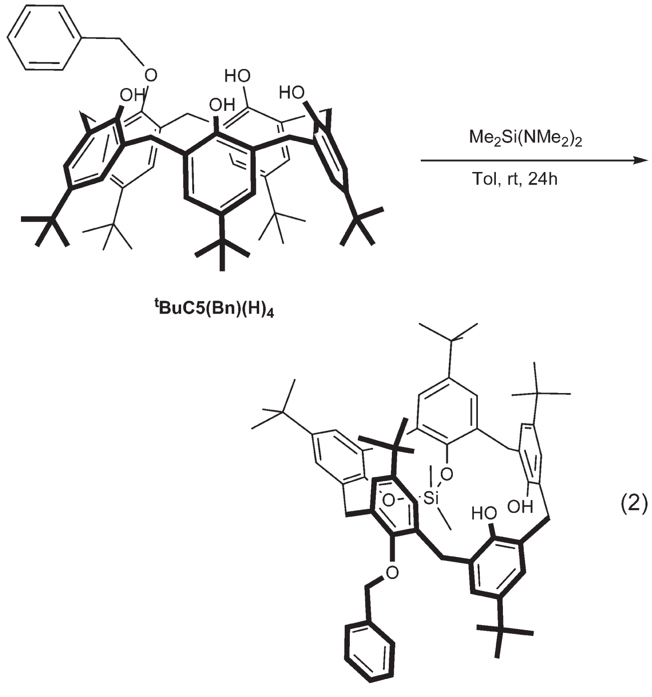
purification. The success of this reaction could be due to the use of a true dianionic precursor that favors the insertion of a single -SiR_2 moiety in the lower rim of the calixarene.

With these successful results, we decided to utilize the calixanion methodology for the preparation of silylated versions of the **^{t}BuC5(Bn)(H)$_4$** ligand. When the in situ prepared dianionic Na_2·**^{t}BuC5Bn(H)$_2$** salt (using 2 equiv of NaO^{t}Bu) was reacted with 1 equiv of $RR'SiCl_2$, the reaction mixture showed only traces of the desired product in addition to parent calixarene. The large amount of unreacted parent calixarene suggested that the deprotonation of the parent ligand with NaO^{t}Bu was not as efficient as in the case of **^{t}BuC5(H)$_5$**.[25]

An alternate procedure for the preparation of silylated calix[4]arenes consists of the deprotonation of the calixarene ligand with triethylamine (Et_3N) followed by addition of $SiCl_4$ or $RSiCl_3$.[27,32,33] We employed this pathway by treating the **^{t}BuC5(Bn)(H)$_4$** ligand with 2 equiv of Et_3N followed by the addition of the appropriate silane dichloride. The ^{1}H NMR spectra in this case showed a smaller amount of unreacted **^{t}BuC5Bn(H)$_4$**, but a complex mixture of products was observed. It was necessary to treat **^{t}BuC5(Bn)(H)$_4$** with 1 equiv of $Me_2Si(NMe_2)_2$ in toluene to afford the desired **^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$** ligand (**6**). The reaction mixture showed quantitative conversion to the silylated ligand **6**, and after recrystallization from hexane an isolated yield of 78% was attained (eq 2).



^{t}BuC5(Bn)(H)$_4$

^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$ 6

(2)

We attempted the preparation of analogous silylated complexes of **^{t}BuC5Bn(H)$_4$** containing bulkier -$SiPh_2$ or -Si^{i}Pr$_2$ groups by the addition of $R_2Si(NMe)_2$ to the parent calixarene, but in all cases we observed a mixture of mono and disubstituted ligands that were hard to separate.

Silylated ligands **1**–**5** are all white solids, soluble in most organic solvents, and stable up to 3 weeks in air.

1.2. Synthesis of Bi(III) and Sb(III) Complexes Supported by ^{t}BuC5(SiRR′)(H)$_3$ Ligands (1–5). The addition of a silicon group in the 1,2 positions of the calix[5]arene ligands left three neighboring hydroxyl groups available for reactivity. We expected that the disposition of the remaining OH groups could facilitate the lower rim coordination of the bismuth(III) and antimony(III) centers. However, we observed that the choice of the right metal reagent is critical for obtaining the desired products.

Relatively few examples of the insertion of main group or transition metals to silylated calixarenes can be found in literature. Ladipo and co-workers reported that complexation of Ti(IV) centers to several **RC4(SiR$_2$)(H)$_2$** ligands was achieved after the stoichiometric addition of $TiCl_4$ at low temperature.[19] Following this methodology, we treated the **^{t}BuC5(SiRR′)(H)$_3$** ligands with 1 equiv of MCl_3 (M = Bi, Sb) in tetrahydrofuran (THF) at −78 °C. The ^{1}H NMR spectra in all cases showed only a trace of new products in mixture with parent calixarene. Our attempts to improve the yield of the products by increasing the temperature or the number of MCl_3 equivalents failed in all cases. We believe that the poor performance observed in these reactions could be related to the release of HCl (protonating agent) that may be responsible for the regeneration of parent calixarene.

The most common pathway for the preparation of main group calix[*n*]arenes (*n* = 4, 6, 8) involves the reaction of the parent calix[*n*]arene ligands with metal amides, organometals, or metal alkoxides in exchange reactions.[15,34–39] Lattman et al. have shown that monophosphorus substituted ligands of the type **^{t}BuC5(PNMe$_2$)(H)$_3$** readily react with transition metal amides (M = Ti, Zr, W) to produce metalated complexes of the type [M{**^{t}BuC5(PNMe$_2$)**}].[23,24] We have reported that M(O^{t}Bu)$_3$ (M = Bi, Sb) or $Sb(NMe_2)_3$ are excellent reagents for the preparation of metallocalix[*n*]arenes (*n* = 4–8).[18,26,40]

We decided to employ the latter routes by treating the **^{t}BuC5(SiRR′)(H)$_3$** ligands with 1 equiv of M(O^{t}Bu)$_3$ (M = Bi, Sb) or $Sb(NMe_2)_2$ in THF or toluene, as depicted in eq 3. Under these reaction conditions, the formation of the metalated calixarenes **7**–**16** was readily achieved (eq 3). The products were obtained in moderate to good yields (52–91%) as yellow (Bi) and white (Sb) solids after purification by recrystallization from THF or DME. As desired, the complexes **7**–**16** displayed excellent solubility in most organic solvents including alkanes (pentane and hexane), and no decomposition was observed after 12 h in

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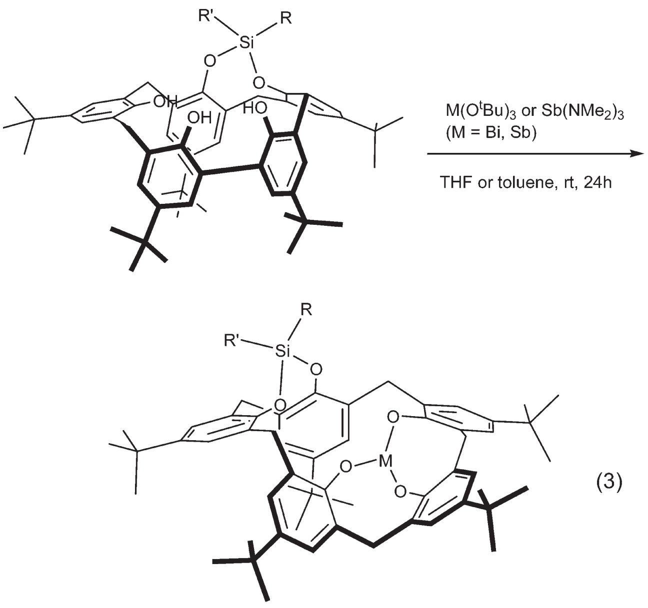
air. Most of the complexes are stable in solution, but complexes **13**, **14**, and **16** start to decompose to parent silylated ligand after 2 h in benzene.



(3)

R, R' = Me	M = Bi **7**		R, R' = ^{i}Pr	M = Bi **13**
R, R' = Me	M = Sb **8**		R, R' = ^{i}Pr	M = Sb **14**
R = Me, R' = Ph	M = Bi **9**		R = Me, R' = C_2H_3	M = Bi **15**
R = Me, R' = Ph	M = Sb **10**		R = Me, R' = C_2H_3	M = Sb **16**
R, R' = Ph	M = Bi **11**			
R, R' = Ph	M = Sb **12**			

1.3. Synthesis of Bi(III) and Sb(III) Complexes Supported by the ^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$ Ligand (6). The silylated calix[5]arene **^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$** (**6**) resembles the **RC4(SiR$_2$)(H)$_2$** ligands by containing two unreacted OH groups, but the larger cavity size in **6** allows the calixarene ring to adopt a partial cone conformation rather than 1,2-alternate. In the partial cone conformation, the two unreacted OH groups in **6** point in different directions so the insertion of a metal could be difficult.

Experimentally, we observed that the treatment of **^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$** with 1 equiv of $M(O^tBu)_3$ (M = Bi, Sb) or $Sb(NMe_2)_3$ in toluene readily yielded the expected complexes **17**−**19**, as shown in eq 4.

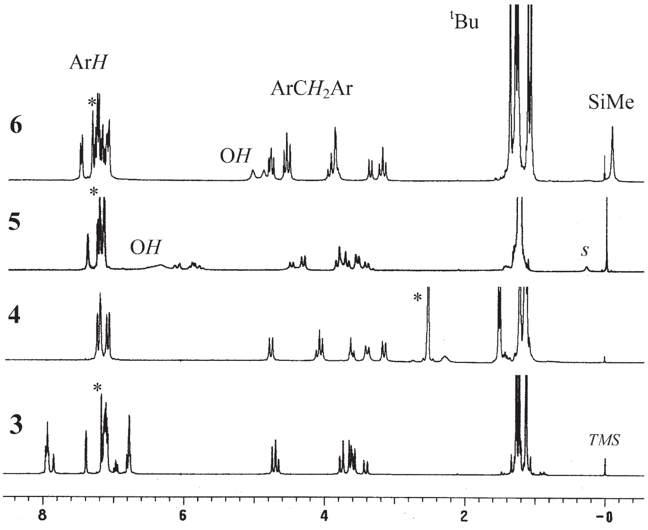
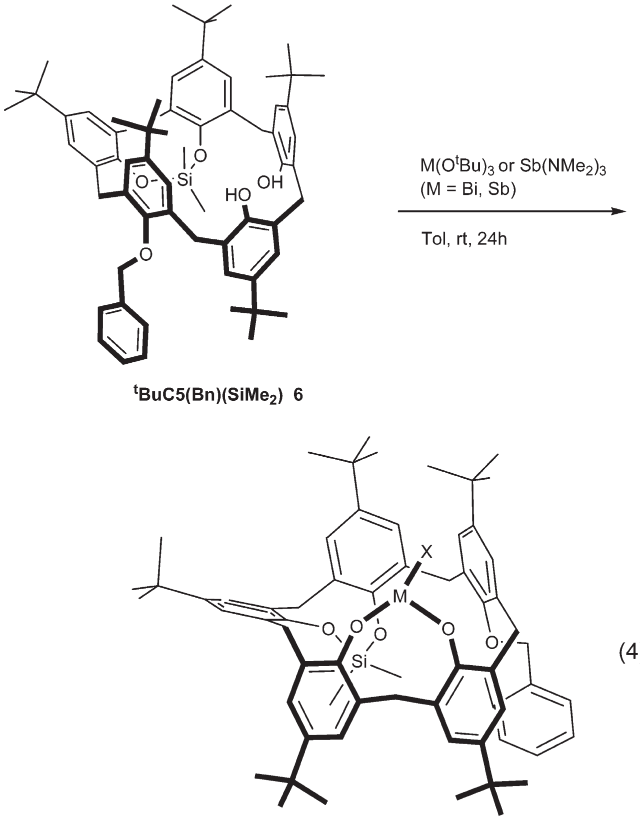


Figure 1. ^{1}H NMR spectra for ligands **3**, **5**, and **6** in *C_6D_6 and **4** in *DMSO-d_6. Second SiMe group in **6** is not shown. *s* = residual solvent.



^{t}BuC5(Bn)(SiMe$_2$) 6

(4)

M = Bi, X = O^{t}Bu **17**
M = Sb, X = O^{t}Bu **18**
M = Sb, X = NMe$_2$ **19**

The crude reaction mixture showed quantitative conversion to the products at room temperature. Recrystallization at −35 °C from concentrated pentane/THF (or DME) gave the complexes in 83−87% yields. Compounds **17**−**19** are soluble in most organic solvents and moderately air and moisture sensitive (decomposition to silylated ligands is observed after 2 days in air).

2. NMR Spectroscopy

The excellent solubility of complexes **1**−**19** allowed their solution analysis by ^{1}H NMR spectroscopy. The monosilylated ligands **1**−**5** all give very similar patterns (Figure 1). Three pairs of doublets for the methylene protons (geminal coupling due to nonequivalent methylene hydrogens), in a 1:2:2 ratio, range from 3.13 to 4.73 ppm.[41] Ligands **1**−**5** display three *tert*-butyl resonances (with 2:2:1 intensities) located between 1.13 to 1.31 ppm. Overall the ^{1}H NMR spectra for ligands **1**−**5** are similar to those observed in phosphorus and silicon calix[5]arene complexes reported in literature, and consistent with a C_s symmetry.[29,42]

The groups attached to the silicon atoms are chemically nonequivalent (*endo* and *exo* orientation), giving two different signals in the ^{1}H NMR spectra. The methyl groups in

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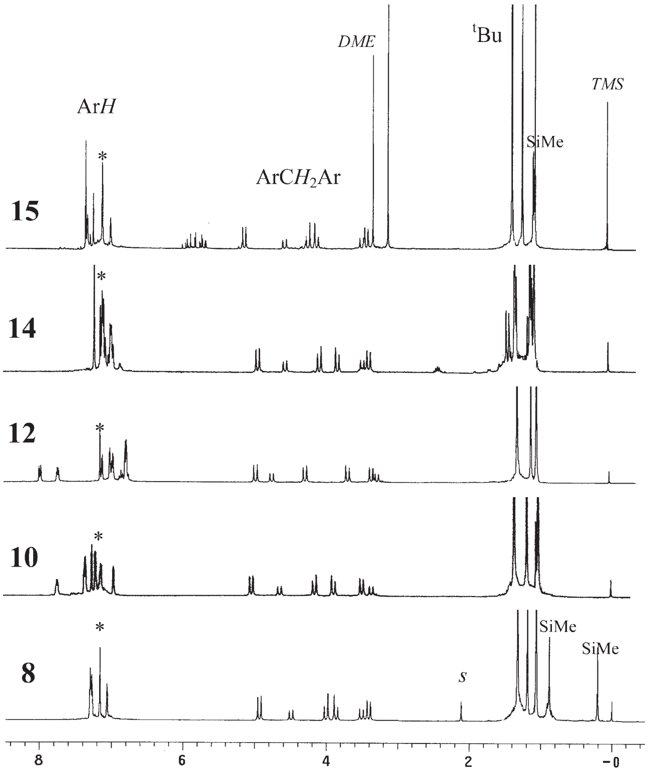

Figure 2. Representative ^{1}H NMR spectra of the M^{III} (M^{III} = Bi, Sb) complexes supported by **^{t}BuC5(SiRR')(H)$_3$** ligands in *C$_6$D$_6$. *s* = residual solvent, DME = dimethoxyethane.

ligands **1**, **2**, and **5** are located in high fields ranging from −2.03 to −0.11 ppm. The OH groups can only be observed for ligands **1** and **5** as the OH signals for ligands **2**−**4** are too broad to be observed at room temperature.

An interesting conformational behavior was observed for ligand **^{t}BuC5(Si^{i}Pr$_2$)(H)$_3$** (**4**). When the ^{1}H NMR spectrum of **4** is taken in C$_6$D$_6$, the pattern indicates the presence of two different conformations in an approximate 1:3 ratio. Each conformer displays a set of three ^{t}Bu peaks and three pairs of doublets for the ArCH$_2$Ar groups. On the other hand, if the ^{1}H NMR of ligand **4** is taken in DMSO-d$_6$, the spectrum shows only a single conformer (Figure 1) probably because of the binding of the dimethyl sulfoxide (DMSO) inside the cavity of the calixarene. This ^{1}H NMR behavior could also be related to the influence of the solvent polarity on the rate of conformational inversion in calixarene complexes.[25,43]

The presence of the benzyl group in the lower rim of ligand **6** changes the patterns of its ^{1}H NMR spectrum with respect to ligands **1**−**5**. Five single peaks for the ^{t}Bu groups, eight doublets in the methylene area, and two broad signals for the unreacted OH groups are observed (Figure 1). The complicated ^{1}H NMR spectrum in ligand **6** resembles the patterns observed in some bimetallic calix[5]arene antimony complexes reported recently by our group.[26] The methylene protons of the benzyl group appear as a singlet at 3.87 ppm and the methyl groups attached to the silicon atoms are nonequivalent, appearing at −2.45 and −0.11 ppm.

The metalated complexes **7**−**16** all display similar ^{1}H NMR patterns to those of their parent ligands (Figure 2).

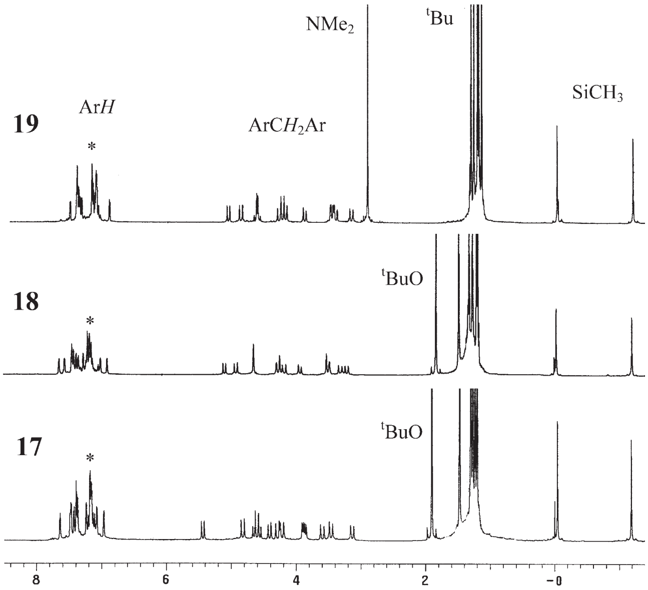

Figure 3. ^{1}H NMR spectra of complexes **17**−**19** in *C$_6$D$_6$.

The presence of the metals resolves the *tert*-butyl peaks as three sharp singlets ranging from 0.97 to 1.38 ppm, and the six methylene doublets range from 3.32 to 5.30 ppm. The SiMe groups in complexes **7** and **8** are nonequivalent, resonating upfield in a range from 0.13 to 0.92 ppm.

Complexes **17**−**19** show similar ^{1}H NMR patterns (Figure 3) to those for the **^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$** ligand **6** (Figure 1). However, the metalation in complexes **17** and **19** resolves the calixarene methylene groups into five pairs of doublets. Likewise, the methylene hydrogens from the benzyl group are no longer equivalent, appearing as a pair of doublets. The *endo* -SiMe groups in **17**−**19** are strongly shielded with chemical shifts of −1.19, −1.20, and −1.16 ppm, respectively. A *tert*-butyl group belonging to the remaining M-O^{t}Bu bond is observed for complexes **17** and **18** at 1.90 and 1.82 ppm, respectively, and in the case of complex **19** a singlet at 2.96 ppm belongs to the Sb-NMe$_2$ group. The presence of reactive -O^{t}Bu and -NMe$_2$ groups in complexes **17**−**19** may be useful for the preparation of more complex structures.

3. Crystal and Molecular Structures

3.1. Monosilylated Ligands. Crystal structures of the ligands **^{t}BuC5(SiPh$_2$)(H)$_3$** (**3**) and **^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$** (**6**) are illustrated in Figures 4 and 5, respectively, and selected bond distances and angles are shown in Table 1. Ligands **3** and **6** are monomeric units with a silicon center located in the lower rim of the cavity. The silicon center displays a tetrahedral geometry with O−Si−O, C−Si−O, and C−Si−C angles ranging from 104.8 to 117.8°, close to the expected 109°.

The silicon centers each form an eight membered ring by bonding to two aryloxide groups from the calixarene ligand. The conformation of the eight membered rings could be described as twisted boat (TB) in the case of ligand **3**, while for ligand **6** the conformation is close to boat chair (BC).[44] These conformations are similar to those observed in silicon, phosphorus, and antimony

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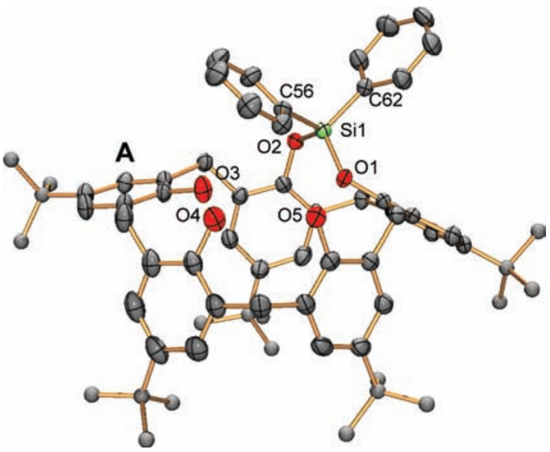

Figure 4. Crystal structure of ligand **3** with thermal ellipsoids at the 50% probability level. H atoms and noncoordinated solvent are omitted for clarity.

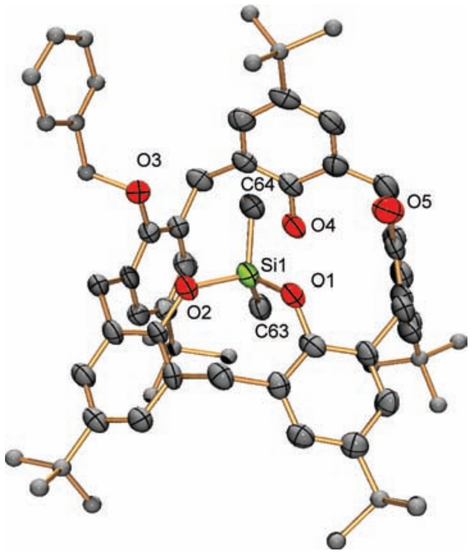

Figure 5. Crystal structure of ligand **6** with thermal ellipsoids at the 50% probability level. H atoms and noncoordinated solvent are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Ligands **3** and **6**

3		6	
Si(1)−O(1)	1.6454(18)	Si(1)−O(1)	1.661(6)
Si(1)−O(2)	1.6590(19)	Si(1)−O(2)	1.652(5)
Si(1)−C(56)	1.858(3)	Si(1)−C(63)	1.825(8)
Si(1)−C(62)	1.856(3)	Si(1)−C(64)	1.819(7)
O(1)−Si(1)−O(2)	109.64(9)	O(1)−Si(1)−O(2)	107.6(3)
O(1)−Si(1)−C(56)	106.04(10)	O(1)−Si(1)−C(63)	108.6(3)
O(1)−Si(1)−C(62)	114.31(11)	O(1)−Si(1)−C(64)	106.3(3)
O(2)−Si(1)−C(56)	107.19(11)	O(2)−Si(1)−C(63)	111.2(3)
O(2)−Si(1)−C(62)	107.17(11)	O(2)−Si(1)−C(64)	104.8(3)
C(56)−Si(1)−C(62)	112.29(12)	C(63)−Si(1)−C(64)	117.8(4)

^{t}**BuC5(H)$_5$** complexes[26,29,42] and in some silicon bisphenolates.[45] The Si−OAr bond lengths are in the range of 1.6454(18) to 1.661(6) Å while the Si−C bond distances range from 1.819(7) to 1.858(3) Å. All these distances fall in the normal ranges for silicon calixarene complexes.[19−22,27,29,46−48] The methyl groups attached to the silicon center are *endo* and *exo* oriented, consistent with their ^{1}H NMR analyses.

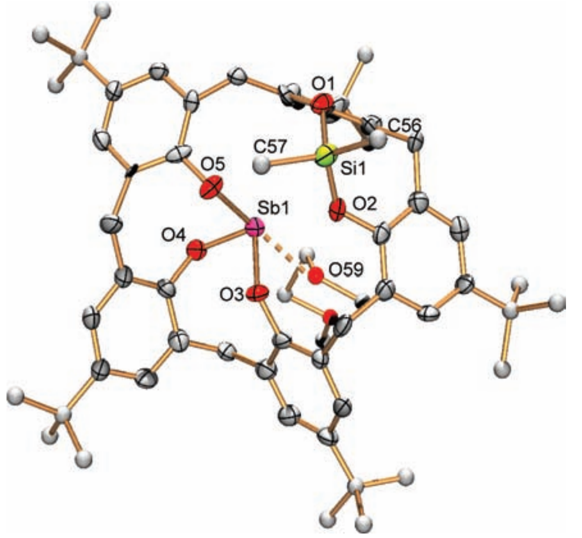

Figure 6. Crystal structure of complex **8** with thermal ellipsoids at the 50% probability level. H atoms and noncoordinated solvent are omitted for clarity.

The calixarene ring in **3** displays a distorted cone conformation with the ring **A** close to the plane of the lower rim (Figure 4). In ligand **6** the presence of the monobenzyl ether moiety causes the ligand to adopt a partial cone conformation (Figure 5) similar to that observed in the mono-*n*-propyl calix[5]arene ether.[41]

3.2. Bi(III) and Sb(III) Complexes with ^{t}BuC5(SiRR′)(H)$_3$ Ligands. The crystal structures of complexes **8**, **9**, **12**, **15**, and **16** are illustrated in Figures 6−8 and selected bond distances and angles are presented in Table 2. Complexes **9**, **12**, **15**, and **16** all crystallize in the triclinic $P\overline{1}$ space group while complex **8** crystallizes in the orthorhombic space group $Pna2_1$. All monometallic complexes **8**, **9**, **12**, **15**, and **16** are monomeric units with the calixarene ligand in an approximate 1,2-alternate conformation. This conformation is similar to that observed in [W(N^{t}Bu)(HN^{t}Bu){^{t}**BuC5(PNMe$_2$)**}] and [Ti(NMe$_2$){^{t}**BuC5(PNMe$_2$)**}].[23,24]

The silicon centers remain tetrahedral as in the parent ligands with their R and R′ groups coordinated *endo* and *exo* with respect to the calixarene lower rim, consistent with their ^{1}H NMR spectra. All the Si−O and Si−C bond distances and O−Si−O and C−Si−O angles fall in the normal ranges for silylated calixarene[27,29] and aryloxide[45,49−52] complexes (Table 2). The conformation of the

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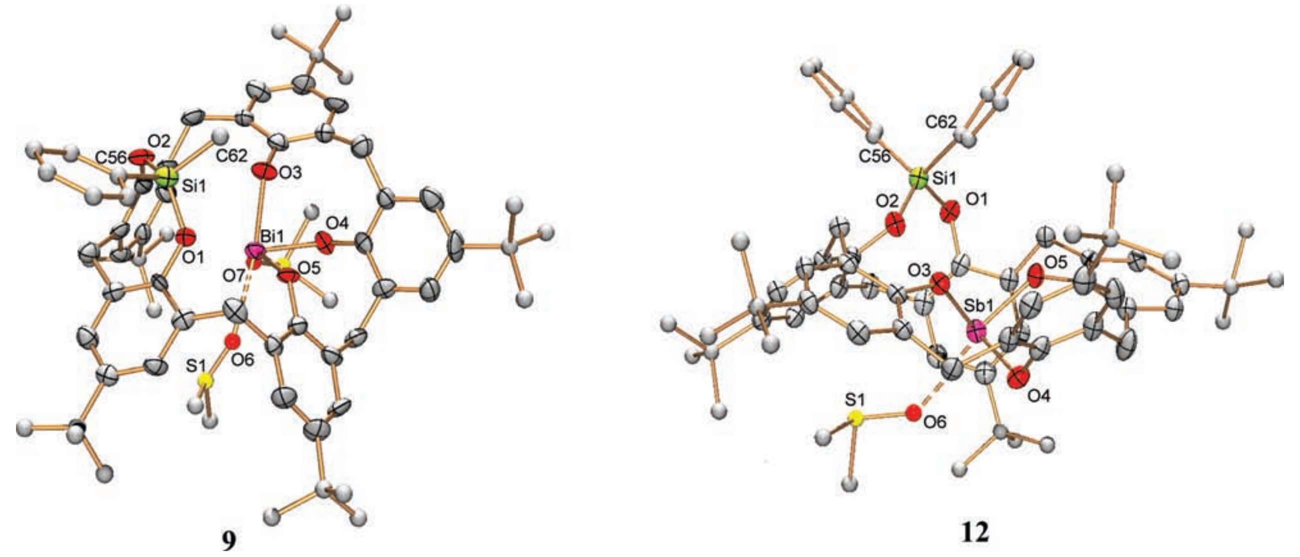

Figure 7. Crystal structures of complexes **9** and **12** with thermal ellipsoids at the 50% probability level. H atoms and noncoordinated solvent are omitted for clarity.

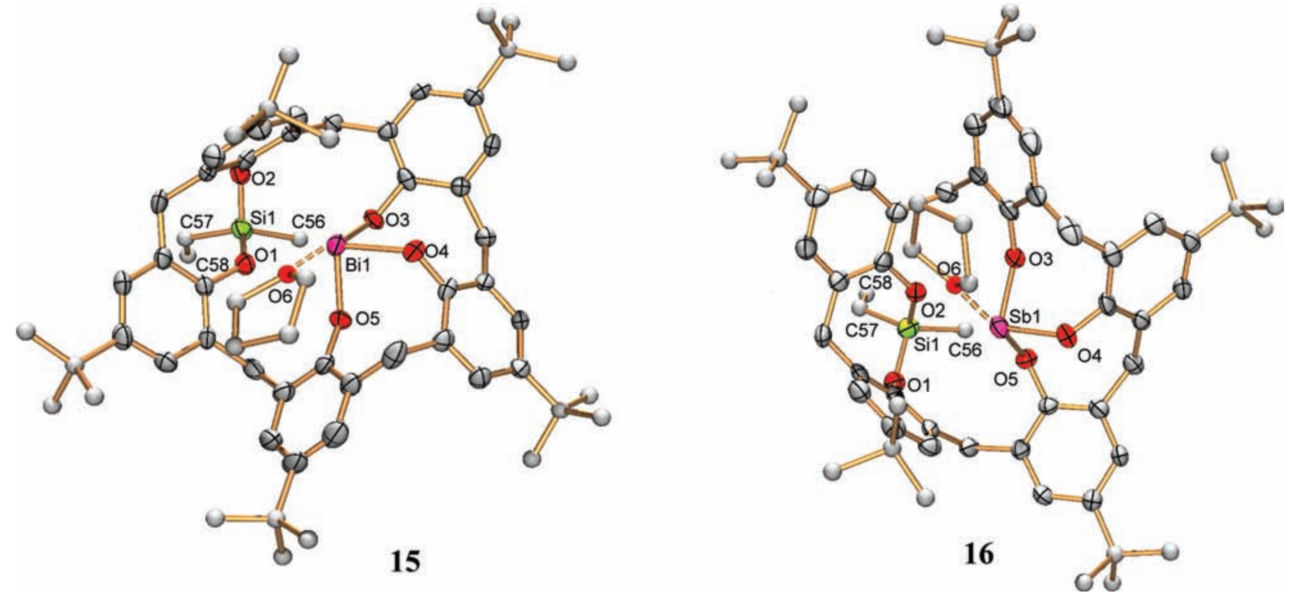

Figure 8. Crystal structures of complexes **15** and **16** with thermal ellipsoids at the 50% probability level. H atoms and noncoordinated solvent are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complexes **8**, **9**, **12**, **15**, and **16**

	8	**9**	**12**	**15**	**16**
Si(1)−OAr	1.644(7), 1.645(7)	1.646(9), 1.666(9)	1.630(3), 1.651(3)	1.640(6), 1.650(5)	1.643(4), 1.648(4)
Si(1)−C	1.826(10), 1.840(11)	1.821(18), 1.831(14)	1.848(5), 1.850(4)	1.833(10), 1.844(8)	1.830(8), 1.852(7)
O(1)−Si−O(2)	106.2(3)	104.4(4)	105.94(14)	105.3(3)	105.3(2)
C−Si−OAr	107.3(5)−114.8(5)	108.5(6)−112.1(6)	105.51(18)−116.78(18)	107.5(3)−113.0(4)	107.3(3)−112.6(3)
C−Si−C	111.1(6)	110.6(7)	110.1(2)	112.8(4)	112.7(4)
M−O(3)	1.959(6)	2.207(8)	1.988(2)	2.131(5)	1.959(4)
M−O(4)	1.969(6)	2.125(8)	1.985(3)	2.094(5)	1.971(4)
M−O(5)	2.013(6)	2.119(7)	2.011(3)	2.069(5)	2.010(4)
ArO−M−OAr	89.9(3)−94.8(2)	83.5(3)−90.5(3)	89.41(11)−95.22(11)	86.99(19)−92.68(18)	89.82(16)−93.49(16)
$M-O_{solvent}$	3.028(12)	2.53(2)− 2.73(2)	2.565(3)	2.981(9)	3.128(14)

eight-membered rings formed around the silicon center in **8**, **9**, **12**, **15**, and **16** is twisted boat (TB) in all cases regardless of the R,R′ groups attached to the silicon atom, or the metal center coordinated in the lower rim.

The metal centers in complexes **8**, **12**, **15**, and **16** are tetracoordinated having primary bonds with three aryloxides, and have a secondary interaction with one solvent molecule (DME for **8**, DMSO for **12**, and THF for **15** and **16**), to give an overall seesaw geometry. The antimony center in complex **8** is weakly coordinated to one DME molecule with a bond distance of 3.028(4) Å, while complex **12** contains a Sb−O(DMSO) bond distance of 2.565(3) Å similar to those observed in [Sb_2Cl_2\{**RC4**\}] and [Sb_2O\{**RC5(H)**\}] complexes [2.503(7)−2.569(2) Å].[18,26] The effect of solvent coordination is noticed in the slight elongation of bonds [Sb−O(5) 2.013(6) and Sb−O(5) 2.011(3) Å] in **8** and **12**, respectively. The metal centers in complexes **15** and **16** are weakly coordinated to one THF molecule each with bond distances of 2.981(9) and 3.128(14) Å, respectively. These Sb−O(THF) bond distances are much longer than that observed in the calixarene complex [Sb_2Cl_2\{**^{t}BuC4**\}]·4THF [2.631(2) Å], indicating relatively weak coordination.[53] A similar solvent coordination effect in complexes **15** and **16** is evidenced by the elongation of the Bi−O(3) and Sb−O(5) bonds with distances of 2.131(5) and 2.010(4) Å, respectively.

In complex **9** two DMSO molecules coordinate to the bismuth center, providing a distorted square-based pyramidal geometry. This geometry is similar to the one observed in the central rings of bismuth calixarene clusters of the type [Bi_2O\{**RC5(H)**\}]$_2$ and [Bi_4O_2\{**RC8**\}]$_2$.[26,53] The Bi−O(7) bond distance is 2.589(10) Å while Bi−(O6) and Bi−O(6A) bond distances from the disordered DMSO molecule are 2.53(2) and 2.73(2) Å, respectively (2.63 Å average).

The conformation of the calixarene ligands in complexes **8**, **9**, **12**, **15**, and **16** allows metal π−arene interactions with a single aromatic ring in the calixarene ligand. The M−C(aryl) distances and M···centroid(aryl) distances are shown in Table 3, and they are comparable with those reported in literature.[18,53−60] Because of the 1,2-alternate conformation in the calixarene ring, the silicon atoms and the metal centers are oriented on opposite sides of the ring, avoiding any Si···metal interactions.

3.3. Bi(III) and Sb(III) Complexes with ^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$ Ligand (6). The crystal structures of complexes **17**, **18**, and **19** are depicted in Figures 9 and 10 and selected bond distances and angles are shown in Table 4. Complexes **17**−**19** are all monomeric with an approximate 1,2-alternate conformation. The calixarene ligands in complexes **17**−**19** display a C_1 symmetry, and the two methyl groups in the tetrahedral silicon centers are coordinated *endo* and *exo*, consistent with their ^{1}H NMR spectra. The bismuth center in complex **17** is primarily coordinated to two aryloxides and to one unreacted O^{t}Bu group that faces away from the calixarene cavity. In addition, a secondary interaction with a THF molecule with bond distance of 2.806(16) Å is observed, providing a seesaw geometry. The Bi−O^{t}Bu bond distance is 2.008(8) Å, similar to that in the [Bi(O^{t}Bu)\{**^{t}BuC4(Bn)$_2$**\}] complex [2.061(3) Å] prepared in our lab.[18]

Table 3. Comparison of M−C(aryl) and M···Centroid(aryl) Interactions

	M−C(aryl)/ Å	M···centroid(aryl)/ Å
8	3.502−4.260	3.661
9	3.524−4.042	3.543
12	3.492−4.116	3.562
15	3.411−3.875	3.391
16	3.477−4.073	3.538
17	3.343−4.218	3.537
18	3.358−4.377	3.655
19	3.431−4.390	3.689

The antimony centers in complexes **18** and **19** are bonded to two neighboring aryloxides and one O^{t}Bu and NMe$_2$, respectively, displaying a trigonal pyramidal geometry. This geometry is usually observed in antimony(III) calixarene and aryloxide complexes.[18,26,53,61] The Sb−O^{t}Bu and Sb−NMe$_2$ bond distances are 1.906(3) and 1.976(4) Å, respectively, and as in complex **17**, they point away from the calixarene cavity.

The M−OAr bond distances and O−M−O angles in structures **17**−**19** fall in the normal ranges for bismuth(III) and antimony(III) calixarene complexes.[18,26,40,53] In complexes **17**−**19**, the *endo* coordination (with respect to the lower rim) of the bismuth and antimony centers allows several metal−arene π interactions with ring **A** (Table 3). The Bi−C interactions in **17** are comparable with those observed in complexes **9** and **15** (Table 3), while the Sb−C interactions in complexes **18** and **19** are similar to those observed in [Sb_2Cl_2\{**RC4**\}],[18] [SbX_3·(arene)],[62−65] and organoantimony(III) complexes.[66,67]

4. Conclusion

We have synthesized and fully characterized a series of calix[5]arene bismuth(III) and antimony(III) complexes supported by silylated ligands. The use of calixanions as precursors for the preparation of monosilylated ligands was only successful when using the **^{t}BuC5(H)$_5$** ligand. For the **^{t}BuC5(Bn)(H)$_4$** ligand, the use of Me$_2$Si(NMe$_2$)$_2$ yielded the desired product. The free OH groups in ligands **1**−**6** are reactive, and the addition of M(O^{t}Bu)$_3$ (M = Bi, Sb) or Sb(NMe$_2$)$_3$ readily yields the respective metalated complexes. All of the complexes are monomeric in the solid state with the calixarene ring in cone conformation for ligand **^{t}BuC5(SiPh$_2$)(H)$_3$ (3)** and partial cone for ligand **^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$ (6)**. All bismuth and antimony complexes display distorted 1,2-alternate conformations in the solid state despite the fact that complexes **17**−**19** contain a monobenzyl group in the lower rim. The *endo* coordination of the metal centers and the

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Table 4. Selected Bond Lengths (Å) and Angles (deg) of Complexes **17**−**19**[a]

	17	**18**	**19**
Si(1)−OAr	1.642(6), 1.664(6)	1.640(3), 1.661(3)	1.650(3), 1.663(2)
Si(1)−C	1.814(11), 1.820(10)	1.823(5), 1.830(5)	1.818(4), 1.847(4)
O(1)−Si−O(2)	105.5(3)	106.66(14)	106.65(12)
C−Si−OAr	108.1(4)−112.6(4)	107.19(18)−111.21(18)	108.05(16)−111.89(17)
C−Si−C	109.0(5)	111.6(2)	110.5(2)
M−O(4)	2.124(6)	1.982(3)	1.992(3)
M−O(5)	2.128(6)	1.995(3)	2.014(2)
M−X	2.008(8)	1.906(3)	1.976(4)
O−M−X	93.4(3), 94.0(3)	94.35(12), 94.74(11)	89.06(14), 94.38(13)
O(4)−M−O(5)	92.4(2)	94.52(11)	95.32(10)
$M-O_{solvent}$	2.806(16)		

[a] X = O^tBu, NMe_2.

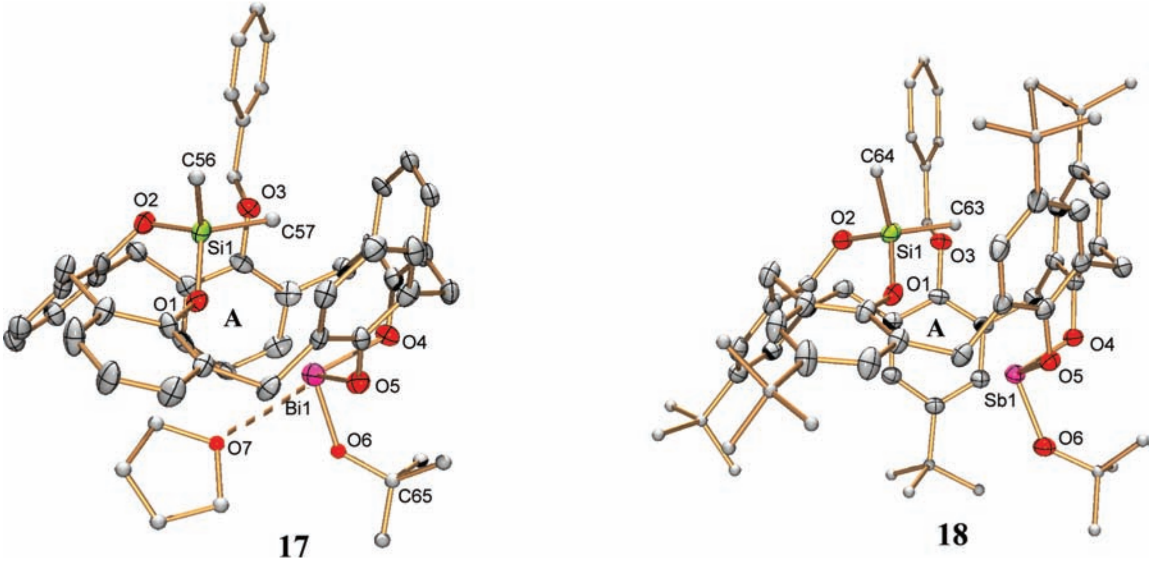

Figure 9. Crystal structures of complexes **17** and **18** with thermal ellipsoids at the 50% probability level. *tert*-Butyl groups in **17**, H atoms, and noncoordinated solvent are omitted for clarity.

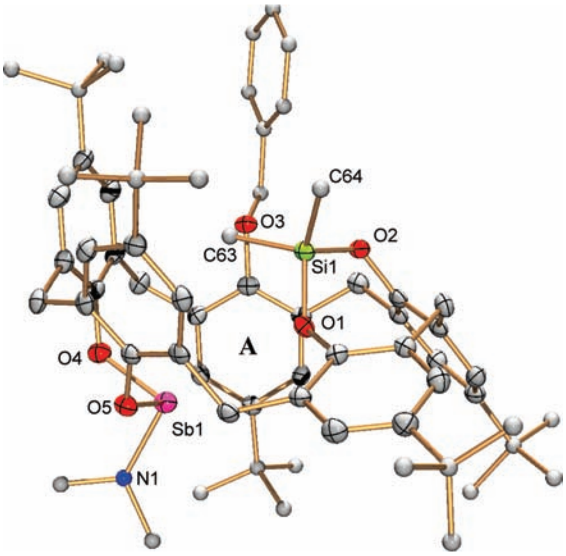

Figure 10. Crystal structure of complex **19** with thermal ellipsoids at the 50% probability level. H atoms and noncoordinated solvent are omitted for clarity.

1,2-alternate conformation of the calixarene rings allow metal−arene π interactions in most of the complexes. The monometallic complexes **7**−**19** have high solubility in most organic solvents making them interesting precursors for more extended structures.

5. Experimental Section

5.1. General Procedures. Unless otherwise noted, all manipulations were carried out in a nitrogen filled glovebox. Starting materials were obtained from commercial suppliers and used without further purification. *p-tert*-Butylcalix[5]arene,[68] monobenzyl-*p-tert*-butylcalix[5]arene,[41] [Na_2·**^{t}BuC5(H)$_3$**],[25] Bi(O^tBu)$_3$,[69] and Sb(O^tBu)$_3$[70] were prepared by the literature procedures. Sb(NMe_2)$_3$ was purchased from Strem Chemicals and used as received. *p-tert*-Butylcalix[5]arene was dried at 110 °C at least 24 h under vacuum before use. THF and toluene were freshly distilled from Na/benzophenone. Other anhydrous solvents were purchased from Aldrich and stored over molecular sieves under nitrogen before using. Deuterated benzene and dimethyl sulfoxide were dried over CaH_2. The melting points of all compounds were taken in sealed and evacuated capillary tubes on a Mel-temp apparatus (Laboratory Devices, Cambridge, MA) using a 500 °C thermometer. A melting temperature preceded by a ” >” sign indicates that the

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Table 5. Crystallographic Data and Summary of Data Collection and Structure Refinement

	3	**6**·0.5C_6H_{14}	**8**·DME	**9**·3DMSO	**12**·DMSO·C_5H_{12}
formula	$C_{67}H_{78}O_5Si$	$C_{67}H_{87}O_5Si$	$C_{61}H_{81}O_7SiSb$	$C_{68}H_{91}O_8S_3SiBi$	$C_{74}H_{93}O_6SSiSb$
Fw	991.38	1000.46	1076.14	1369.66	1260.38
cryst syst	triclinic	monoclinic	orthorhombic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$Pna2_1$	$P\bar{1}$	$P\bar{1}$
T, K	213(2)	228(2)	218(2)	218(2)	228(2)
a, Å	10.980(3)	15.970(4)	27.843(5)	11.377(3)	13.675(3)
b, Å	17.101(5)	15.753(4)	15.306(3)	17.416(4)	13.858(2)
c, Å	18.085(5)	27.162(5)	13.221(2)	20.856(4)	18.553(3)
α, deg	100.073(6)	90	90	112.877(4)	88.196(3)
β, deg	107.479(5)	120.270(10)	90	92.901(4)	77.019(3)
γ, deg	101.844(5)	90	90	102.414(4)	86.717(4)
V, A^3	3066.5(15)	5902(2)	5634.3(18)	3676.8(15)	3419.8(11)
Z	2	4	4	2	2
d_{calcd}, g·cm^{-3}	1.074	1.126	1.264	1.237	1.224
μ, mm^{-1}	0.084	0.088	0.561	2.546	0.501
refl collected	13355	23868	22348	14957	14053
T_{min}/T_{max}	0.996	0.995	0.968	0.860	0.972
N_{measd}	8660	8460	7520	10473	9727
$[R_{int}]$	[0.0367]	[0.0848]	[0.1022]	[0.0823]	[0.0975]
$R\,[I > 2\sigma(I)]$	0.0528	0.1157	0.0574	0.0700	0.0506
$R_w[I > 2\sigma(I)]$	0.1371	0.2860	0.1198	0.1687	0.1300
GOF	0.979	1.074	0.910	0.958	1.020

	15·2THF	**16**·2THF	**17**·THF	**18**·DME	**19**·2.5THF
formula	$C_{66}H_{87}O_7SiBi$	$C_{66}H_{87}O_7SiSb$	$C_{72}H_{95}O_7SiBi$	$C_{72}H_{97}O_8SiSb$	$C_{76}H_{104}NO_{7.5}SiSb$
Fw	1229.43	1142.20	1309.55	1240.38	1301.48
cryst syst	triclinic	triclinic	monoclinic	hexagonal	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{3}$	$P\bar{1}$
T, K	223(2)	223(2)	228(2)	223(2)	223(2)
a, Å	13.033(4)	13.0513(16)	30.143(9)	31.122(3)	16.080(3)
b, Å	15.050(5)	15.1142(19)	31.624(9)	31.222(3)	16.736(3)
c, Å	18.679(6)	18.546(2)	17.105(7)	14.5433(18)	17.447(3)
α, deg	66.401(5)	66.643(2)	90	90	99.445(3)
β, deg	75.309(6)	76.027(2)	93.469(7)	90	116.548(3)
γ, deg	67.587(5)	67.568(2)	90	120	108.152(3)
V, A^3	3081.7(17)	3086.9(6)	16275(9)	12199(2)	3728.4(12)
Z	2	2	8	6	2
d_{calcd}, g·cm^{-3}	1.325	1.229	1.069	1.013	1.159
μ, mm^{-1}	2.930	0.516	2.223	0.392	0.434
refl collected	15150	14195	32203	60352	17582
T_{min}/T_{max}	0.863	0.956	0.875	0.981	0.983
N_{measd}	8831	8860	11671	11707	10608
$[R_{int}]$	[0.0843]	[0.0625]	[0.1144]	[0.0672]	[0.0506]
$R\,[I > 2\sigma(I)]$	0.0474	0.0579	0.0657	0.0488	0.0426
$R_w[I > 2\sigma(I)]$	0.1079	0.1383	0.1617	0.1311	0.1002
GOF	0.979	0.959	0.0902	0.969	0.903

compound starts to decompose at that temperature but appears to actually melt at some higher temperature. ^{1}H NMR and ^{13}C spectra were recorded at room temperature on a Varian XL-300 spectrometer at 300 and 75 MHz, respectively. Analytical samples were dried under vacuum for at least 24 h. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA. IR and UV/vis spectra were obtained with an Infinity Gold FTIR spectrometer and Agilent 8453 spectrophotometer, respectively. Filtrations used a medium sintered glass filter. All X-ray diffraction experiments were performed in a Bruker SMART 1000 CCD detector at variable low temperature using Mo Kα radiation. In most cases the crystals for X-ray diffraction included solvents of crystallization, as shown in Table 5. For analytical samples the crystals were dried under vacuum at room temperature for 24 h.

5.2. General Procedure for Preparation of ^{t}BuC5(SiRR′)(H)$_3$ Ligands. A solution of NaO^{t}Bu (0.102 g, 1.06 mmol) in 4 mL of THF was added dropwise to a solution of **^{t}BuC5(H)$_5$** (0.412 g, 0.508 mmol) in 8 mL of THF, and the reaction mixture was allowed to stir for 24 h. To the resulting yellowish solution of the Na$_2$·**^{t}BuC5(H)$_3$**[25] salt, a colorless solution of the appropriate silane precursor (RR′SiCl$_2$, 0.508 mmol) in 3 mL of THF was added, and the reaction was allowed to stir for 24 h. The resulting cloudy solution was centrifuged (or filtered) to yield a colorless solution that was vacuum-dried to yield a white solid.

R, R′ = Me (1). The white solid was stirred in 15 mL of pentane for 24 h and centrifuged. This washing procedure was repeated to yield 0.374 g of pure **^{t}BuC5(SiMe$_2$)(H)$_3$** as a white powder (0.432 mmol, 85% yield). ^{1}H NMR (C_6D_6): δ −2.03 (bs, 3H, SiC*H*$_3$), −0.10 (bs, 3H, SiC*H*$_3$), 1.15 (s, 18H, C(C*H*$_3$)$_3$), 1.28 (s, 18H, C(C*H*$_3$)$_3$), 1.31 (s, 9H, C(C*H*$_3$)$_3$), 3.34 (d, J = 14.1 Hz, 2H, ArC*H*$_2$Ar), 3.37 (d, J = 13.2 Hz, 1H, ArC*H*$_2$Ar), 3.78 (d, J = 14.1 Hz, 2H, ArC*H*$_2$Ar), 3.89 (d, J = 14.1 Hz, 2H, ArC*H*$_2$Ar), 4.34 (d, J = 14.1 Hz, 2H, ArC*H*$_2$Ar), 4.47 (d, J = 13.2 Hz, 1H, ArC*H*$_2$Ar), 5.53 (b, 3H, O*H*), 7.09 (d, J = 2.4 Hz, 2H, Ar*H*), 7.21 (d, J = 2.4 Hz, 2H, Ar*H*), 7.30 (s, 6H, Ar*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 151.9, 150.4, 149.2, 144.7, 143.8, 142.9, 131.7, 131.4, 127.1, 127.0, 126.7, 126.2, 126.1, 125.9 (aromatic carbons) [two signals missing, probably overlapping with C_6H_6 peaks], 35.6, 34.9 (*C*(CH$_3$)$_3$), 34.0, 33.9 (Ar*C*H$_2$Ar), 31.8 (*C*(CH$_3$)$_3$), 31.6, 31.5, 31.4 (C(*C*H$_3$)$_3$), 30.7 (Ar*C*H$_2$Ar), −2.9, −8.4 (Si*C*H$_3$). IR (KBr, cm^{-1}): 3548bs (OH), 2962vs, 2906vs, 2868vs, 1603m, 1479vs, 1439m, 1402w, 1393w, 1362s, 1310m, 1291s, 1264s, 1202vs, 1125m, 1105w, 1056w, 944m, 927m, 899s, 878s, 824s, 789m. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 281 (1.61×10^4).

R = Me, R′ = Ph (2). The white solid was dissolved in 8 mL of pentane, and the solution was allowed to evaporate slowly to yield 0.382 g of colorless single block crystals of pure **^{t}BuC5(SiMePh)(H)$_3$** (0.411 mmol, 81% yield). ^{1}H NMR (C_6D_6): δ −0.29 (b, 3H, $SiCH_3$), 1.15 (s, 9H, $C(CH_3)_3$), 1.20 (s, 18H, $C(CH_3)_3$), 1.30 (s, 18H, $C(CH_3)_3$), 3.33 (d, J = 14.1 Hz, 1H, $ArCH_2Ar$), 3.53 (d, J = 14.1 Hz, 2H, $ArCH_2Ar$), 3.75 (d, J = 14.7 Hz, 2H, $ArCH_2Ar$), 3.83 (d, J = 14.1 Hz, 2H, $ArCH_2Ar$), 4.39 (d, J = 14.7 Hz, 2H, $ArCH_2Ar$), 4.50 (d, J = 14.1 Hz, 1H, $ArCH_2Ar$), 7.01 (b, 2H, ArH), 7.10 (d, J = 2.4 Hz, 2H, ArH), 7.13 (d, J = 2.4 Hz, 1H, ArH), 7.19 (d, J = 2.4 Hz, 2H, ArH), 7.23 (d, J = 2.4 Hz, 2H, ArH), 7.25 (d, J = 2.4 Hz, 2H, ArH), 7.48 (d, J = 2.4 Hz, 2H, ArH), 7.73−7.76 (m, 2H, ArH). No OH peak was observed at room temperature. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 150.9, 148.7, 148.5, 145.5, 144.2, 143.7, 143.1, 134.4, 133.9, 130.9, 130.6, 130.3, 127.4, 127.5, 127.0, 126.9, 126.7, 126.5, 126.4, 125.9 (aromatic carbons), 35.7, 34.5 ($C(CH_3)_3$), 34.2, 34.0, 33.9 ($ArCH_2Ar$), 32.7 ($C(CH_3)_3$), 31.8, 31.6, 31.5 ($C(CH_3)_3$), −2.7 ($SiCH_3$). IR (KBr, cm^{-1}): 3576m, 3516vs, 3073w, 3049m, 2963vs, 2910vs, 2868vs, 1771w, 1593w, 1512w, 1503m, 1479vs, 1431s, 1392m, 1362s, 1323s, 1291vs, 1258vs, 1202vs, 1124vs, 996w, 931vs, 900vs, 872vs, 813m, 793s, 757m. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 282 (1.63×10^4).

R, R′ = Ph (3). The white solid was dissolved in 8 mL of hexane and allowed to evaporate slowly to yield 0.373 g of **^{t}BuC5(SiPh$_2$)(H)$_3$** as colorless crystals suitable for X-ray diffraction (0.376 mmol, 74% yield). Mp: 273−275 °C. ^{1}H NMR (C_6D_6): δ 1.13 (s, 18H, $C(CH_3)_3$), 1.23 (s, 9H, $C(CH_3)_3$), 1.27 (s, 18H, $C(CH_3)_3$), 3.41 (d, J = 15 Hz, 1H, $ArCH_2Ar$), 3.59 (d, J = 15 Hz, 2H, $ArCH_2Ar$), 3.62 (d, J = 14.1 Hz, 2H, $ArCH_2Ar$), 3.76 (d, J = 14.1 Hz, 2H, $ArCH_2Ar$), 4.67 (d, J = 15 Hz, 1H, $ArCH_2Ar$), 4.72 (d, J = 15 Hz, 2H, $ArCH_2Ar$), 6.76−6.81(m, 4H, ArH), 6.96 (t, J = 7.5 Hz, 1H, ArH), 7.08−7.14 (m, 8H, ArH), 7.39 (d, J = 2.4 Hz, 2H, ArH), 7.85 (s, 1H, ArH), 7.92−7.96 (m, 4H, ArH). The OH peak was too broad to be observed at room temperature. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 149.9, 148.8, 148.4, 145.2, 143.6, 142.6, 134.8, 134.2, 133.4, 132.8, 131.0, 130.7, 129.9, 129.4, 128.6, 128.2, 127.2, 127.1, 126.8, 126.6, 126.4, 126.1, 126.0, 125.7 (aromatic carbons), 36.7 ($C(CH_3)_3$), 34.0, 33.9, 33.8 ($ArCH_2Ar$), 32.4, 32.1 ($C(CH_3)_3$), 31.6, 31.5, 31.3 ($C(CH_3)_3$). IR (KBr, cm^{-1}): 3558s (OH), 3401vs (OH), 3047m, 3007m, 2962vs, 2905vs, 2868vs, 2743w, 2709w, 2591w, 2557w, 1758w, 1592m, 1481vs, 1430s, 1393s, 1363vs, 1297vs, 1247vs, 1201vs, 1123vs, 1027w, 997w, 953s, 928s, 909vs, 889vs. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 283 (1.41×10^4). Anal. Calcd for $C_{67}H_{78}O_5Si$: C 81.17, H 7.93. Found: C 80.90, H 8.06.

R, R′ = ^{i}Pr (4). The white solid was redissolved in 3 mL of pentane and was placed in the freezer at −35 °C overnight to yield 0.127 g of block colorless crystals of pure **^{t}BuC5(Si^{i}Pr$_2$)(H)$_3$** (0.137 mmol, 27% yield). Single crystals were obtained by slow evaporation of a concentrated pentane/DME solution (5:1) of product. Mp: 139−140 °C. ^{1}H NMR (DMSO-d$_6$): δ 1.11 (d, J = 7.5 Hz, 6H, $CH(CH_3)_2$), 1.13 (s, 9H, $C(CH_3)_3$), 1.14 (s, 18H, $C(CH_3)_3$), 1.21 (s, 18H, $C(CH_3)_3$), 1.41 (broad septet, 1H, $CH(CH_3)_2$), 1.49 (d, J = 7.5 Hz, 6H, $CH(CH_3)_2$), 2.26 (broad septet, 1H, $CH(CH_3)_2$), 3.13 (d, J = 13.5 Hz, 2H, $ArCH_2Ar$), 3.36 (d, J = 13.8 Hz, 2H, $ArCH_2Ar$), 3.57 (d, J = 14.1 Hz, 1H, $ArCH_2Ar$), 4.03 (d, J = 13.5 Hz, 2H, $ArCH_2Ar$), 4.07 (d, J = 14.1 Hz, 1H, $ArCH_2Ar$), 4.73 (d, J = 13.8 Hz, 2H, $ArCH_2Ar$), 7.03 (b, 2H, ArH), 7.06 (bs, 2H, ArH), 7.16 (b, 4H, ArH), 7.20 (s, 2H, ArH). OH peak not observed at room temperature. $^{13}C\{^1H\}$ NMR (DMSO-d$_6$): δ 148.9, 143.4, 130.5, 128.9, 128.3, 128.1, 127.3, 126.6, 126.3, 125.9, 125.7 (aromatic carbons, one carbon peak not observed), 36.2 ($C(CH_3)_3$), 34.4, 34.2 ($ArCH_2Ar$), 34.1 ($C(CH_3)_3$), 32.1, 31.9 (two peaks overlapping, $C(CH_3)_3$), 27.9 ($ArCH_2Ar$), 25.8 ($C(CH_3)_3$), 18.6, 18.4 ($CH(CH_3)_2$), 14.8 ($CH(CH_3)_2$) [one ($CH(CH_3)_2$) peak not observed]. IR (KBr, cm^{-1}): 3368m, 3055w, 2962s, 2910m, 2868s, 2717w, 1602w, 1503w, 1481s, 1422m, 1363s, 1296m, 1246m, 1202s, 1126m, 1117m, 1069w, 1046m, 1019w, 995w, 927m, 884s, 820m, 8052w, 795w. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 213 (1.05×10^4), 284 (6.036×10^3). Anal. Calcd for $C_{61}H_{82}O_5Si \cdot C_4H_{10}O_2$: C 77.03, H 9.15. Found: C 77.11, H 9.36.

R = Me, R′ = C$_2$H$_3$ (5). The white solid was stirred for 24 h in 10 mL of pentane and centrifuged to yield a white solid. This washing procedure was repeated to yield 0.277 g of pure **^{t}BuC5(SiMeVinyl)(H)$_3$** as a white powder (0.315 mmol, 62% yield). Mp: 268−270 °C. ^{1}H NMR (C_6D_6): δ −1.05 (b, 3H, $SiCH_3$), 1.22 (bs, 9H, $C(CH_3)_3$), 1.24 (bs, 18H, $C(CH_3)_3$), 1.25 (b, 18H, $C(CH_3)_3$), 3.42 (d, J = 14.1 Hz, 1H, $ArCH_2Ar$), 3.55 (d, J = 14.4 Hz, 2H, $ArCH_2Ar$), 3.69 (d, J = 14.1 Hz, 2H, $ArCH_2Ar$), 3.83 (d, J = 14.1 Hz, 2H, $ArCH_2Ar$), 4.32 (d, J = 14.4 Hz, 2H, $ArCH_2Ar$), 4.48 (d, J = 14.1 Hz, 1H, $ArCH_2Ar$), 5.74−5.93 (m, 2H, $CH{=}CH_2$), 6.11 (dd, J = 4.5 Hz, J = 14.7 Hz, 1H, $CH = CH_2$), 6.36 (b, 3H, OH), 7.22 (b, 6H, ArH), 7.25 (d, J = 2.1 Hz, 2H, ArH), 7.39 (b, 2H, ArH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 150.5, 150.1, 148.8, 145.2, 143.8, 143.2, 136.5, 133.2, 130.9, 130.7, 127.5, 127.4, 127.3, 126.7, 126.4 (aromatic carbons), 126.3 ($CH{=}CH_2$), 126.2 (aromatic carbons), 35.6 ($C(CH_3)_3$), 34.4 ($ArCH_2Ar$), 34.2, 34.1, ($C(CH_3)_3$), 34.0 ($ArCH_2Ar$), 32.5 ($CH = CH_2$), 31.7, 31.6, 31.5 ($C(CH_3)_3$), 22.7 ($ArCH_2Ar$), −5.8 ($SiCH_3$). IR (KBr, cm^{-1}): 3537m (OH), 3047m, 2961vs, 2906vs, 2867s, 2743w, 2702w, 1762w, 1596w, 1479vs, 1393m, 1362s, 1310m, 1291m, 1261m, 1202vs, 1125s, 1104m, 1004m, 961m, 946s, 926m, 899s, 878s, 859m. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 283 (5.68×10^3). Anal. Calcd for $C_{58}H_{74}O_5Si$: C 79.23, H 8.48. Found: C 79.47, H 8.76.

^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$ (6). A colorless solution of $Me_2Si(NMe_2)_2$ in 4 mL of toluene (0.0743 g, 0.508 mmol) was added dropwise to a solution of **^{t}BuC5(Bn)(H)$_4$** (0.458 g, 0.508 mmol) in 8 mL of toluene, and the reaction mixture was allowed to stir for 24 h. The final yellowish solution was vacuum-dried to yield a yellowish solid. This solid was dissolved in 10 mL of hexane, and the solution was allowed to slowly evaporate to give 0.379 g of pure **^{t}BuC5(Bn)(SiMe$_2$)(H)$_2$** as X-ray quality colorless block crystals (0.396 mmol, yield 78%). Mp: 279−281 °C. ^{1}H NMR (C_6D_6): δ −2.45 (s, 3H, $SiCH_3$), −0.11 (s, 3H, $SiCH_3$), 1.06 (s, 9H, $C(CH_3)_3$), 1.10 (s, 9H, $C(CH_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$), 1.28 (s, 9H, $C(CH_3)_3$), 1.36 (s, 9H, $C(CH_3)_3$), 3.17 (d, J = 14.1 Hz, 1H, $ArCH_2Ar$), 3.21 (d, J = 14.1 Hz, 1H, $ArCH_2Ar$), 3.36 (d, J = 13.2 Hz, 1H, $ArCH_2Ar$), 3.85 (partially overlapping, d, J = 13.2 Hz, 1H, $ArCH_2Ar$), 3.87 (s, 2H, OCH_2Ar), 3.95 (d, J = 13.2 Hz, 1H, $ArCH_2Ar$), 4.54 (d, J = 14.1 Hz, 2H, $ArCH_2Ar$), 4.58 (d, J = 11.4 Hz, 1H, $ArCH_2Ar$), 4.77 (d, J = 14.1 Hz, 1H, $ArCH_2Ar$), 4.80 (d, J = 11.4 Hz, 1H, $ArCH_2Ar$), 4.88 (b, 1H, OH), 5.05 (b, 1H, OH), 7.12 (b, 2H, ArH), 7.15 (d, J = 2.4 Hz, 1H, ArH), 7.18 (b, 1H, ArH), 7.21 (d, J = 2.4 Hz, 1H, ArH), 7.24 (b, 1H, ArH), 7.26 (b, 2H, ArH), 7.28 (b, 2H, ArH), 7.31 (d, J = 2.4 Hz, 1H, ArH), 7.36 (b, 2H, ArH), 7.51 (d, J = 6.9 Hz, 2H, ArH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 153.5, 152.3, 150.1, 149.5, 149.4, 146.4, 144.2, 144.1, 143.4, 143.0, 137.9, 133.6, 132.3, 132.1 (two signals overlapping), 131.9, 131.8, 129.1, 128.8 (three signals overlapping), 128.0 (two signals overlapping) 127.6, 127.3, 127.2, 127.1, 126.3, 126.2, 126.0, 125.8, 125.7, 125.5, 125.3 (aromatic carbons), 75.5 (OCH_2Ar), 36.5, 36.1 ($C(CH_3)_3$), 34.8 ($ArCH_2Ar$), 34.1, 34.0, 33.96 ($C(CH_3)_3$), 33.9, 33.8 ($ArCH_2Ar$), 31.63, 31.61, 31.5, 31.4, 31.3 ($C(CH_3)_3$), 29.7, 28.8 ($ArCH_2Ar$), −3.55, −9.79 ($SiCH_3$). IR (KBr, cm^{-1}): 3535bs (OH), 3032m, 2960vs, 2867vs, 2750w, 2716w, 1763w, 1601m, 1513m, 1478vs, 1392m, 1372m, 1363s, 1310s, 1290vs, 1257vs, 1201vs, 1122s, 1107m, 987m, 943m, 902vs, 879s, 822s, 787m. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 284 (2.36×10^4). Anal. Calcd for $C_{64}H_{80}O_5Si$: C 80.29, H 8.42. Found: C 79.90, H 8.77.

5.3. General Synthesis of Silylated Bismuth and Antimony Complexes of the Type [M{^{t}BuC5(SiRR′)}]. A solution of $M(O^tBu)_3$ (M = Bi, Sb) or $Sb(NMe_2)_3$ (0.126 mmol) in 4 mL of toluene was added dropwise to a colorless solution of the **^{t}BuC5(SiRR′)(H)$_3$** ligand (0.125 mmol) in 10 mL of toluene.

The resulting yellow (Bi) or colorless (Sb) solution was allowed to stir for 24 h at room temperature. The solvent was vacuum removed to yield the crude products as white (antimony) or yellow (bismuth) solids. The crude product was dissolved in 2 mL of pentane and centrifuged to remove the small amount of insoluble material. To the resulting solution 0.5 mL of THF (or dimethoxyethane) were added and then placed in the freezer at −35 °C for 4 days to yield pure products as crystalline powders.

[Bi{^{t}BuC5(SiMe$_2$)}] (7). Single crystals of **7** (poor quality) were obtained from a mixture of pentane/DMSO (2:0.3 mL) at room temperature. Yield 83% (0.104 mmol, 0.111 g). Mp: 258−260 °C. ^{1}H NMR (C_6D_6): δ 0.13 (s, 3H, $\mathrm{SiC}H_3$), 0.92 (s, 3H, $\mathrm{SiC}H_3$), 1.03 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.20 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.35 (s, 18H, $\mathrm{C(C}H_3)_3$), 3.42 (d, $J = 13.8$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 3.47 (d, $J = 15.0$ Hz, 1H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.11 (d, $J = 15.3$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.24 (d, $J = 15.3$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.40 (d, $J = 15.0$ Hz, 1H, $\mathrm{Ar}CH_2\mathrm{Ar}$), 5.12 (d, $J = 13.8$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 7.04 (d, $J = 2.1$ Hz, 2H, $\mathrm{Ar}H$), 7.28 (s, 2H, $\mathrm{Ar}H$), 7.37 (d, $J = 2.1$ Hz, 2H, $\mathrm{Ar}H$), 7.39 (s, 4H, $\mathrm{Ar}H$). ^{13}C{^{1}H} NMR (C_6D_6): δ 152.7, 152.3, 148.6, 146.7, 144.6, 135.9, 135.4, 135.2, 134.3, 131.3, 129.2, 126.6, 125.7, 125.6, 125.2, 123.4 (aromatic carbons), 36.4, 35.9 ($C\mathrm{(CH_3)_3}$), 34.1 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 33.7 ($C\mathrm{(CH_3)_3}$), 33.5 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 32.0 (two peaks overlapping), 31.3 ($\mathrm{C(}C\mathrm{H_3)_3}$), 30.1 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 1.0, −1.5 ($\mathrm{Si}C\mathrm{H_3}$). IR (KBr, cm^{-1}): 3042m, 2970vs, 2922vs, 2870vs, 1606m, 1481vs, 1397s, 1296vs, 1256vs, 1196vs, 1123s, 1053w, 1029w, 989w, 946s, 930m, 894m, 873s, 825m, 753w. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 283 (1.72×10^4). Anal. Calcd for $C_{57}H_{71}O_5BiSi \cdot 1.5C_2H_6SO$: C 60.54, H 6.77. Found: C 60.84, H 6.65.

[Sb{^{t}BuC5(SiMe$_2$)}] (8). Single crystals of **8** were obtained from a mixture of pentane/DME (2:0.3 mL) at −35 °C. Yield 87% (0.109 mmol, 0.107 g). Mp: 344−346 °C. ^{1}H NMR (C_6D_6): δ 0.20 (s, 3H, $\mathrm{SiC}H_3$), 0.88 (s, 3H, $\mathrm{SiC}H_3$), 1.06 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.18 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.32 (s, 18H, $\mathrm{C(C}H_3)_3$), 3.40 (d, $J = 13.8$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 3.51 (d, $J = 15.0$ Hz, 1H, $\mathrm{ArC}H_2\mathrm{Ar}$), 3.86 (d, $J = 15.0$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.00 (d, $J = 15.0$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.49 (d, $J = 15.0$ Hz, 1H, $\mathrm{Ar}CH_2\mathrm{Ar}$), 4.93 (d, $J = 13.8$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 7.06 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 7.26 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 7.28−7.30 (m, 6H, $\mathrm{Ar}H$). ^{13}C{^{1}H} NMR (C_6D_6): δ 152.2, 151.1, 148.7, 146.2, 144.6, 144.3, 134.4, 134.2, 133.6, 131.3, 131.2, 126.6, 126.4, 126.1, 125.7, 124.4 (aromatic carbons), 36.8, 36.6 ($C\mathrm{(CH_3)_3}$), 34.1 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 33.9 ($C\mathrm{(CH_3)_3}$), 33.9, 31.8 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 31.6, 31.5, 31.4 ($\mathrm{C(}C\mathrm{H_3)_3}$), 0.9, −1.3 ($\mathrm{Si}C\mathrm{H_3}$). IR (KBr, cm^{-1}): 3054w, 2960vs, 2866vs, 1598w, 1477vs, 1422w, 1392m, 1362s, 1291s, 1239s, 1187vs, 1122s, 1052w, 904m, 873m, 801w, 736m. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 283 (5.57×10^3). Anal. Calcd for $C_{57}H_{71}O_5SbSi \cdot 0.5C_4H_{10}O_2$: C 68.73, H 7.43. Found: C 68.87, H 7.74.

[Bi{^{t}BuC5(SiMePh)}] (9). Single crystals of **9** were obtained from a mixture of pentane/DMSO (2:0.3 mL) at room temperature. Yield 81% (0.101 mmol, 0.115 g). Mp: 215−217 °C. ^{1}H NMR (C_6D_6): δ 0.97 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.13 (s, 3H, $\mathrm{SiC}H_3$), 1.21 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.38 (s, 18H, $\mathrm{C(C}H_3)_3$), 3.32 (d, $J = 15.0$ Hz, 1H, $\mathrm{ArC}H_2\mathrm{Ar}$), 3.47 (d, $J = 13.8$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.13 (d, $J = 15.3$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.27 (d, $J = 15.3$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.50 (d, $J = 15.0$ Hz, 1H, $\mathrm{Ar}CH_2\mathrm{Ar}$), 5.25 (d, $J = 13.8$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 6.87 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 7.02−7.04 (m, 3H, $\mathrm{Ar}H$), 7.31 (s, 2H, $\mathrm{Ar}H$), 7.32 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 7.40 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 7.42 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 7.57 (d, $J = 2.4$ Hz, 1H, $\mathrm{Ar}H$), 7.60 (d, $J = 2.4$ Hz, 1H, $\mathrm{Ar}H$). ^{13}C{^{1}H} NMR (C_6D_6): δ 152.6, 152.4, 148.6, 146.7, 144.7, 144.6, 136.0, 135.4, 134.9, 134.2, 133.5, 133.4, 131.4, 129.2, 128.4, 126.3, 125.6, 125.5, 125.3, 123.4 (aromatic carbons), 36.4, 36.0 ($C\mathrm{(CH_3)_3}$), 34.1, 33.8 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 33.5 ($C\mathrm{(CH_3)_3}$), 32.0, 31.9 ($\mathrm{C(}C\mathrm{H_3)_3}$), 31.6 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 31.2 ($\mathrm{C(}C\mathrm{H_3)_3}$), 1.6 ($\mathrm{Si}C\mathrm{H_3}$). IR (KBr, cm^{-1}): 3049w, 3109w, 2961vs, 2867vs, 2717w, 1759w, 1591m, 1504m, 1474vs, 1429s, 1412s, 1393s, 1362vs, 1299s, 1250s, 1196vs, 1121vs, 1028w, 990w, 949s, 924vs, 894vs, 877vs, 817vs, 808s. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 279 (3.71×10^4), 347 (1.46×10^3). Anal. Calcd for $C_{62}H_{73}O_5BiSi \cdot C_4H_{10}O_2$: C 64.69, H 6.83. Found: C 64.97, H 7.10.

[Sb{^{t}BuC5(SiMePh)}] (10). Yield 77% (0.0964 mmol, 0.101 g). Mp: 367−369 °C. ^{1}H NMR (C_6D_6): δ 1.01 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.04 (s, 3H, $\mathrm{SiC}H_3$), 1.17 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.35 (s, 18H, $\mathrm{C(C}H_3)_3$), 3.32 (d, $J = 14.7$ Hz, 1H, $\mathrm{ArC}H_2\mathrm{Ar}$), 3.46 (d, $J = 14.4$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 3.85 (d, $J = 15.0$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.11 (d, $J = 15.0$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.59 (d, $J = 14.7$ Hz, 1H, $\mathrm{Ar}CH_2\mathrm{Ar}$), 4.99 (d, $J = 14.4$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 6.90 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 7.06−7.08 (m, 3H, $\mathrm{Ar}H$), 7.15 (s, 2H, $\mathrm{Ar}H$), 7.20 (s, 2H, $\mathrm{Ar}H$), 7.29 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 7.31 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 7.67 (d, $J = 2.1$ Hz, 1H, $\mathrm{Ar}H$), 7.69 (d, $J = 2.1$ Hz, 1H, $\mathrm{Ar}H$). ^{13}C{^{1}H} NMR (C_6D_6): δ 151.5, 151.4, 148.5, 146.1, 144.6, 144.5, 134.3, 134.1, 134.0, 133.5, 133.2, 131.5, 131.3, 130.7, 129.2, 128.4, 126.7, 125.5, 125.4, 124.5 (aromatic carbons), 36.9, 36.4 ($C\mathrm{(CH_3)_3}$), 34.1 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 34.0 ($C\mathrm{(CH_3)_3}$), 33.9, 31.9 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 31.7, 31.5, 31.3 ($\mathrm{C(}C\mathrm{H_3)_3}$), 1.2 ($\mathrm{Si}C\mathrm{H_3}$). IR (KBr, cm^{-1}): 3051w, 2961vs, 2868vs, 1775w, 1604w, 1474vs, 1392m, 1362s, 1293s, 1243s, 1198vs, 1115m, 1050w, 910m, 874m, 820s, 796m. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 289 (2.84×10^4). Anal. Calcd for $C_{62}H_{73}O_5SbSi \cdot 2C_4H_8O$: C 70.52, H 7.52. Found: C 70.23, H 7.25.

[Bi{^{t}BuC5(SiPh$_2$)}] (11). Yield 92% (0.115 mmol, 0.138 g). Mp: 245−246 °C. ^{1}H NMR (C_6D_6): δ 1.02 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.19 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.36 (s, 18H, $\mathrm{C(C}H_3)_3$), 3.38 (d, $J = 14.7$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 3.40 (d, $J = 15.0$ Hz, 1H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.10 (d, $J = 15.3$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.44 (d, $J = 15.3$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.74 (d, $J = 15.0$ Hz, 1H, $\mathrm{Ar}CH_2\mathrm{Ar}$), 5.30 (d, $J = 14.7$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 6.96 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 6.99−7.01 (m, 3H, $\mathrm{Ar}H$), 7.05−7.06 (m, 3H, $\mathrm{Ar}H$), 7.15 (s, 2H, $\mathrm{Ar}H$), 7.27 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 7.36 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 7.44 (s, 2H, $\mathrm{Ar}H$), 7.80 (dd, $J = 2.4$ Hz, $J = 6.9$ Hz, 2H, $\mathrm{Ar}H$), 8.23 (dd, $J = 2.4$ Hz, $J = 6.9$ Hz, 2H, $\mathrm{Ar}H$). ^{13}C{^{1}H} NMR (C_6D_6): δ 154.1, 150.6, 149.1, 146.2, 145.2, 144.5, 136.0, 135.7, 135.4, 134.9, 134.4, 133.2, 132.3, 132.0, 131.3, 131.2, 129.7, 128.42, 128.40, 125.8, 125.7, 125.6, 125.3, 123.4 (aromatic carbons), 36.5, 36.1 ($C\mathrm{(CH_3)_3}$), 34.1, 33.7 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 33.6 ($C\mathrm{(CH_3)_3}$), 32.0, 31.9 ($\mathrm{C(}C\mathrm{H_3)_3}$), 31.8 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 31.3 ($\mathrm{C(}C\mathrm{H_3)_3}$). IR (KBr, cm^{-1}): 3049m, 2959vs, 2906s, 2867s, 1592m, 1505w, 1474vs, 1429m, 1413m, 1392m, 1362m, 1300m, 1250m, 1198vs, 1076w, 1045w, 1030w, 996w, 952m, 952m, 925s, 896m, 876m, 853m, 823s, 807w, 787m, 764w. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 279 (1.42×10^4), 356 (7.70×10^3). Anal. Calcd for $C_{67}H_{75}O_5BiSi \cdot C_4H_{10}O_2$: C 66.23, H 6.65. Found: C 65.96, H 6.73.

[Sb{^{t}BuC5(SiPh$_2$)}] (12). Single crystals of **12** can be obtained from a mixture of pentane/DMSO (2:0.3 mL) at room temperature. Yield 80% (0.100 mmol, 0.111 g). Mp: 105−106 °C. ^{1}H NMR (C_6D_6): δ 1.05 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.13 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.32 (s, 18H, $\mathrm{C(C}H_3)_3$), 3.33 (d, $J = 14.4$ Hz, 1H, $\mathrm{ArC}H_2\mathrm{Ar}$), 3.41 (d, $J = 15.3$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 3.75 (d, $J = 15.0$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.37 (d, $J = 15.0$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.84 (d, $J = 14.4$ Hz, 1H, $\mathrm{Ar}CH_2\mathrm{Ar}$), 5.07 (d, $J = 15.3$ Hz, 2H, $\mathrm{ArC}H_2\mathrm{Ar}$), 6.92 (d, $J = 2.4$ Hz, 4H, $\mathrm{Ar}H$), 6.94 (b, 2H, $\mathrm{Ar}H$) 7.11−7.13 (m, 4H, $\mathrm{Ar}H$), 7.17 (s, 2H, $\mathrm{Ar}H$), 7.27 (d, $J = 2.4$ Hz, 2H, $\mathrm{Ar}H$), 7.30 (s, 2H, $\mathrm{Ar}H$), 7.91 (dd, $J = 2.4$ Hz, $J = 6.9$ Hz, 2H, $\mathrm{Ar}H$), 8.16 (dd, $J = 2.4$ Hz, $J = 6.9$ Hz, 2H, $\mathrm{Ar}H$). ^{13}C{^{1}H} NMR (C_6D_6): δ 152.2, 149.9, 148.9, 145.8, 144.9, 144.5, 135.3, 134.3, 133.61, 133.59, 133.4, 133.2, 133.2, 131.4, 131.0, 130.9, 129.2, 128.5, 128.4, 127.2, 126.7, 125.2, 124.8, 124.5 (aromatic carbons), 36.9, 36.5 ($C\mathrm{(CH_3)_3}$), 34.1, 33.9 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 33.9 ($C\mathrm{(CH_3)_3}$), 32.5 ($\mathrm{Ar}C\mathrm{H_2Ar}$), 31.6, 31.5, 31.4 ($\mathrm{C(}C\mathrm{H_3)_3}$). IR (KBr, cm^{-1}): 3049w, 2962vs, 2869vs, 1759w, 1592m, 1478vs, 1431s, 1393m, 1363vs, 1295vs, 1252vs, 1199vs, 1121vs, 1054w, 994w, 955m, 929s, 876m, 822m, 807w, 777m. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 281 (2.17×10^4). Anal. Calcd for $C_{67}H_{75}O_5SbSi \cdot 0.25C_2H_6SO$: C 71.77, H 6.83. Found: C 71.73, H 7.05.

[Bi{^{t}BuC5(Si^{i}Pr$_2$)}] (13). Single crystals of **13** (poor quality) can be obtained from a mixture of pentane/DMSO (2:0.3 mL) at room temperature. Yield 81% (0.101 mmol, 0.114 g). Mp: 260−262 °C. ^{1}H NMR (C_6D_6): δ 1.16 (s, 18H, C(CH_3)$_3$), 1.26 (s, 9H, C(CH_3)$_3$), 1.33 (d, J = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.37 (s, 18H, C(CH_3)$_3$), 1.63 (d, J = 7.2 Hz, 6H, CH(CH_3)$_2$), 2.51 (broad septet, 1H), 2.72 (broad septet, 1H), 3.38 (d, J = 14.4 Hz, 2H, ArCH_2Ar), 3.51 (d, J = 14.7 Hz, 1H, ArCH_2Ar), 4.08 (d, J = 15.3 Hz, 2H, ArCH_2Ar), 4.23 (d, J = 15.3 Hz, 2H, ArCH_2Ar), 4.65 (d, J = 14.7 Hz, 1H, ArCH_2Ar), 5.00 (d, J = 14.4 Hz, 2H, ArCH_2Ar), 7.03 (d, J = 2.4 Hz, 2H, ArH), 7.27 (s, 2H, ArH), 7.29 (s, 2H, ArH), 7.37 (s, 4H, ArH). ^{13}C NMR not available because of fast decomposition in solution. IR (KBr, cm^{-1}): 3045w, 2961vs, 2910vs, 2868vs, 1759w, 1602w, 1504w, 1467vs, 1413m, 1392m, 1362s, 1299s, 1251s, 1199vs, 1123m, 1117m, 1071w, 1020m, 994w, 924s, 883s, 822m, 805w, 784w. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 281 (1.66×10^4), 340 (4.40×10^3). Anal. Calcd for $C_{61}H_{79}O_5BiSi \cdot 1.5C_2H_6SO$: C 61.67, H 7.12. Found: C 61.65, H 7.18.

[Sb{^{t}BuC5{(Si^{i}Pr$_2$)}] (14). Yield 52% (0.0651 mmol, 0.0678 g). Mp: 188−189 °C. ^{1}H NMR (C_6D_6): δ 1.07 (s, 18H, C(CH_3)$_3$), 1.13 (s, 9H, C(CH_3)$_3$), 1.135 (broad septet, 1H, CH(CH$_3$)$_2$), 1.14 (d, J = 11.7 Hz, 6H, CH(CH_3)$_2$), 1.34 (s, 18H, C(CH_3)$_3$), 1.44 (d, J = 11.7 Hz, 6H, CH(CH_3)$_2$), 2.42 (broad septet, 1H, CH(CH$_3$)$_2$), 3.39 (d, J = 14.4 Hz, 2H, ArCH_2Ar), 3.48 (d, J = 14.7 Hz, 1H, ArCH_2Ar), 3.84 (d, J = 15.3 Hz, 2H, ArCH_2Ar), 4.09 (d, J = 15.3 Hz, 2H, ArCH_2Ar), 4.58 (d, J = 14.7 Hz, 1H, ArCH_2Ar), 4.96 (d, J = 14.4 Hz, 2H, ArCH_2Ar), 7.04 (d, J = 2.4 Hz, 2H, ArH), 7.13 (s, 2H, ArH), 7.18 (s, 2H, ArH), 7.27 (s, 4H, ArH). ^{13}C NMR not available because of fast decomposition in solution. IR (KBr, cm^{-1}): 3048m, 2964vs, 2906vs, 2869vs, 1602w, 1585w, 1503m, 1475vs, 1413m, 1392s, 1363s, 1302s, 1248s, 1195vs, 1153s, 1056w, 1020m, 996w, 952m, 925s, 882s, 827s. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 282 (1.44×10^4). Anal. Calcd for $C_{61}H_{79}O_5SiSb$: C 70.30, H 7.64. Found: C 70.56, H 7.44.

[**Bi**{^{t}**BuC5(SiMeVinyl)**}] **(15).** Single crystals of **15** were obtained from a mixture of pentane/THF (2:0.3 mL) at −35 °C. Yield 67% (0.0838 mmol, 0.0909 g). Mp: 236−237 °C. ^{1}H NMR (C_6D_6): δ 1.03 (s, 18H, C(CH_3)$_3$), 1.05 (s, 3H, SiCH_3), 1.21 (s, 9H, C(CH_3)$_3$), 1.35 (s, 18H, C(CH_3)$_3$), 3.42 (d, J = 13.5 Hz, 2H, ArCH_2Ar), 3.48 (d, J = 15.3 Hz, 1H, ArCH_2Ar), 4.12 (d, J = 15.3 Hz, 2H, ArCH_2Ar), 4.24 (d, J = 15.3 Hz, 2H, ArCH_2Ar), 4.57 (d, J = 15.3 Hz, 1H, ArCH_2Ar), 5.14 (d, J = 13.5 Hz, 2H, ArCH_2Ar), 5.68−5.84 (m, 2H, CH=CH_2), 5.90−6.02 (m, 1H, CH = CH$_2$), 7.04 (d, J = 2.1 Hz, 2H, ArH), 7.29 (s, 2H, ArH), 7.37 (d, J = 2.1 Hz, 2H, ArH), 7.40 (s, 4H, ArH). ^{13}C{^{1}H} NMR (C_6D_6): δ 152.5, 148.7, 146.9, 144.7, 138.1, 137.9, 136.1, 135.5, 135.2, 134.5, 134.1, 132.3, 131.3, 126.8, 125.8 (aromatic carbons), 125.4 (CH$_2$=CH), 123.5 (aromatic carbons), 36.5, 36.2 (C(CH$_3$)$_3$), 36.1, 34.4, 34.3 (ArCH$_2$Ar), 33.9 (CH = CH$_2$), 33.7 (C(CH$_3$)$_3$), 32.1 (two carbons overlapping), 31.4 (C(CH$_3$)$_3$), −1.0 (SiCH$_3$). IR (KBr, cm^{-1}): 3050w, 2961vs, 2906vs, 2868vs, 1596w, 1504w, 1475vs, 1413m, 1393m, 1362s, 1295s, 1251s, 1201vs, 1123m, 1006w, 928m, 903m, 879m, 819m, 809m, 744w. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 280 (2.03×10^4), 332 (7.05×10^3). Anal. Calcd for $C_{58}H_{71}O_5BiSi \cdot C_4H_8O$: C 64.34, H 6.88. Found: C 64.19, H 7.17.

[**Sb**{^{t}**BuC5(SiMeVinyl)**}] **(16).** Single crystals of **16** were obtained from a mixture of pentane/THF (2:0.3 mL) at −35 °C. Yield 79% (0.0988 mmol, 0.0986 g). Mp: 180−181 °C. ^{1}H NMR (C_6D_6): δ 1.06 (s, 18H, C(CH_3)$_3$), 1.18 (s, 9H, C(CH_3)$_3$), 1.24 (s, 3H, SiCH_3), 1.32 (s, 18H, C(CH_3)$_3$), 3.40 (d, J = 14.1 Hz, 2H, ArCH_2Ar), 3.51 (d, J = 15.3 Hz, 1H, ArCH_2Ar), 3.86 (d, J = 15.3 Hz, 2H, ArCH_2Ar), 4.01 (d, J = 15.3 Hz, 2H, ArCH_2Ar), 4.66 (d, J = 15.3 Hz, 1H, ArCH_2Ar), 4.95 (d, J = 14.1 Hz, 2H, ArCH_2Ar), 5.72−5.91 (m, 2H, CH=CH_2), 6.05 (dd, J = 4.5 Hz, J = 14.5 Hz, 1H, CH = CH$_2$), 7.05 (d, J = 2.1 Hz, 2H, ArH), 7.19 (s, 2H, ArH), 7.22 (d, J = 2.1 Hz, 2H, ArH), 7.27 (b, 4H, ArH). No ^{13}C NMR available because of fast decomposition of product in solution. IR (KBr, cm^{-1}): 3050m, 2963vs, 2905vs, 2869s, 1759w, 1560w, 1478vs, 1414m, 1393m, 1363s, 1293s, 1257s, 1202vs, 1122s, 1056m, 1008m, 930s, 904s, 879s, 809s, 788m, 749m, 680m. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 282 (1.56×10^4). Anal. Calcd for $C_{58}H_{71}O_5SiSb \cdot C_4H_{10}O_2$: C 68.43, H 7.50. Found: C 68.70, H 7.41.

[**Bi(O^{t}Bu)**{^{t}**BuC5(Bn)(SiMe$_2$)**}] **(17).** Single crystals of **17** were obtained from a mixture of pentane/THF (2:0.3 mL) at −35 °C. Yield 85% (0.106 mmol, 0.131 g). Mp: 244−245 °C. ^{1}H NMR (C_6D_6): δ −1.19 (s, 3H, SiCH_3), −0.04 (s, 3H, SiCH_3), 1.20 (s, 9H, C(CH_3)$_3$), 1.24 (s, 9H, C(CH_3)$_3$), 1.27 (s, 9H, C(CH_3)$_3$), 1.30 (s, 9H, C(CH_3)$_3$), 1.48 (s, 9H, C(CH_3)$_3$), 1.90 (s, 9H, OC(CH_3)$_3$), 3.13 (d, J = 14.4 Hz, 1H, ArCH_2Ar), 3.46 (d, J = 15.3 Hz, 1H, ArCH_2Ar), 3.60 (d, J = 16.2 Hz, 1H, ArCH_2Ar), 3.87 (d, J = 13.2 Hz, 1H, ArCH_2Ar), 3.89 (d, J = 12.3 Hz, 1H, ArCH_2Ar), 4.22 (d, J = 15.3 Hz, 1H, ArCH_2Ar), 4.29 (d, J = 16.2 Hz, 1H, ArCH_2Ar), 4.41 (d, J = 13.2 Hz, 1H, ArCH_2Ar), 4.56 (d, J = 11.4 Hz, 1H, OCH_2Ar), 4.65 (d, J = 11.4 Hz, 1H, OCH_2Ar), 4.82 (d, J = 14.4 Hz, 1H, ArCH_2Ar), 5.44 (d, J = 12.3 Hz, 1H, ArCH_2Ar), 6.97 (d, J = 2.4 Hz, 1H, ArH), 7.07 (d, J = 2.1 Hz, 1H, ArH), 7.16−7.18 (m, 4H, ArH), 7.24 (d, J = 2.4 Hz, 1H, ArH), 7.37−7.39 (m, 3H, ArH), 7.43 (d, J = 2.4 Hz, 1H, ArH), 7.47−7.49 (m, 3H, ArH), 7.64 (d, J = 2.1 Hz, 1H, ArH). ^{13}C{^{1}H} NMR (C_6D_6): δ 155.1, 153.2, 151.9, 150.0, 149.5, 147.7, 144.8, 143.9, 143.5, 143.4, 137.8, 137.4, 136.6, 136.1, 134.8, 133.0, 131.8, 131.2, 129.7 (two signals overlapping), 128.7 (two signals overlapping), 128.6, 128.5, 128.4, 128.1, 127.4, 126.8, 126.5, 126.4, 126.1, 125.6, 124.6, 121.7 (aromatic carbons), 80.3 (OC(CH$_3$)$_3$), 74.2 (OCH$_2$Ar), 38.4, 36.8 (C(CH$_3$)$_3$), 35.5 (OC(CH$_3$)$_3$), 34.9 (C(CH$_3$)$_3$), 34.0, 33.9, 33.7 (ArCH$_2$Ar), 31.84, 31.81, 31.7, 31.6, 31.5 (C(CH$_3$)$_3$), 30.6, 29.4 (C(CH$_3$)$_3$), 29.3, 28.2 (ArCH$_2$Ar), −0.56, −0.98 (SiCH$_3$). IR (KBr, cm^{-1}): 3031m, 2963vs, 2868vs, 2737w, 2712w, 1757w, 1601w, 1513w, 1493s, 1476vs, 1417s, 1392s, 1362vs, 1293vs, 1258vs, 1201vs, 1122vs, 1106m, 1085m, 1018m, 1000w, 942s, 931s, 899vs, 879vs, 821vs, 790w, 742m, 728m, 694m, 675w. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 284 (1.35×10^4). Anal. Calcd for $C_{68}H_{87}O_6BiSi$: C 66.00, H 7.09. Found: C 65.73, H 7.34.

[**Sb(O^{t}Bu)**{^{t}**BuC5(Bn)(SiMe$_2$)**}] **(18).** Single crystals of **18** were obtained from a mixture of pentane/DME (2:0.3 mL) at −35 °C. Yield 87% (0.109 mmol, 0.125 g). Mp: 186−188 °C. ^{1}H NMR (C_6D_6): δ −1.20 (s, 3H, SiCH_3), −0.03 (s, 3H, SiCH_3), 1.18 (s, 9H, C(CH_3)$_3$), 1.20 (s, 9H, C(CH_3)$_3$), 1.26 (s, 9H, C(CH_3)$_3$), 1.31 (s, 9H, C(CH_3)$_3$), 1.47 (s, 9H, C(CH_3)$_3$), 1.82 (s, 9H, OC(CH_3)$_3$), 3.19 (d, J = 14.1 Hz, 1H, ArCH_2Ar), 3.29 (d, J = 16.2 Hz, 1H, ArCH_2Ar), 3.49 (d, J = 13.2 Hz, 2H, ArCH_2Ar), 3.91 (d, J = 13.5 Hz, 1H, ArCH_2Ar), 4.16 (d, J = 16.2 Hz, 1H, ArCH_2Ar), 4.25 (d, J = 13.2 Hz, 2H, ArCH_2Ar), 4.63 (s, 2H, OCH_2Ar), 4.90 (d, J = 14.1 Hz, 1H, ArCH_2Ar), 5.08 (d, J = 13.5 Hz, 1H, ArCH_2Ar), 6.88 (d, J = 2.1 Hz, 1H, ArH), 6.99 (d, J = 2.4 Hz, 1H, ArH), 7.13 (d, J = 2.4 Hz, 2H, ArH), 7.19 (b, 3H, ArH), 7.25 (d, J = 2.4 Hz, 1H, ArH), 7.33 (d, J = 2.4 Hz, 1H, ArH), 7.36 (d, J = 2.1 Hz, 1H, ArH), 7.40 (b, 1H, ArH), 7.42−7.44 (two doublets overlapping, 2H, ArH), 7.54 (d, J = 2.4 Hz, 1H, ArH), 7.62 (d, J = 2.1 Hz, 1H, ArH). ^{13}C{^{1}H} NMR (C_6D_6): δ 155.1, 151.5, 150.0, 149.9, 149.7, 147.4, 144.4, 143.8, 143.7, 143.6, 138.0, 136.0, 135.7, 134.9, 133.6, 132.2, 131.1, 130.8, 129.9, 129.7, 129.2, 128.7, 128.6, 128.4, 128.0, 127.9, 127.8, 127.4, 127.0, 126.4, 126.0, 125.9, 124.8, 122.1 (aromatic carbons), 80.9 (OC(CH$_3$)$_3$), 74.4 (OCH$_2$Ar), 38.7, 36.8, 34.7 (C(CH$_3$)$_3$), 34.1, 34.0, 33.9, 33.8 (ArCH$_2$Ar), 33.7 (OC(CH$_3$)$_3$), 33.4, 31.9 (C(CH$_3$)$_3$), 31.8, 31.63, 31.62, 31.5, 31.4 (C(CH$_3$)$_3$), 28.0 (ArCH$_2$Ar), −0.57, −0.81 (SiCH$_3$). IR (KBr, cm^{-1}): 3030m, 2963vs, 2910vs, 2867vs, 1755w, 1602w, 1478vs, 1416m, 1392m, 1363vs, 1292s, 1260vs, 1200vs, 1121s, 1108m, 1055w, 1021w, 994s, 934s, 905s, 879s, 822s, 810m, 790m, 747m, 729m. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 272 (1.56×10^4), 283 (2.25×10^4). Anal. Calcd for $C_{68}H_{87}O_6SiSb \cdot 1.5C_4H_{10}O_2$: C 69.14, H 8.00. Found: C 69.49, H 7.80.

[Sb(NMe$_2$)\{^{t}BuC5(Bn)(SiMe$_2$)\}] (19). Single crystals of **19** were obtained from a mixture of pentane/THF (2:0.3 mL) at −35 °C. Yield 83% (0.104 mmol, 0.117 g). Mp: 175−176 °C. ^{1}H NMR (C_6D_6): δ −1.16 (s, 3H, SiCH_3), 0.02 (s, 3H, SiCH_3), 1.19 (s, 9H, C(CH_3)$_3$), 1.24 (s, 9H, C(CH_3)$_3$), 1.26 (s, 9H, C(CH_3)$_3$), 1.31 (s, 9H, C(CH_3)$_3$), 1.36 (s, 9H, C(CH_3)$_3$), 2.96 (s, 6H, N(CH_3)$_2$), 3.21 (d, J = 14.4 Hz, 1H, ArCH_2Ar), 3.45 (d, J = 13.8 Hz, 1H, ArCH_2Ar), 3.50 (d, J = 12.6 Hz, 1H, OCH_2Ar), 3.51 (d, J = 12.6 Hz, 1H, OCH_2Ar), 3.93 (d, J = 13.8 Hz, 1H, ArCH_2Ar), 4.20−4.35 (three doublets overlapping, 3H, ArCH_2-Ar), 4.64 (d, J = 16.8 Hz, 1H, ArCH_2Ar), 4.68 (d, J = 16.8 Hz, 1H, ArCH_2Ar), 4.92 (d, J = 14.4 Hz, 1H, ArCH_2Ar), 5.11 (d, J = 12.3 Hz, 1H, ArCH_2Ar), 6.94 (d, J = 2.4 Hz, 1H, ArH), 7.11−7.17 (m, 3H, ArH), 7.20 (s, 1H, ArH), 7.22 (b, 3H, ArH), 7.37 (d, J = 2.4 Hz, 1H, ArH), 7.40 (d, J = 2.4 Hz, 1H, ArH), 7.42 (s, 1H, ArH), 7.45 (b, 2H, ArH), 7.46 (s, 1H, ArH), 7.55 (d, J = 2.4 Hz, 1H, ArH). ^{13}C\{^{1}H\} NMR (C_6D_6): δ 155.0, 152.6, 151.0, 150.2, 149.8, 146.6, 144.4, 143.7, 143.5, 143.1, 138.1, 135.8, 135.2, 134.6, 133.4, 131.5, 131.4, 130.6, 130.3, 129.9, 129.5, 129.2, 128.7, 128.5, 128.4, 128.3, 128.0, 127.0, 126.6, 126.5, 126.1, 126.0, 124.6, 122.1 (aromatic carbons), 74.4 (OCH$_2$Ar), 38.9 (C(CH$_3$)$_3$), 38.4 (N(CH$_3$)$_2$), 37.4, 37.0, 34.5 (C(CH$_3$)$_3$), 34.1, 34.0, 33.9 (ArCH$_2$Ar), 33.9 (C(CH$_3$)$_3$), 32.9 (ArCH$_2$Ar), 31.62 (two peaks overlapping), 31.59 (two peaks overlapping), 31.4 (C(CH$_3$)$_3$), 28.1 (ArCH$_2$Ar), −0.41, −1.02 (SiCH$_3$). IR (KBr, cm^{-1}): 3031m, 2961vs, 2905vs, 2868s, 1767w, 1600w, 1479vs, 1416m, 1393m, 1362s, 1293s, 1259s, 1202vs, 1122s, 1019w, 945m, 904s, 879s, 823s, 729m. UV/vis λ_{max}/nm (C_6H_6) (ε/dm^3 mol^{-1} cm^{-1}): 283 (1.80×10^4). Anal. Calcd for $C_{66}H_{84}NO_5SbSi \cdot C_4H_8O$: C 70.45, H 7.77. Found: C 70.18, H 7.49.

5.4. General X-ray Structure Information. X-ray data for **3**, **6**, **8**, **9**, **12**, **15**, **16**, and **17**−**19** were collected on a SMART Bruker 1000 CCD detector diffractometer at low temperature using Mo Kα radiation. The crystallographic data and some details of the data collection and refinement of the structures are given in Table 5. Absorption corrections in all cases were applied by SADABS.[71] All structures were solved by direct methods and subsequent difference Fourier syntheses and refined by full matrix least-squares methods against F^2 (SHELX 97).[72] Disorder for some *tert*-butyl groups was due to a 2-fold axis and was modeled using partial occupancies (PART instruction).[72] The O(6) and S(1) atoms in a DMSO molecule of complex **9** presented disorder and were modeled using a 50/50% atom occupancy. Some other disordered molecules and solvents were refined using a combination of restraints on the distances while keeping the disordered parts similar (use of the SADI and SAME instructions).[72] All non-hydrogen atoms were refined with anisotropic displacement coefficients, except atoms of disordered fragments, which were refined with isotropic thermal parameters. The H atoms in structures were taken in calculated positions. In the crystal structures of complexes **18** and **19**, highly disordered molecules (6 DME molecules in **18** and 1 THF molecule in **19**) were treated with the program SQUEEZE.[73] Corrections of the X-ray data for **18** and **19** by SQUEEZE (309 and 42 electron cell, respectively), were close to the required values (300 and 40 electron cell, respectively). The programs ORTEP32[74] and POV-ray[75] were used to generate the X-ray structural diagrams pictured in this article.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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