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Synthesis and Structure of Silyl-Substituted Bis(cyclopentadienyl) Scandium(III) Halide Complexes

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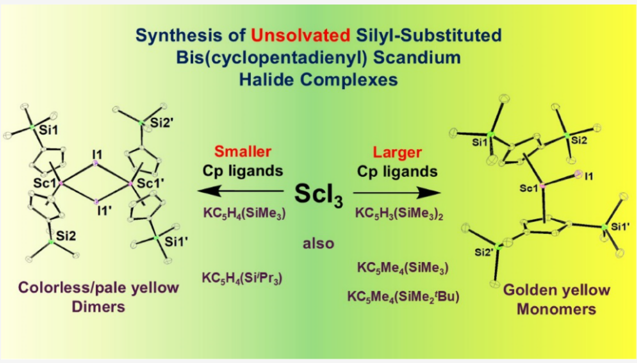
ABSTRACT: Despite the importance of bis(cyclopentadienyl) scandium(III) halide complexes as precursors in the development of scandium metallocene chemistry, relatively few examples of this class have been structurally characterized. Since the cyclopentadienyl ring substitution pattern and the halide identity can have a major influence on organoscandium complex synthesis and reactivity, it is critical to have a variety of well-characterized $[(C_5R_5)_2ScX]_n$ starting materials (R = H, alkyl, silyl; X = halide) available for exploration of this area. To remedy this deficiency, reactions between ScX_3 (X = Cl and I) and 2 equiv of a variety of potassium cyclopentadienide reagents have been examined. This has provided, in good crystalline yield, the compounds $[C_5H_3(SiMe_3)_2]_2ScI$, $[C_5Me_4(SiMe_3)]_2ScI$, $[C_5Me_4(SiMe_2{}^tBu)]_2ScI$, $\{[C_5H_4(SiMe_3)]_2Sc(\mu\text{-}I)\}_2$, $\{[C_5H_4(Si^iPr_3)]_2Sc(\mu\text{-}I)\}_2$, and $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}Cl)\}_2$, each of which has been characterized by X-ray crystallography, elemental analysis, NMR spectroscopy (^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, and ^{45}Sc), and infrared spectroscopy. The study has also revealed the facile cocrystallization of the oxide $\{[C_5H_3(SiMe_3)_2]_2Sc\}_2(\mu\text{-}O)$ and hydroxide $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}OH)\}_2$ impurities from preparations of $[C_5H_3(SiMe_3)_2]_2ScI$ using samples of ScI_3 that presumably contain an oxide contaminant.



■ INTRODUCTION

Bis(cyclopentadienyl) scandium(III) halide complexes represent an important class of starting materials for organoscandium chemistry due to the ease with which the halide ligand can be replaced.[1−12] However, relatively few examples have been characterized by X-ray diffraction. Atwood and Smith reported the first synthesis and crystallographic characterization of the dimeric Sc(III) complex $[(C_5H_5)_2Sc(\mu\text{-}Cl)]_2$[1] in 1973, while the trimeric fluoride analogue $[(C_5H_5)_2Sc(\mu\text{-}F)]_3$[2] was synthesized over a decade later by Bottomley et al. in 1985. In 1998, the mixed cyclopentadienyl complex, $(C_5Me_4H)(C_5H_4CH_2CH_2NMe_2)ScCl$,[5] was characterized by Schumann and co-workers, and Conley and co-workers obtained the X-ray crystal structures[11] of the unsolvated monometallic $(C_5Me_5)_2ScX$ complexes (X = F, Cl, Br, and I[3]) in 2018. The X-ray crystal structure of the unsolvated $(C_5H_2{}^tBu_3)_2ScI$[13] was also recently reported, however there are no further examples of unsolvated Sc(III) $[(C_5R_5)_2ScX]_n$ (R = H, alkyl, silyl; X = halide) complexes in the literature to our knowledge. The THF-solvated complexes $(C_5Me_5)_2ScCl(THF)$[14] and $(C_5Me_4H)_2ScCl(THF)$[15] have been structurally characterized as well as the ansa-metallocene "ate" salt $\{Me_2Si[C_5H_2(CHMe_2)_2]_2\}Sc(\mu\text{-}Cl)_2Li(THF)_2$.[6]

Recently, the bis(1,2,4-tri-*tert*-butylcyclopentadienyl) scandium iodide complex $(C_5H_2{}^tBu_3)_2ScI$ proved to be a critical precursor in the potassium graphite (KC_8) reduction reaction that generated the first crystallographically characterized neutral Sc(II) metallocene $(C_5H_2{}^tBu_3)_2Sc$.[13] The steric bulk of the cyclopentadienyl ligand and its substitution pattern is evidently important in this system because KC_8 reductions of the analogous $(C_5Me_5)_2ScI$ and $[C_5H_3(SiMe_3)_2]_2ScI$ did not give isolable $(C_5R_5)_2Sc$ products, although the latter complex provided the anionic Sc(II) metallocene, $\{[C_5H_3(SiMe_3)_2]_2ScI\}^{1-}$.[13] The identity of the halide also appears to be important because the KC_8 reduction of "$[C_5H_3(SiMe_3)_2]_2ScCl$" has not generated a crystallizable Sc(II) product. The present study was initiated to remedy the deficiency in the literature of unsolvated crystallographically characterized $[(C_5R_5)_2ScX]_n$ complexes with a variety of cyclopentadienyl ligands.

The bis(cyclopentadienyl) Sc(III) halide complex $[C_5H_3(SiMe_3)_2]_2ScI$ was originally reported by Lappert and co-workers in 2012 and was prepared from the reaction between $ScI_3(THF)_3$ and 2 equiv of $NaC_5H_3(SiMe_3)_2$ followed

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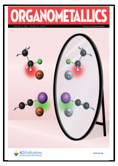

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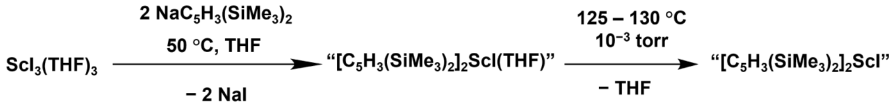
Scheme 1. Original Preparation of "$[C_5H_3(SiMe_3)_2]_2ScI$" Reported by Lappert and Co-Workers[9]



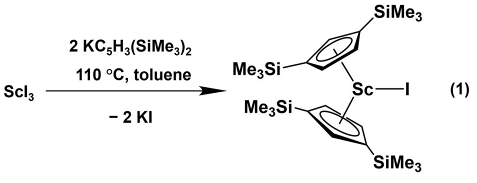
by desolvation under reduced pressure at elevated temperatures, as shown in Scheme 1.[9] Although it was reported that the THF-solvated complex $[C_5H_3(SiMe_3)_2]_2ScI(THF)$ could be isolated as nearly colorless crystals and the solvent-free complex $[C_5H_3(SiMe_3)_2]_2ScI$ could be isolated as yellow crystals, X-ray crystal structures for neither complex were provided to our knowledge.

Our initial attempts to characterize $[C_5H_3(SiMe_3)_2]_2ScI$ by X-ray diffraction surprisingly led to a crystal structure containing presumably a mixture of the oxide $\{[C_5H_3(SiMe_3)_2]_2Sc\}_2(\mu\text{-}O)$ and hydroxide $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}OH)\}_2$ (see below), which initiated this study.

Since $[(C_5R_5)_2ScX]_n$ complexes are critical to the rapidly developing chemistry of Sc(II), we revisited the synthesis of $[C_5H_3(SiMe_3)_2]_2ScI$ and examined the synthesis of the chloride variation $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}Cl)\}_2$, and four cyclopentadienyl variations of $[(C_5R_5)_2ScI]_n$ complexes. We describe here a general synthesis for these unsolvated bis(cyclopentadienyl) Sc(III) halide complexes and their corresponding crystal structures that should put this area of organoscandium precursors on a firm basis of structurally characterized compounds.

RESULTS

X-ray Crystal Structure of Monometallic $[C_5H_3(SiMe_3)_2]_2ScI$, 1. Previously, it was found that the reaction between ScI_3[16] and 2 equiv of $KC_5H_2{}^tBu_3$ in toluene at 110 °C gave unsolvated $(C_5H_2{}^tBu_3)_2ScI$ in good yields.[13] In a preparation analogous to that procedure, ScI_3 was treated with 2 equiv of $KC_5H_3(SiMe_3)_2$ in a sealed vessel in toluene at 110 °C over 16 h. This generated light-yellow solids upon workup identified as $[C_5H_3(SiMe_3)_2]_2ScI$, **1**, by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy when compared to Lappert's initial report, as shown in eq 1.[9]



1

Crystallization from saturated toluene solutions stored at −35 °C yielded pale-yellow crystals of monometallic **1** in 50% crystalline yield suitable for study by X-ray diffraction, as shown in Figure 1.

Complex **1** crystallizes as a monomer in the *P*2/*c* space group with half of a molecule in the asymmetric unit. The molecule is located on a 2-fold rotation axis that is coincident with the Sc−I bond such that the two cyclopentadienyl ligands are crystallographically equivalent. Complex **1** has a bent metallocene structure with a Sc−Cnt distance (Cnt = cyclopentadienyl ring centroid) of 2.146 Å and a Cnt−Sc−Cnt angle of 134.8° (Table 1). The average Sc−Cnt distance of **1** is similar to the 2.164 Å analogous distance of $(C_5Me_5)_2ScI$[11] and shorter than the 2.229 Å distance in $(C_5H_2{}^tBu_3)_2ScI$.[13] However, the Cnt−Sc−Cnt angle of **1** is smaller than that of both $(C_5Me_5)_2ScI$[11] (140.5°) and $(C_5H_2{}^tBu_3)_2ScI$[13] (147.0°). The 2.800(4) Å Sc−I distance of **1** is in a range typical for Sc(III) complexes containing iodide ligands; e.g., $(C_5Me_5)_2ScI$[11] and $(C_5H_2{}^tBu_3)_2ScI$[13] have analogous distances of 2.8194(3) Å and 2.8569(3) Å, respectively.

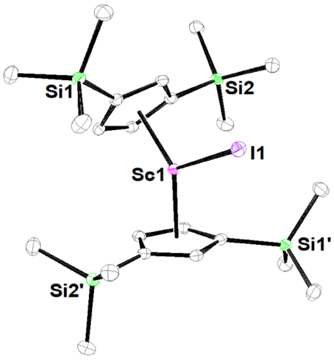
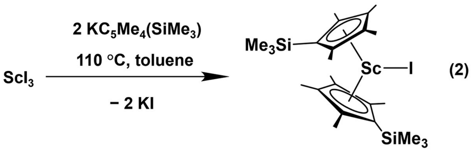


Figure 1. Molecular structure of $[C_5H_3(SiMe_3)_2]_2ScI$, **1**, with ellipsoids drawn at the 50% probability level and selective atom labeling. Hydrogen atoms are not shown for clarity.

Monometallic $[C_5Me_4(SiMe_3)]_2ScI$, 2 and $[C_5Me_4(SiMe_2{}^tBu)]_2ScI$, 3. Trialkylsilyl variants of the common $(C_5Me_5)^{1-}$ ligand were also examined for comparison with the known monometallic $(C_5Me_5)_2ScI$[11] and $(C_5H_2{}^tBu_3)_2ScI$[13] complexes. Thus, the reaction between ScI_3 and 2 equiv of $KC_5Me_4(SiMe_3)$ produced bright yellow solids that crystallized from saturated hexane solutions stored at −35 °C as the monometallic bis(cyclopentadienyl) Sc(III) iodide complex $[C_5Me_4(SiMe_3)]_2ScI$, **2**, in 53% crystalline yield, as shown in Figure 2, eq 2.



2

The $[C_5Me_4(SiMe_2{}^tBu)]^{1-}$ ligand was also explored because recent studies of uranium metallocenes with this ligand revealed that its complexes had significantly different chemistry compared to analogous complexes of $(C_5Me_5)^{1-}$.[17] To examine $[C_5Me_4(SiMe_2{}^tBu)]^{1-}$ chemistry with the much smaller rare-earth metal scandium, ScI_3 was treated with 2 equiv of $KC_5Me_4(SiMe_2{}^tBu)$ using the same procedure that was used to prepare **2** as described in eq 2. This reaction afforded $[C_5Me_4(SiMe_2{}^tBu)]_2ScI$, **3**, which was crystallized as bright yellow blocks from saturated hexane solutions stored at −35 °C in 54% crystalline yield, as shown in Figure 3 and eq 3.

Complexes **2** and **3** both crystallize as monomers in the *Pbcn* and *C*2/*c* space groups, respectively, with half of a molecule in the asymmetric unit. As with the structure of complex **1**,

Table 1. Selected Interatomic Distances (Å) and Angles (deg) of Crystallographically Characterized Monometallic Unsolvated Bis(cyclopentadienyl) Scandium Halide Complexes Ordered in Increasing Sc−Cnt Distance

Sc(III) complex	Sc−Cnt (av.)	Cnt−Sc−Cnt	Sc−X	Cnt−Sc−X
$[C_5H_3(SiMe_3)_2]_2ScI$, **1**	2.146	134.8	2.800(4)	112.6
$(C_5Me_5)_2ScBr$[11]	2.157	141.7	2.584(4)	108.9, 109.4
$(C_5Me_5)_2ScCl$[11,a]	2.158	142.0	2.417(2)	109.0
$(C_5Me_5)_2ScI$[11]	2.164	140.4	2.819(3)	108.9, 109.6
$(C_5Me_5)_2ScF$[11]	2.164	143.4	1.927(1)	108.3
$[C_5Me_4(SiMe_3)]_2ScI$, **2**	2.165	139.1	2.860(5)	110.4
$[C_5Me_4(SiMe_2{}^tBu)]_2ScI$, **3**	2.181	143.5	2.802(6)	108.3
$(C_5H_2{}^tBu_3)_2ScI$[13]	2.229	147.0	2.857(3)	105.9, 107.1

[a] Values were averaged between each crystallographically unique scandium complex in the asymmetric unit.

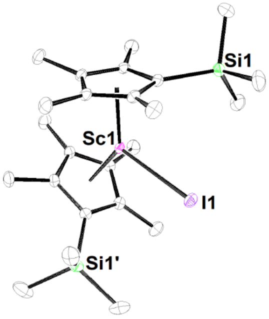


Figure 2. Molecular structure of $[C_5Me_4(SiMe_3)]_2ScI$, **2**, with ellipsoids drawn at 50% probability level and selective atom labeling. Hydrogen atoms are not shown for clarity.

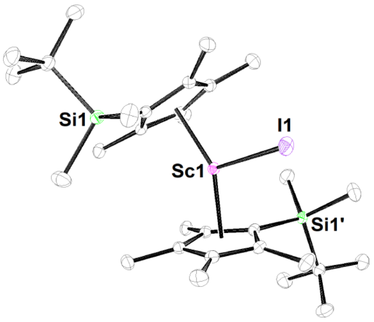
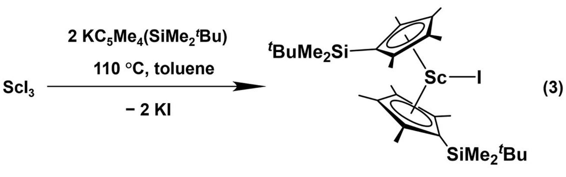


Figure 3. Molecular structure of $[C_5Me_4(SiMe_2{}^tBu)]_2ScI$, **3**, with ellipsoids drawn at 50% probability level and selective atom labeling. Hydrogen atoms are not shown for clarity.



3

complexes **2** and **3** are each located on a 2-fold rotation axis that is collinear with the Sc−I bond. Complex **2** has an average Sc−Cnt distance of 2.165 Å and a Cnt−Sc−Cnt angle of 139.1°, while complex **3** has a similar analogous distance of 2.181 Å and a wider angle of 143.5°. Table 1 shows that the average Sc−Cnt distances of **2** and **3** are longer than those of **1** but similar to those of $(C_5Me_5)_2ScI$[11] and shorter than those of $(C_5H_2{}^tBu_3)_2ScI$.[13] This is consistent with the difference in steric bulk between the cyclopentadienyl ligands and the fact that $(C_5H_2{}^tBu_3)_2ScI$ has the widest Cnt−Sc−Cnt angle of all of the bis(cyclopentadienyl) scandium halide complexes discussed in this paper.

Bimetallic $\{[C_5H_4(SiMe_3)]_2Sc(\mu\text{-}I)\}_2$, 4 and $\{[C_5H_4(Si^iPr_3)]_2Sc(\mu\text{-}I)\}_2$, 5. To compare the scandium chemistry of the *bis*(trimethylsilyl)cyclopentadienyl ligand to that of the smaller *mono*(trimethylsilyl)cyclopentadienyl ligand, the synthesis of "$[C_5H_4(SiMe_3)]_2ScI$" was pursued. The reaction between ScI_3 and 2 equiv of $KC_5H_4(SiMe_3)$ using the same procedure as described for the synthesis of **1** gave colorless solids upon workup rather than the light-yellow solids described for complex **1**. Crystallization from saturated toluene solutions stored at −35 °C yielded colorless X-ray quality crystals of the dimeric species $\{[C_5H_4(SiMe_3)]_2Sc(\mu\text{-}I)\}_2$, **4**, as shown in Figure 4 and eq 4.

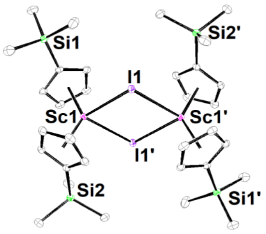
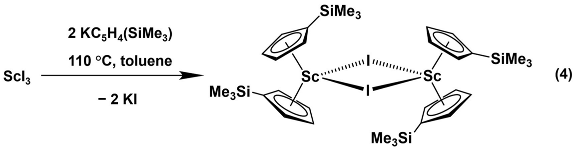


Figure 4. Molecular structure of $\{[C_5H_4(SiMe_3)]_2Sc(\mu\text{-}I)\}_2$, **4**, with ellipsoids drawn at the 50% probability level and selective atom labeling. Hydrogen atoms are not shown for clarity.



4

Complex **4** crystallizes as a centrosymmetric dimer in the $P\bar{1}$ space group. The molecule lies on an inversion center that is located in the center of the plane formed by the iodine and scandium atoms. Each scandium atom binds two cyclopentadienyl ligands in an η^5 fashion and two bridging iodide ligands in a distorted tetrahedral geometry with respect to the cyclopentadienyl ring centroids and iodide ligands. The average Cnt−Sc−I angle of 107.9° is close to the 109.5° angle of a tetrahedral compound, however the Cnt−Sc−Cnt angle is 131.5° and the I−Sc−I angle is 82.9 (1)° (Table 2). This leads to a τ_4 value of 0.85 with respect to the scandium atoms, where τ_4 = 1.00 for a perfect tetrahedral geometry.[18] The 2.182 Å average Sc−Cnt distance in **4** is similar to that in

Table 2. Selected Bond Distances (Å) and Angles (deg) of Crystallographically Characterized Bimetallic Bis(cyclopentadienyl) Scandium Halide and Oxide Complexes in Order of Increasing Sc−Cnt Distance

Sc(III) complex	Sc−Cnt (av.)	Cnt−Sc−Cnt	Sc−X (X = O, Cl, I)	Cnt−Sc−X (X = O, Cl, I)	Sc···Sc
$[(C_5H_5)_2Sc(\mu\text{-}Cl)]_2$[1]	2.170	129.5, 131.5, 130.5	2.583(5), 2.584(4), 2.581(5), 2.559(5), 2.57(2), 2.565(2)	109.5, 108.3, 108.8, 108.7, 106.7, 107.1, 109.2, 109.2, 109.1, 107.6, 108.6, 108.6	3.92(1), 3.89(1)
$\{[C_5H_4(Si^iPr_3)]_2Sc(\mu\text{-}I)\}_2$, **5**	2.181	133.8	2.969(3), 2.976(3)	108.5, 105.9, 105.1, 108.4	4.424(3)
$\{[C_5H_4(SiMe_3)]_2Sc(\mu\text{-}I)\}_2$, **4**	2.182	131.5	2.955(2), 3.002(4)	109.0, 107.4, 106.2, 109.1	4.466(7)
$\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}Cl)\}_2$, **6**	2.202	131.2	2.545(7), 2.548(7)	109.7, 109.6, 106.8, 106.5	3.845(8)
$[(C_5Me_4H)_2Sc]_2(\mu\text{-}O)$[15]	2.205	132.5, 132.8	1.910(5), 1.925(5)	113.9, 113.6, 113.3, 113.7	3.830(2)
$\{[C_5H_3(SiMe_3)_2]_2Sc\}_2(\mu\text{-}O)$, 7	2.224	130.8	1.868(4)	111.5 117.8	3.736(6)

1, but the 2.955(2) and 3.002(4) Å Sc−I distances are longer, which is typical of bridging versus terminal ligands.

Given the surprising differences in the Th(III) chemistry of the $[C_5H_4(SiMe_3)]^{1-}$ ligand versus its triisopropyl analogue $[C_5H_4(Si^iPr_3)]^{1-}$,[19] the synthesis and structure of a bis(cyclopentadienyl) scandium iodide complex of the latter ligand were also pursued. Like the synthesis of complex **4**, the reaction between ScI_3 and 2 equiv of $KC_5H_4(Si^iPr_3)$ in toluene at 110 °C provided colorless solids upon workup. Crystallization from saturated toluene solutions stored at −35 °C yielded colorless X-ray quality crystals of the dimeric species $\{[C_5H_4(Si^iPr_3)]_2Sc(\mu\text{-}I)\}_2$, **5**, as shown in Figure 5 and eq 5.

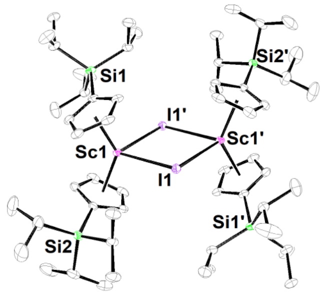
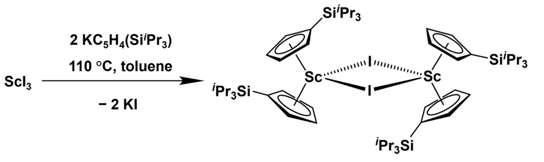


Figure 5. Molecular structure of $\{[C_5H_4(Si^iPr_3)]_2Sc(\mu\text{-}I)\}_2$, **5**, with ellipsoids drawn at the 50% probability level and selective atom labeling. Hydrogen atoms are not shown for clarity.



(5)

5

Complex **5** crystallizes as a centrosymmetric dimer in the $P\overline{1}$ space group, as was found for **4**, with the molecule on an inversion center located in the center of the plane formed by the iodine and scandium atoms. Complex **5** has a similar molecular structure and metrical data compared to **4**, with a similar τ_4 value of 0.83 (Table 2) despite the difference in steric bulk of the cyclopentadienyl ligands.[19]

Bimetallic $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}Cl)\}_2$, 6.

In pursuit of another crystalline bis(cyclopentadienyl) scandium halide with the $[C_5H_3(SiMe_3)_2]^{1-}$ ligand, the synthesis of the analogous scandium chloride complex "$[C_5H_3(SiMe_3)_2]_2ScCl$" was explored. The reaction between $ScCl_3$ and 2 equiv of $KC_5H_3(SiMe_3)_2$ in toluene at 110 °C yielded off-white solids upon workup. Saturated toluene solutions of this material stored at −18 °C yielded X-ray quality crystals that were identified as the dimeric complex $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}Cl)\}_2$, **6**, in 88% crystalline yield, as shown in Figure 6 and eq 6.

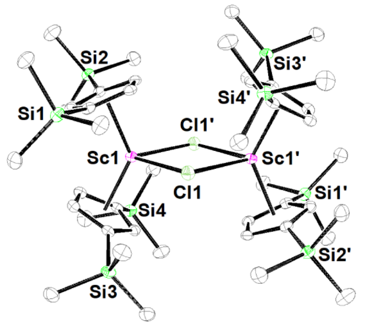
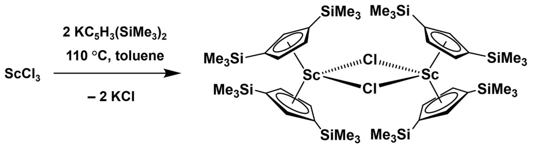


Figure 6. Molecular structure of $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}Cl)\}_2$, **6**, with ellipsoids drawn at the 50% probability level and selective atom labeling. Hydrogen atoms are not shown for clarity.



(6)

6

The bimetallic $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}Cl)\}_2$, **6**, crystallizes in the $P2_1/n$ space group, again with half of the molecule in the asymmetric unit. An inversion center is located in the middle of the chlorine and scandium atoms in the asymmetric unit. In contrast to complex **1**, complex **6** crystallizes as a dimeric species in the solid state when the halide is switched from an iodide to a chloride ligand. The 2.202 Å average Sc−Cnt distance of the formally eight-coordinate dimeric chloride complex **6** is larger than the 2.146 Å analogous distance in the seven-coordinate iodide complex of the same ligand $[C_5H_3(SiMe_3)_2]_2ScI$, **1**, which is consistent with the larger coordination number. The 131.2° Cnt−Sc−Cnt angle is slightly more bent than the 134.8° angle of **1**. Compared to complexes **4** and **5**, the 3.845(8) Å Sc···Sc distance in the chloride-bridged **6** is shorter than the Sc···Sc distances in the iodide-bridged complexes **4** (4.466(7) Å) and **5** (4.424(3) Å), which is consistent with the difference in the ionic radii of the halide atoms.[20] Furthermore, complex **6** has a τ_4 value of 0.84, which is very similar to those of **4** and **5**.

Bimetallic Oxide $\{[C_5H_3(SiMe_3)_2]_2Sc\}_2(\mu\text{-}O)$, 7, and Hydroxide $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}OH)\}_2$, 8. Our initial attempts to synthesize and obtain crystals of $[C_5H_3(SiMe_3)_2]_2ScI$, **1**, following the procedure described above resulted in the isolation of X-ray quality crystals of a bridging oxo complex $\{[C_5H_3(SiMe_3)_2]_2Sc\}_2(\mu\text{-}O)$, **7** (Figure 7), which cocrystallized presumably with the bridging hydroxide complex $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}OH)\}_2$, **8** (Figure S64). The crystallographic data were modeled as a 75:25 mixture of **7**:**8**. Further attempts to synthesize and grow X-ray quality crystals of **1** with the same batch of ScI_3 made from Sc metal and NH_4I[16] yielded similar results. Since it was known that the ScI_3 preparation required stringent methods to obtain pure material,[16] a new batch of ScI_3 was generated and used to form complex **1** free of oxide **7** and hydroxide **8**. Consequently, we suspect that the earlier sample of ScI_3 was contaminated with an oxygen-containing impurity that can be eliminated with the proper procedure.[16] Evidently, the bimetallic oxide **7** and the hydroxide **8** were the least soluble and most readily crystallizable materials in a mixture of **1**, **7**, and **8**. We include **7** and **8** in this paper to show how sensitive these organometallic scandium complexes are to oxygen-containing impurities.

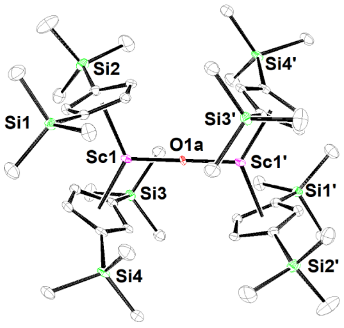


Figure 7. Molecular structure of $\{[C_5H_3(SiMe_3)_2]_2Sc\}_2(\mu\text{-}O)$, **7**, drawn at the 50% probability level with selective atom labeling. Hydrogen atoms are not shown for clarity. The bridging hydroxide $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}OH)\}_2$, **8**, is not shown here.

Complex **7** is an example of an oxo-bridged bis(cyclopentadienyl) bimetallic complex that is commonly encountered in the organometallic chemistry of the oxophilic rare-earth metals.[21−25] For example, most reactions of $(C_5Me_5)_2Sm$ can use the NMR peak of the $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$[21] oxide impurity at 0.06 ppm in C_6D_6 to calibrate the spectrum of the main product since the oxide is almost always formed as a byproduct. Similarly, the synthesis of the sterically crowded $(C_5Me_5)_3La$ was previously reported to be commonly complicated by the generation of $[(C_5Me_5)_2La]_2(\mu\text{-}O)$.[26] Hydroxide complexes like **8** have previously been observed as hydrolysis products in rare-earth organometallic chemistry, however relatively few X-ray crystal structures have been reported.[27−31] To the best of our knowledge, there are no other crystallographically characterized examples of bis(cyclopentadienyl) scandium(III) hydroxide complexes.

The cocrystallization of a bimetallic oxide or hydroxide with another bimetallic complex of similar structure is also a common problem with oxygen-containing contaminants. For example, the oxide complexes of Nd[32] and Gd,[33] $[K_2(18\text{-crown-}6)_3][\{(R_2N)_3Ln\}_2(\mu\text{-}O)]$, cocrystallize with the $(N{=}N)^{2-}$ complexes, $[K_2(18\text{-crown-}6)_3][\{(R_2N)_3Ln\}_2(\mu\text{-}\eta^x{:}\eta^x\text{-}N_2)]$ (Ln = Nd, Gd; R = $SiMe_3$). In another example, cocrystallization of $\{[C_5H_4(SiMe_3)]_2Nd(\mu\text{-}OH)\}_2$ with $[C_5H_4(SiMe_3)]_3NdGa(C_5Me_5)$ was observed.[34] Also, a pair of closely related scandium oxide and hydroxide complexes of a pentadentate pyridine-based pyrazolylborate ligand system has been reported by Piers and co-workers.[35]

Complexes **7** and **8** cocrystallize in the $P2_1/n$ space group with half of the dimeric molecule in the asymmetric unit. An inversion center is located on the bridging oxygen atom of **7** which is also between the scandium atoms and the two μ-hydroxide ligands (see Supporting Information). Complex **7** comprises about 75% of the crystal structure and has a 180° Sc−O−Sc angle and a Sc−O distance of 1.868(4) Å, whereas for the minor component, **8**, which has a 111.4(3)° Sc−O−Sc angle, the analogous average Sc−O distance is longer at 2.261(6) Å. For comparison, the only other previously reported bimetallic bis(cyclopentadienyl) scandium oxo complex is $[(C_5Me_4H)_2Sc]_2(\mu\text{-}O)$[15] which has a similar average Sc−O distance of 1.917(5) Å and a close to linear O−Sc−O angle of 174.1(3). Both the 2.224 Å average Sc−Cnt distance and the 130.8 °Cnt−Sc−Cnt angle of **7** are similar to the values in $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}Cl)\}_2$, **6** (Table 2). However, the 3.736(6) Å Sc···Sc distance of **7** is shorter than the 3.845(4) Å distance of **6**.

NMR Analyses. Complexes **1**−**4** exhibit diamagnetic ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra containing resonances for just one type of cyclopentadienyl environment. This indicates that the cyclopentadienyl ligands are all equivalent in solution for these Sc(III) complexes and no monomer−dimer equilibria are observed at room temperature.

Solution-phase ^{45}Sc NMR data were also obtained for complexes **1**−**6** and the chemical shifts and associated line width at half-height values are summarized in Table 3 along with data on other previously reported bis(cyclopentadienyl) Sc(III) complexes. In addition, data are reported on samples of **1**−**6** in deuterobenzene (C_6D_6) to which a few drops of THF were added. These samples are labeled **1+THF** to **6+THF**, and the expected compositions based on the ^1H, $^{13}C\{^1H\}$, and ^{29}Si NMR spectra are noted.

In general, the ^{45}Sc NMR spectra for monomeric complexes **1**−**3** show one broad resonance in neat C_6D_6 at room temperature in the range of 200−270 ppm with line widths of approximately 3200−4300 Hz. These data are similar to those of the unsolvated bis(cyclopentadienyl) Sc(III) halides that have been studied previously by Conley and co-workers.[11] For bimetallic complex **4**, the ^{45}Sc NMR signal has a much lower chemical shift at 71.2 ppm and a line width value of about 1900 Hz that is narrower than those of the monometallic complexes. The sharper line width and lower chemical shift are consistent with a Sc(III) metal center that has a higher symmetry local environment and higher coordination number than that of complexes **1**−**3**.[38,39] For example, Gauvin et al.

Table 3. ^{45}Sc NMR Chemical Shifts (ppm) and Line Widths at Half-Height Values (Hz) for Selected Bis(cyclopentadienyl) Sc(III) Complexes Ordered in Decreasing Chemical Shift

Complex	Chemical Shift (ppm)	$\Delta\nu_{1/2}$ (Hz)
$[C_5Me_4(SiMe_3)]_2ScI$, **2**	264.2	3200
$[C_5Me_4(SiMe_2{}^tBu)]_2ScI$, **3**	263.8	3300
$(C_5Me_5)_2ScI$[11]	256.9	-
$[C_5H_3(SiMe_3)_2]_2ScI$, **1**	208.3	4300
$(C_5Me_5)_2ScBr$[11]	203.3	-
$[(C_5Me_4H)_2Sc][(\mu\text{-Ph})BPh_3]$[15]	190	7800
$[C_5Me_4(SiMe_3)]_2ScI(THF)$, **2+THF**	176.3	340
$\{[C_5H_4(Si^iPr_3)]_2Sc(\mu\text{-I})\}_2$, **5**	172.8[a]	7000[a]
$[C_5Me_4(SiMe_2{}^tBu)]_2ScI(THF)$, **3+THF**	167.5	850
$(C_5Me_4H)_2Sc(\eta^3\text{-}C_3H_5)$[15]	153	350
$\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-Cl})\}_2$, **6**	138.3[a]	2700[a]
$[C_5H_3(SiMe_3)_2]_2ScI(THF)$, **1+THF**	81.9	370
$\{[C_5H_4(SiMe_3)]_2Sc(\mu\text{-I})\}_2$, **4**	71.2[b]	1900[b]
$[C_5H_4(Si^iPr_3)]_2ScI(THF)$, **5+THF**	68.9	540
$(C_5H_5)_2Sc(BH_4)$[36]	67.5	250
$(C_5Me_5)_2ScF$[11]	65.7	-
$[C_5H_4(SiMe_3)]_2ScI(THF)$, **4+THF**	59.7	160
$(C_5Me_4H)_2ScCl(THF)$[15]	55	400
$\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-Cl})\}_2$, **6**	43.3[b]	1900[b]
$\{[C_5H_4(Si^iPr_3)]_2Sc(\mu\text{-I})\}_2$, **5**	34.5[b]	2600[b]
$[C_5H_3(SiMe_3)_2]_2ScCl(THF)$, **6+THF**	29.9	940
$\{(C_5H_5)_2Sc(\mu\text{-Cl})\}_2$[37]	−9.5	85

[a] Resonance assigned to the monomeric species in neat C_6D_6. [b] Resonance assigned to the dimeric species in neat C_6D_6.

reported that coordination of the neutral Lewis base triphenylphosphine oxide to $Sc[N(SiMe_3)_2]_3$ shifted the ^{45}Sc NMR resonance from 396 to 350 ppm.[38] Their studies on Sc(III) amide complexes grafted onto silica also showed peak sharpening in the ^{45}Sc NMR spectra upon coordination of triphenylphosphine oxide.[38]

The ^{1}H NMR spectra for complexes **5** and **6** display two different resonances with different line widths (see Supporting Information). These spectra presumably arise due to the presence of both monomeric and dimeric species in equilibrium in neat C_6D_6 at room temperature. The higher chemical shift resonance with a broader line width is assigned to the monomeric form, and the lower chemical shift resonance with the sharper line width is assigned to the dimeric form on the basis that higher coordinate scandium complexes are observed to have relatively lower chemical shifts and sharper line widths (Table 3).[38,39] The dynamic nature of bridging cyclopentadienyl Sc(III) complexes in solution has been previously observed and studied using ^{45}Sc NMR by McGlinchey and co-workers.[37] The single resonance observed for **4** suggests that it remains predominantly dimeric in solution in C_6D_6 at room temperature.

Addition of a few drops of THF to C_6D_6 solutions of either **5** or **6** produced ^{45}Sc NMR spectra that do not contain the original two broad signals, but show the presence of one new Sc(III) compound with a different chemical shift and a sharper line width in each spectrum. In addition, the ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectra of complexes **5** and **6** after being treated with THF show clean conversion to new Sc(III) complexes that have only one unique type of cyclopentadienyl environment. This is presumably due to the quantitative formation of the higher coordinate monomeric THF adducts, $[C_5H_4(Si^iPr_3)]_2ScI(THF)$, **5+THF**, and $[C_5H_3(SiMe_3)_2]_2ScCl(THF)$, **6+THF**. Indeed, addition of a few drops of THF to C_6D_6 solutions of monomeric **1**, **2**, **3** and dimeric **4** produced ^{45}Sc NMR spectra that show the presence of new Sc(III) complexes consistent with the formation of THF-solvated complexes (Table 3). In the case of complexes **2** and **3**, there appears to be a mixture of both the unsolvated and THF-solvated complexes, as evidenced by the presence of two distinct resonances with the signal for the THF-solvated complex appearing with a lower chemical shift and with a sharper line width relative to that of the unsolvated complex (see Supporting Information).

The ^{1}H NMR spectrum of the sample of **1** in toluene-d_8 (see Supporting Information and Experimental) that also had crystals containing a mixture of the oxide $\{[C_5H_3(SiMe_3)_2]_2Sc\}_2(\mu\text{-O})$, **7** and the hydroxide $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-OH})\}_2$, **8** contains resonances corresponding to one major product with resonances at +7.77, +7.07, and +0.21 ppm assignable to the cyclopentadienyl and trimethylsilyl substituent protons, respectively. Also, there is at least one other identifiable $[C_5H_3(SiMe_3)_2]^{1-}$ containing minor product with resonances at +7.46, +7.13, and +0.40 ppm analogous to complex **1**, which may be assignable to complex **7** or **8**. Presumably, the major product is complex **1** as it was found that this oxide-containing impure sample of $[C_5H_3(SiMe_3)_2]_2ScI$ gave the Sc(II) metallocene complex $\{[C_5H_3(SiMe_3)_2]_2ScI\}^{1-}$ in good yields when treated with KC_8.[13] Therefore, it may be likely that **7** and **8** are only minor byproducts of reactions forming **1** using samples of ScI_3-containing oxide impurities, yet are readily crystallizable.

Guzei Analysis. The extent of steric saturation for the scandium atom in its primary coordination sphere for each metal complex described in this paper was evaluated using the Guzei solid angle method that provides *G*, an estimation of the percentage of the coordination sphere of the metal that is protected by ligands.[40] All Guzei *G* values in Table 4 were calculated on X-ray crystal structures that include hydrogen atoms. For the bimetallic molecules, only the coordination sphere of one metal was used for the calculations, i.e.,

Table 4. Solid *G* Values for Selected Crystallographically Characterized Bis(cyclopentadienyl) Scandium Halide Complexes in Increasing *G*(Complex) Value

Sc(III) Complex	*G*(Cp) (av.)	*G*(X = F, O, Cl, Br, I)	*G*(complex)
$[(C_5H_5)_2Sc(\mu\text{-Cl})]_2$[1,a]	28	11	78
$[(C_5Me_4H)_2Sc]_2(\mu\text{-O})$[15,a]	33	18	81
$(C_5Me_5)_2ScI$[11]	34	14	81
$(C_5Me_5)_2ScCl$[11]	35	13	81
$(C_5Me_5)_2ScBr$[11]	34	15	82
$(C_5Me_5)_2ScF$[11]	35	16	83
$[C_5Me_4(SiMe_3)]_2ScI$, **2**	38	13	88
$[C_5Me_4(SiMe_2{}^tBu)]_2ScI$, **3**	38	14	88
$\{[C_5H_4(SiMe_3)]_2Sc(\mu\text{-I})\}_2$, **4**	33	12	89
$\{[C_5H_3(SiMe_3)_2]_2Sc\}_2(\mu\text{-O})$, **7**	35	19	89
$[C_5H_3(SiMe_3)_2]_2ScI$, **1**	38	14	90
$\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-Cl})\}_2$, **6**	35	11	90
$\{[C_5H_4(Si^iPr_3)]_2Sc(\mu\text{-I})\}_2$, **5**	35	12	92
$(C_5H_2{}^tBu_3)_2ScI$[13]	40	13	92

[a] Values were averaged between each crystallographically unique scandium metal center in the asymmetric unit.

$[(C_5R_5)_2ScX_2]^{1-}$ for the halides (R = H, alkyl, trialkylsilyl; X = Cl, I) and $[(C_5R_5)_2Sc(\mu\text{-}O)]^{1-}$ for the oxides.

The analysis of this set of complexes shows the variation in the ligand *G* values as a function of the specific crystal structure. For example, iodide ligand *G* values are typically 13–14% for terminal iodides and 12% in the bridging complexes. The analogous terminal and bridging chloride *G* values of 13% and 11%, respectively, are numerically less as expected for a smaller ligand, but it only differs by 1% from the iodide, which may be within the accuracy of these calculations. Further examination of the series of $(C_5Me_5)_2ScX$ (X = F, Cl, Br, and I)[11] complexes shows that the *G* values for the fluoride (16%) and bromide (15%) ligands do not necessarily follow the same periodic trend as the ionic size of the halogens. The *G* values vary from 38% for the $[C_5H_3(SiMe_3)_2]^{1-}$ ligands in monomeric **1** to 28% for the $(C_5H_5)^{1-}$ ligands in the dimeric $[(C_5H_5)_2Sc(\mu\text{-}Cl)]_2$.[1] Overall, the *G* values for the complexes are in the high range, i.e., 88–92%, as is expected for stable sterically saturated compounds.[19,41–43]

DISCUSSION

Bis(cyclopentadienyl)scandium iodide complexes can be readily synthesized and crystallographically characterized with a variety of ligands including $(C_5Me_5)^{1-}$,[11] $(C_5H_2{}^tBu_3)^{1-}$,[13] and the $[C_5H_3(SiMe_3)_2]^{1-}$, $[C_5Me_4(SiMe_3)]^{1-}$, $[C_5Me_4(SiMe_2{}^tBu)]^{1-}$, $[C_5H_4(SiMe_3)]^{1-}$, and $[C_5H_4(Si^iPr_3)]^{1-}$ examples described here when the synthesis starts with pure samples of ScI_3. As shown by the isolation of crystals of the oxide $\{[C_5H_3(SiMe_3)_2]_2Sc\}_2(\mu\text{-}O)$, **7**, and hydroxide $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}OH)\}_2$, **8**, from reactions designed to form $[C_5H_3(SiMe_3)_2]_2ScI$, **1**, oxide impurities in a metal halide starting material can give different products and compounds that are more readily crystallized. This is a good cautionary tale of both starting materials and crystallographic characterization. One should always be aware that small impurities in starting reagents can lead to preferentially crystallized products and that an isolated X-ray crystal structure may not be representative of the bulk material.

The solution NMR data on complexes **1**–**6** suggest that the ^{45}Sc NMR chemical shift and line width are highly sensitive to the ligand environment and coordination number around the scandium metal center.[38,39,44] Monomeric and dimeric species as well as unsolvated and solvated species appear to be discernible based on this set of data due to the variable range of chemical shifts and line width values in the ^{45}Sc NMR spectra. The ^{45}Sc NMR chemical shift also seems to vary depending on the electron-donating properties of the ligands. For the $(C_5Me_5)_2ScX$ (X = F, Cl, Br, and I) complexes, the ^{45}Sc NMR chemical shifts increase with the less electronegative halides. As an example, the peak for $(C_5Me_5)ScF$ has a chemical shift of 65.7 ppm, whereas for $(C_5Me_5)ScI$, it is 256.9 ppm (Table 3). Similarly, with more electron-donating cyclopentadienyl ligands,[45] the ^{45}Sc NMR shift increases. For example, the resonances for $[C_5H_3(SiMe_3)_2]_2ScI$, **1** and $(C_5Me_5)ScI$ are 208.3 and 256.9 ppm, respectively (Table 3). Moreover, the fact that complexes $[C_5Me_4(SiMe_3)]_2ScI$, **2** and $[C_5Me_4(SiMe_2{}^tBu)]_2ScI$, **3** have very similar chemical shifts is consistent with this observation as one would not expect a significant difference in electron-donating ability between the $[C_5Me_4(SiMe_3)]^{1-}$ and $[C_5Me_4(SiMe_2{}^tBu)]^{1-}$ ligands. This type of method can be useful to study the dynamic speciation of different scandium complexes in solution or electronic effects when conventional methods such as ^{1}H NMR or ^{13}C{^{1}H} NMR do not produce easily resolvable signals due to minute differences in the proton and carbon environments.

The structural analysis of the complexes shows that both monomeric and dimeric complexes can form, depending on the size of the ligands. Complexes of the larger cyclopentadienyl and halide ligands, specifically $[C_5H_3(SiMe_3)_2]_2ScI$, **1**, $[C_5Me_4(SiMe_3)]_2ScI$, **2**, $[C_5Me_4(SiMe_2{}^tBu)]_2ScI$, **3**, and $(C_5H_2{}^tBu_3)_2ScI$[13] crystallize as monometallic species that achieve steric saturation of the metal center, as shown by high 88–92% *G* values, without coordination of another halide. The 81% *G* value for $(C_5Me_5)_2ScI$[11] is a curious outlier and is consistent with the fact that it forms a complex with THF. It is worth noting that although $[C_5H_3(SiMe_3)_2]_2ScI$, **1** has a relatively high *G* value of 90%, it can still complex with THF, as shown previously by Lappert and co-workers.[9] In addition, $[(C_5H_5)_2Sc(\mu\text{-}Cl)]_2$[1] can be isolated and crystallized even though it has a low *G* value of 78% as expected due to the small size of the $(C_5H_5)^{1-}$ ligand. Therefore, these values should not be used as a definitive measure of the reactivity of a complex.[42] The suitability of the monomer versus dimer for reductive formation of Sc(II) complexes remains to be determined, but the identity of these Sc(III) starting materials is well-established.

CONCLUSION

A series of bis(cyclopentadienyl) scandium halide complexes have been synthesized in good yields and high purity and structurally characterized to provide a firm basis for available starting materials for the elaboration of organometallic scandium chemistry. Syntheses must be started from precursors free of oxide impurities that could readily form oxide complexes such as $\{[C_5H_3(SiMe_3)_2]_2Sc\}_2(\mu\text{-}O)$, **7**, or hydroxide complexes such as $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu\text{-}OH)\}_2$, **8**. Further studies on this set of silyl-substituted bis(cyclopentadienyl) scandium halide complexes are currently being investigated to determine the importance of the identity of the cyclopentadienyl ligand and halide on the resulting reduction chemistry.

EXPERIMENTAL DETAILS

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 atmosphere. Solvents were sparged with UHP (99.999%) argon before drying and collection using an S2 Grubbs-type[46] solvent purification system (JC Meyer) and stored over activated molecular sieves overnight prior to use. Deuterated NMR solvents were degassed and dried over activated molecular sieves before use. NMR spectra were recorded on a Bruker GN500 or AVANCE600 spectrometer at 298 K unless otherwise stated, and ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were referenced internally to residual protio-solvent resonances. ^{29}Si{^{1}H} NMR spectra were referenced externally to $SiMe_4$. ^{45}Sc NMR spectra were referenced externally to $ScCl_3$ dissolved in D_2O. Infrared spectra were recorded as compressed solids on an Agilent Cary 630 ATR-FTIR instrument under an argon atmosphere. Elemental analyses were conducted on a Thermo Scientific FlashSmart CHNS/O elemental analyzer at UC Irvine Materials Research Institute's TEMPR facility in Irvine, California. ScI_3,[16] $KC_5Me_4(SiMe_2{}^tBu)$,[17] $KC_5H_4(Si^iPr_3)$,[19] $KC_5H_4(SiMe_3)$,[47] and $KC_5H_3(SiMe_3)_2$[48] were synthesized according to literature procedures. $ScCl_3$ was synthesized via a modification of a literature procedure.[49] $KC_5Me_4(SiMe_3)$ was synthesized by treating $\mathrm{HC_5Me_4(SiMe_3)}$[50] with $\mathrm{KN(SiMe_3)_2}$ in toluene.

Synthesis of $\mathbf{[C_5H_3(SiMe_3)_2]_2ScI}$, 1. In an argon-containing glovebox, a 100 mL Schlenk flask fitted with a Teflon stopper was charged with $\mathrm{ScI_3}$ (116 mg, 0.272 mmol), solid $\mathrm{KC_5H_3(SiMe_3)_2}$ (135 mg, 0.543 mmol), and toluene (ca. 15 mL). The flask was sealed, brought out of the glovebox, and was allowed to stir at ca. 110 °C for 16 h to produce a yellow mixture containing a colorless precipitate. The mixture was then cooled to room temperature and brought back into an argon-containing glovebox. Insoluble solids, presumably KI, were removed via centrifugation, followed by filtration through a Kimwipe-packed pipet to produce a clear yellow supernatant. The solution was concentrated to ca. 2 mL and stored at −35 °C. Pale-yellow crystals of $\mathrm{[C_5H_3(SiMe_3)_2]_2ScI}$, **1**, suitable for study by X-ray diffraction were grown overnight (80 mg, 50% crystalline yield). ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$): δ 7.84 (s, 2H, cyclopentadienyl H), 7.10 (s, 4H, cyclopentadienyl H), 0.23 (s, 36H, $\mathrm{Si}Me_3$). ^{13}C{^{1}H} NMR (125 MHz, $\mathrm{C_6D_6}$): δ 138.9 (cyclopentadienyl C), 135.1 (cyclopentadienyl C), 125.7 (cyclopentadienyl C), 0.14 ($\mathrm{Si}Me_3$). ^{29}Si{^{1}H} NMR (119 MHz, $\mathrm{C_6D_6}$): δ −9.0 ($Si\mathrm{Me_3}$). ^{45}Sc NMR (145 MHz, $\mathrm{C_6D_6}$): δ 208.3 (br, $\Delta\nu_{1/2}$ = 4300 Hz). IR: 3068w, 2950m, 2894w, 1441w, 1403w, 1318w, 1256m, 1241vs, 1206w, 1087s, 1064m, 921s, 874m, 824vs, 801vs, 749vs, 688s cm^{-1}. Anal. Calcd for $\mathrm{C_{22}H_{42}Si_4ScI}$: C, 44.73; H, 7.17. Found: C, 44.50; H, 7.04. Addition of excess THF to $\mathrm{C_6D_6}$ solutions of **1** quantitatively shows the conversion of $\mathrm{[C_5H_3(SiMe_3)_2]_2ScI}$, **1**, to $\mathrm{[C_5H_3(SiMe_3)_2]_2ScI(THF)}$, **1+THF**, by NMR spectroscopy. ^{1}H NMR (600 MHz, $\mathrm{C_6D_6}$): δ 7.04 (s, 2H, cyclopentadienyl H), 6.67 (s, 4H, cyclopentadienyl H), 3.57 (m, 4H, α-carbon of THF), 1.43 (m, 4H, β-carbon of THF), 0.36 (s, 36H, $\mathrm{Si}Me_3$). ^{13}C{^{1}H} NMR (151 MHz, $\mathrm{C_6D_6}$): δ 137.2 (cyclopentadienyl C), 126.1 (cyclopentadienyl C), 122.7 (cyclopentadienyl C), 68.0 (α-carbon of THF), 25.8 (β-carbon of THF), 1.0 ($\mathrm{Si}Me_3$). ^{29}Si{^{1}H} NMR (119 MHz, $\mathrm{C_6D_6}$): δ −8.6 ($Si\mathrm{Me_3}$). ^{45}Sc NMR (145 MHz, $\mathrm{C_6D_6}$): δ 81.6 (br, $\Delta\nu_{1/2}$ = 370 Hz).

Synthesis of $\mathbf{[C_5Me_4(SiMe_3)]_2ScI}$, 2. In an argon-containing glovebox, a 100 mL Schlenk flask fitted with a Teflon stopper was charged with $\mathrm{ScI_3}$ (100 mg, 0.235 mmol), $\mathrm{KC_5Me_4(SiMe_3)}$ (109 mg, 0.470 mmol), and toluene (ca. 15 mL). The flask was sealed, brought out of the glovebox, and allowed to stir at ca. 110 °C for 16 h to produce a golden yellow mixture containing a colorless precipitate. The mixture was then cooled to room temperature and brought back into an argon-containing glovebox. Insoluble solids, presumably KI, were removed via centrifugation, followed by filtration through a Kimwipe-packed pipet to produce a golden yellow supernatant. Volatiles were removed under reduced pressure to yield waxy yellow solids. The yellow solids were extracted into hexane (ca. 10 mL) and filtered through a Kimwipe-packed pipet. Volatiles were removed from the supernatant under reduced pressure to yield a yellow crude solid, which was then washed with cold $\mathrm{SiMe_4}$ (ca. 1 mL) and dried under reduced pressure to yield $\mathrm{[C_5Me_4(SiMe_3)]_2ScI}$, **2** as a yellow powder (118 mg, 90% crude yield). Yellow crystals of $\mathrm{[C_5Me_4(SiMe_3)]_2ScI}$, **2** suitable for study by X-ray diffraction were grown from saturated hexane solutions stored at −35 °C overnight (70 mg, 53% crystalline yield). ^{1}H NMR (600 MHz, $\mathrm{C_6D_6}$): δ 2.44 (s, 12H, $\mathrm{C_5}Me_4\mathrm{SiMe_3}$), 1.76 (s, 12H, $\mathrm{C_5}Me_4\mathrm{SiMe_3}$), 0.27 (s, 18H, $\mathrm{Si}Me_3$). ^{13}C{^{1}H} NMR (151 MHz, $\mathrm{C_6D_6}$): δ 135.4 ($C_5\mathrm{Me_4SiMe_3}$), 127.7 ($C_5\mathrm{Me_4SiMe_3}$), 124.9 ($C_5\mathrm{Me_4SiMe_3}$), 17.9 ($\mathrm{C_5}Me_4\mathrm{SiMe_3}$), 12.0 ($\mathrm{C_5}Me_4\mathrm{SiMe_3}$), 1.9 ($\mathrm{Si}Me_3$). ^{29}Si{^{1}H} NMR (119 MHz, $\mathrm{C_6D_6}$): δ −9.7 ($Si\mathrm{Me_3}$). ^{45}Sc NMR (145 MHz, $\mathrm{C_6D_6}$): δ 264.2 (br, $\Delta\nu_{1/2}$ = 3200 Hz). IR: 2948w, 2894w, 1461w, 1429w, 1405w, 1380w, 1325m, 1241s, 1129w, 1019m, 831vs, 755s, 686s cm^{-1}. Anal. Calcd for $\mathrm{C_{24}H_{42}Si_2ScI}$: C, 51.60; H, 7.58. Found: C, 51.81; H, 7.66. Addition of excess THF to $\mathrm{C_6D_6}$ solutions of **2** partially converted $\mathrm{[C_5Me_4(SiMe_3)]_2ScI}$, **2**, to $\mathrm{[C_5Me_4(SiMe_3)]_2ScI}$, **2+THF**, as determined by ^{45}Sc NMR spectroscopy. ^{1}H NMR (600 MHz, $\mathrm{C_6D_6}$): δ 3.57 (m, 4H, α-carbon of THF), 2.42 (s, 12H, $\mathrm{C_5}Me_4\mathrm{SiMe_3}$), 1.77 (s, 12H, $\mathrm{C_5}Me_4\mathrm{SiMe_3}$), 1.43 (m, 4H, β-carbon of THF), 0.25 (s, 18H, $\mathrm{Si}Me_3$). ^{13}C{^{1}H} NMR (151 MHz, $\mathrm{C_6D_6}$): δ 135.4 ($C_5\mathrm{Me_4SiMe_3}$), 127.7 ($C_5\mathrm{Me_4SiMe_3}$), 124.9 ($C_5\mathrm{Me_4SiMe_3}$), 67.8 (α-carbon of THF), 25.8 (β-carbon of THF), 17.8 ($\mathrm{C_5}Me_4\mathrm{SiMe_3}$), 12.0 ($\mathrm{C_5}Me_4\mathrm{SiMe_3}$), 1.8 ($\mathrm{Si}Me_3$). ^{29}Si{^{1}H} NMR (119 MHz, $\mathrm{C_6D_6}$): δ −9.7 ($Si\mathrm{Me_3}$). ^{45}Sc NMR (145 MHz, $\mathrm{C_6D_6}$): δ 176.3 (br, $\Delta\nu_{1/2}$ = 340 Hz).

Synthesis of $\mathbf{[C_5Me_4(SiMe_2{}^tBu)]_2ScI}$, 3. In an argon-containing glovebox, a 100 mL Schlenk flask fitted with a Teflon stopper was charged with $\mathrm{ScI_3}$ (132 mg, 0.310 mmol), $\mathrm{KC_5Me_4(SiMe_2{}^{\mathit{t}}Bu)}$ (170 mg, 0.620 mmol), and toluene (ca. 15 mL). The flask was sealed, brought out of the glovebox, and allowed to stir at ca. 110 °C for 16 h to produce a golden yellow containing a colorless precipitate. The mixture was then cooled to room temperature and dried under reduced pressure to yield yellow and colorless solids before it was sealed and brought back into an argon-containing glovebox. The product was extracted into hexane (ca. 10 mL) and centrifuged, then filtered through a Kimwipe-packed pipet to remove insoluble solids, presumably KI. Volatiles were removed under reduced pressure from the golden yellow supernatant to yield waxy yellow solids. The solids were then washed with cold $\mathrm{SiMe_4}$ (ca. 1 mL) and dried under reduced pressure to yield $\mathrm{[C_5Me_4(SiMe_2{}^{\mathit{t}}Bu)]_2ScI}$, **3** as a bright yellow powder (150 mg, 75% crude yield). Yellow crystals of $\mathrm{[C_5Me_4(SiMe_2{}^{\mathit{t}}Bu)]_2ScI}$, **3** suitable for study by X-ray diffraction were grown from saturated hexane solutions stored at −35 °C overnight (108 mg, 54% crystalline yield). ^{1}H NMR (600 MHz, $\mathrm{C_6D_6}$): δ 2.58 (s, 12H, $\mathrm{C_5}Me_4\mathrm{SiR_3}$), 1.76 (s, 12H, $\mathrm{C_5}Me_4\mathrm{SiR_3}$), 0.80 (s, 18H, $\mathrm{SiMe_2}{}^tBu$), 0.40 (s, 12H, $\mathrm{Si}Me_2{}^t\mathrm{Bu}$). ^{13}C{^{1}H} NMR (151 MHz, $\mathrm{C_6D_6}$): δ 136.5 ($C_5\mathrm{Me_4SiR_3}$), 128.0 ($C_5\mathrm{Me_4SiR_3}$), 124.2 ($C_5\mathrm{Me_4SiR_3}$), 27.8 ($C\mathrm{Me_3}$), 20.6 ($\mathrm{C}Me_3$), 18.9 ($\mathrm{C_5}Me_4\mathrm{SiR_3}$), 12.2 ($\mathrm{C_5}Me_4\mathrm{SiR_3}$), −1.0 ($\mathrm{Si}Me_2{}^t\mathrm{Bu}$). ^{29}Si{^{1}H} NMR (119 MHz, $\mathrm{C_6D_6}$): δ −2.4 ($Si\mathrm{Me_2}{}^t\mathrm{Bu}$). ^{45}Sc NMR (145 MHz, $\mathrm{C_6D_6}$): δ 263.9 (br, $\Delta\nu_{1/2}$ = 3300 Hz). IR: 2928m, 2853m, 1463m, 1379w, 1314m, 1247s, 1124w, 1012m, 956w, 805vs, 762vs, 742s, 677vs cm^{-1}. Anal. Calcd for $\mathrm{C_{30}H_{54}Si_2ScI}$: C, 56.06; H, 8.47. Found: C, 55.86; H, 8.51. Addition of excess THF to $\mathrm{C_6D_6}$ solutions of **3** partially converted $\mathrm{[C_5Me_4(SiMe_2{}^{\mathit{t}}Bu)]_2ScI}$, **3**, to $\mathrm{[C_5Me_4(SiMe_2{}^{\mathit{t}}Bu)]_2ScI(THF)}$, **3+THF**, as determined by ^{45}Sc NMR spectroscopy. ^{1}H NMR (600 MHz, $\mathrm{C_6D_6}$): δ 3.57 (m, 4H, α-carbon of THF), 2.57 (s, 12H, $\mathrm{C_5}Me_4\mathrm{SiR_3}$), 1.76 (s, 12H, $\mathrm{C_5}Me_4\mathrm{SiR_3}$), 1.43 (m, 4H, β-carbon of THF), 0.79 (s, 18H, $\mathrm{SiMe_2}{}^tBu$), 0.39 (s, 12H, $\mathrm{Si}Me_2{}^t\mathrm{Bu}$). ^{13}C{^{1}H} NMR (151 MHz, $\mathrm{C_6D_6}$): δ 136.5 ($C_5\mathrm{Me_4SiR_3}$), 128.0 ($C_5\mathrm{Me_4SiR_3}$), 124.2 ($C_5\mathrm{Me_4SiR_3}$), 67.9 (α-carbon of THF), 27.8 ($C\mathrm{Me_3}$), 25.8 (β-carbon of THF), 20.6 ($\mathrm{C}Me_3$), 18.9 ($\mathrm{C_5}Me_4\mathrm{SiR_3}$), 12.1 ($\mathrm{C_5}Me_4\mathrm{SiR_3}$), −1.0 ($\mathrm{Si}Me_2{}^t\mathrm{Bu}$). ^{29}Si{^{1}H} NMR (119 MHz, $\mathrm{C_6D_6}$): δ −2.4 ($Si\mathrm{Me_2}{}^t\mathrm{Bu}$). ^{45}Sc NMR (145 MHz, $\mathrm{C_6D_6}$): δ 167.5 (br, $\Delta\nu_{1/2}$ = 850 Hz).

Synthesis of $\mathbf{\{[C_5H_4(SiMe_3)]_2Sc(\mu\text{-}I)\}_2}$, 4. In an argon-containing glovebox, a 100 mL Schlenk flask fitted with a Teflon stopper was charged with $\mathrm{ScI_3}$ (202 mg, 0.475 mmol), $\mathrm{KC_5H_4(SiMe_3)}$ (167 mg, 0.947 mmol), and toluene (ca. 15 mL). The flask was sealed, brought out of the glovebox, and allowed to stir at ca. 110 °C for 16 h to produce a yellow-orange mixture containing colorless precipitate. The flask was then sealed, cooled to room temperature, and brought back into an argon-containing glovebox. The mixture was then centrifuged and filtered through a Kimwipe-packed pipet to remove insoluble solids, presumably KI. Volatiles were removed under reduced pressure to yield brown and white solids. The solids were then washed with cold hexane (ca. 2 mL) and dried under reduced pressure to yield $\mathrm{\{[C_5H_4(SiMe_3)]_2Sc(\mu\text{-}I)\}_2}$, **4** as colorless solids (133 mg, 63%). Colorless X-ray quality crystals of **4** can be grown from saturated toluene solutions of **4** stored at −35 °C overnight. ^{1}H NMR (600 MHz, $\mathrm{C_6D_6}$): δ 7.05 (m, 8H, $\mathrm{C_5}H_4\mathrm{SiMe_3}$), 6.58 (m, 8H, $\mathrm{C_5}H_4\mathrm{SiMe_3}$), 0.31 (s, 36H, $\mathrm{Si}Me_3$). ^{13}C{^{1}H} NMR (151 MHz, $\mathrm{C_6D_6}$): δ 124.3 ($C_5\mathrm{H_4SiMe_3}$), 123.3 ($C_5\mathrm{H_4SiMe_3}$), 118.7 ($C_5\mathrm{H_4SiMe_3}$), 0.5 ($\mathrm{Si}Me_3$). ^{29}Si{^{1}H} NMR (119 MHz, $\mathrm{C_6D_6}$): δ −8.6 ($Si\mathrm{Me_3}$). ^{45}Sc NMR (145 MHz, $\mathrm{C_6D_6}$): δ 71.2 (br, $\Delta\nu_{1/2}$ = 1900 Hz). IR: 2948w, 2889w, 1444w, 1403w, 1366m, 1316w, 1243s, 1174s, 1044s, 904s, 859w, 829vs, 792vs, 751vs, 688s cm^{-1}. Anal. Calcd for $\mathrm{C_{32}H_{52}Si_4Sc_2I_2}$: C, 43.05; H, 5.87. Found: C, 43.27; H, 6.07. Addition of excess THF to $\mathrm{C_6D_6}$ solutions of **4** quantitatively shows the conversion of $\mathrm{\{[C_5H_4(SiMe_3)]_2Sc(\mu\text{-}I)\}_2}$, **4**, to $\mathrm{[C_5H_4(SiMe_3)]_2ScI(THF)}$, **4+THF**, by NMR spectroscopy. ^{1}H NMR (600 MHz, $\mathrm{C_6D_6}$): δ 6.66 (br s, 4H, $\mathrm{C_5}H_4\mathrm{SiMe_3}$), 6.19 (s, 4H, $\mathrm{C_5}H_4\mathrm{SiMe_3}$), 3.55 (m, 4H,

α-carbon of THF), 1.44 (m, 4H, β-carbon of THF), 0.36 (s, 18H, $\mathrm{Si}Me_3$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (151 MHz, $\mathrm{C_6D_6}$): δ 123.8 ($C_5\mathrm{H_4SiMe_3}$), 121.7 ($C_5\mathrm{H_4SiMe_3}$), 115.6 (br, $C_5\mathrm{H_4SiMe_3}$), 67.9 (α-carbon of THF), 25.8 (β-carbon of THF), 0.63 ($\mathrm{Si}Me_3$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (119 MHz, $\mathrm{C_6D_6}$): δ −8.6 ($Si\mathrm{Me_3}$). $^{45}\mathrm{Sc}$ NMR (145 MHz, $\mathrm{C_6D_6}$): δ 59.7 (br, $\Delta\nu_{1/2}$ = 160 Hz).

Synthesis of $\{[\mathrm{C_5H_4(Si^iPr_3)}]_2\mathrm{Sc}(\mu\text{-I})\}_2$, 5. In an argon-containing glovebox, a 100 mL Schlenk flask fitted with a Teflon stopper was charged with $\mathrm{ScI_3}$ (100 mg, 0.235 mmol), $\mathrm{KC_5H_4(Si^iPr_3)}$ (122 mg, 0.470 mmol), and toluene (ca. 15 mL). The flask was sealed, brought out of the glovebox, and allowed to stir at ca. 110 °C for 16 h to produce a pale-yellow mixture containing a colorless precipitate. The flask was then cooled to room temperature and brought back into an argon-containing glovebox. The mixture was centrifuged and filtered through a Kimwipe-packed pipet to remove insoluble solids, presumably KI. Volatiles were removed under reduced pressure to yield waxy, off-white solids. The solids were then washed with cold hexane (ca. 2 mL) and dried under reduced pressure to yield $\{[\mathrm{C_5H_4(Si^iPr_3)}]_2\mathrm{Sc}(\mu\text{-I})\}_2$, **5**, as colorless solids (98 mg, 94%). Colorless X-ray quality crystals can be grown from saturated toluene solutions of **5** stored at −35 °C overnight. ^{1}H NMR (600 MHz, $\mathrm{C_6D_6}$): δ 7.38 (m, 8H, $\mathrm{C_5}H_4\mathrm{Si^iPr_3}$), 6.53 (m, 8H, $\mathrm{C_5}H_4\mathrm{Si^iPr_3}$), 1.28 (m, 12H, C$H$ of $\mathrm{Si^iPr_3}$), 1.09 (m, 72H, CH_3 of $\mathrm{Si^iPr_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (151 MHz, $\mathrm{C_6D_6}$): δ 126.1 ($C_5\mathrm{H_4Si^iPr_3}$), 124.3 ($C_5\mathrm{H_4Si^iPr_3}$), 119.0 ($C_5\mathrm{H_4Si^iPr_3}$), 19.6 ($C\mathrm{H_3}$ of $\mathrm{Si^iPr_3}$), 12.5 (CH of $\mathrm{Si^iPr_3}$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (119 MHz, $\mathrm{C_6D_6}$): δ 0.8 ($Si\mathrm{^iPr_3}$). $^{45}\mathrm{Sc}$ NMR (145 MHz, $\mathrm{C_6D_6}$): δ 172.8 (br, $\Delta\nu_{1/2}$ = 7000 Hz), 34.5 (br, $\Delta\nu_{1/2}$ = 2600 Hz). IR: 2939m, 2861s, 1459m, 1366w, 1362w, 1239w, 1167m, 1046s, 1001m, 880s, 790vs, 652vs cm^{-1}. Anal. Calcd for $\mathrm{C_{56}H_{100}Si_4Sc_2I_2}$: C, 54.71; H, 8.20. Found: C, 54.55; H, 8.26. Addition of excess THF to $\mathrm{C_6D_6}$ solutions of **5** quantitatively shows the conversion of $\{[\mathrm{C_5H_4(Si^iPr_3)}]_2\mathrm{Sc}(\mu\text{-I})\}_2$, **5**, to $[\mathrm{C_5H_4(Si^iPr_3)}]_2\mathrm{ScI(THF)}$, **5+THF**, by NMR spectroscopy. ^{1}H NMR (600 MHz, $\mathrm{C_6D_6}$): δ 6.75 (m, 4H, $\mathrm{C_5}H_4\mathrm{Si^iPr_3}$), 6.31 (m, 4H, $\mathrm{C_5}H_4\mathrm{Si^iPr_3}$), 3.56 (m, 4H, α-carbon of THF), 1.56 (sept, 6H, CH of $\mathrm{Si^iPr_3}$, $^3J_{\mathrm{HH}}$ = 7.2 Hz), 1.45 (m, 4H, β-carbon of THF), 1.18 (d, 36H, CH_3 of $\mathrm{Si^iPr_3}$, $^3J_{\mathrm{HH}}$ = 7.2 Hz). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (151 MHz, $\mathrm{C_6D_6}$): δ 125.0 ($C_5\mathrm{H_4Si^iPr_3}$), 120.5 ($C_5\mathrm{H_4Si^iPr_3}$), 115.7 ($C_5\mathrm{H_4Si^iPr_3}$), 67.9 (α-carbon of THF), 25.8 (β-carbon of THF), 19.7 ($C\mathrm{H_3}$ of $\mathrm{Si^iPr_3}$), 12.8 (CH of $\mathrm{Si^iPr_3}$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (119 MHz, $\mathrm{C_6D_6}$): δ −0.6 ($Si\mathrm{^iPr_3}$). $^{45}\mathrm{Sc}$ NMR (145 MHz, $\mathrm{C_6D_6}$): δ 68.9 (br, $\Delta\nu_{1/2}$ = 540 Hz).

Synthesis of $\{[\mathrm{C_5H_3(SiMe_3)_2}]_2\mathrm{Sc}(\mu\text{-Cl})\}_2$, 6. In an argon-containing glovebox, a 100 mL Schlenk flask fitted with a Teflon stopper was charged with $\mathrm{ScCl_3}$ (116 mg, 0.767 mmol), $\mathrm{KC_5H_3(SiMe_3)_2}$ (381 mg, 1.33 mmol), and toluene (ca. 15 mL). The flask was sealed, brought out of the glovebox, and allowed to stir at ca. 110 °C for 16 h to yield a cloudy brown-yellow mixture containing colorless precipitate. Removal of the solvent under reduced pressure yielded off-white solids. The Schlenk flask was then brought back into an argon-containing glovebox, and toluene (ca. 15 mL) was added. The resulting cloudy brown-yellow mixture was centrifuged and filtered through a pipet packed with Kimwipe tissue to yield a clear brown solution. Removal of the solvent under reduced pressure yielded light brown solids. The solids were then washed with cold hexane (ca. 2 mL) and subsequently dried under reduced pressure to yield $\{[\mathrm{C_5H_3(SiMe_3)_2}]_2\mathrm{Sc}(\mu\text{-Cl})\}_2$, **6**, as colorless solids (128 mg, 33%). Yellow X-ray quality crystals of **6** can be grown from saturated toluene solutions of **6** stored at −18 °C overnight. The ^{1}H and $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra of **6** in neat $\mathrm{C_6D_6}$ at room temperature presumably contain an equilibrium mixture of isomers and monomeric and dimeric species, so assignments could not be definitively determined. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (119 MHz, $\mathrm{C_6D_6}$): δ −9.0 (br, $Si\mathrm{Me_3}$). $^{45}\mathrm{Sc}$ NMR (145 MHz, $\mathrm{C_6D_6}$): δ 138.3 (br, $\Delta\nu_{1/2}$ = 2700 Hz), 43.3 (br, $\Delta\nu_{1/2}$ = 1900 Hz). IR: 2948w, 2893w, 1437w, 1398w, 1321w, 1242s, 1217w, 1209w, 1077s, 917s, 865m, 821s, 799s, 746s, 686m cm^{-1}. EA: Anal. Calcd for $\mathrm{C_{44}H_{84}Si_8Sc_2Cl_2}$: C, 52.92; H, 8.48. Found: C, 43.78; H, 6.98. C, 42.34; H, 6.74. C, 37.53; H, 6.18. Low C and H values were observed across multiple runs and suggest incomplete combustion.[43,51−55] The C/H ratios in the analytical data give formulas of $\mathrm{C_{44}H_{83.4}}$, $\mathrm{C_{44}H_{83.3}}$, and $\mathrm{C_{44}H_{86}}$, respectively, close to the calculated ratio of $\mathrm{C_{44}H_{84}}$. Addition of excess THF to $\mathrm{C_6D_6}$ solutions of **6** quantitatively show the conversion of $\{[\mathrm{C_5H_3(SiMe_3)_2}]_2\mathrm{Sc}(\mu\text{-Cl})\}_2$, **6**, to $[\mathrm{C_5H_3(SiMe_3)_2}]_2\mathrm{ScCl(THF)}$, **6+THF**, by NMR spectroscopy. ^{1}H NMR (600 MHz, $\mathrm{C_6D_6}$): δ 6.73 (m, 2H, cyclopentadienyl H), 6.64 (m, 4H, cyclopentadienyl H), 3.57 (m, 4H, α-carbon of THF), 1.44 (m, 4H, β-carbon of THF), 0.35 (s, 36H, CH_3 of $\mathrm{SiMe_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (151 MHz, $\mathrm{C_6D_6}$): δ 134.6 (cyclopentadienyl C), 125.7 (cyclopentadienyl C), 121.9 (cyclopentadienyl C), 68.1 (α-carbon of THF), 25.8 (β-carbon of THF), 0.8 ($\mathrm{CH_3}$ of $\mathrm{SiMe_3}$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (119 MHz, $\mathrm{C_6D_6}$): δ −9.0 ($Si\mathrm{Me_3}$). $^{45}\mathrm{Sc}$ NMR (145 MHz, $\mathrm{C_6D_6}$): δ 29.9 (br, $\Delta\nu_{1/2}$ = 940 Hz).

Synthesis of $[\mathrm{C_5H_3(SiMe_3)_2}]_2\mathrm{ScI}$, 1 Containing $\{[\mathrm{C_5H_3(SiMe_3)_2}]_2\mathrm{Sc}\}_2(\mu\text{-O})$, 7 and $\{[\mathrm{C_5H_3(SiMe_3)_2}]_2\mathrm{Sc}(\mu\text{-OH})\}_2$, 8. In an argon-containing glovebox, $\mathrm{ScI_3}$ (500 mg, 1.17 mmol), presumably containing an oxide impurity, and $\mathrm{KC_5H_3(SiMe_3)_2}$ (490 mg, 2.35 mmol) were combined in toluene (ca. 40 mL) in a 100 mL Schlenk flask containing a Teflon-coated stir bar and fitted with a Teflon stopcock. The reaction mixture was heated to ca. 60 °C in an oil bath and was allowed to stir for 24 h. Solvent was removed under reduced pressure to yield a yellow/green oil that was then brought back into the glovebox for continued workup. The residue was then extracted into hexane (ca. 15 mL) and centrifuged to yield a white precipitate, presumably KI, and a golden yellow supernatant. The supernatant was collected and dried under reduced pressure to yield flaky golden solids (598 mg). Colorless crystals of a mixture of $\{[\mathrm{C_5H_3(SiMe_3)_2}]_2\mathrm{Sc}\}_2(\mu\text{-O})$, **7**, and $\{[\mathrm{C_5H_3(SiMe_3)_2}]_2\mathrm{Sc}(\mu\text{-OH})\}_2$, **8**, were grown from saturated toluene solutions stored at −18 °C overnight. NMR data for **1**: ^{1}H NMR (600 MHz, $\mathrm{C_7D_8}$): δ 7.77 (m, 2H, cyclopentadienyl H), 7.07 (m, 4H, cyclopentadienyl H), 0.21 (s, 36H, $\mathrm{Si}Me_3$). NMR data for **7**: ^{1}H NMR (600 MHz, $\mathrm{C_7D_8}$): δ 7.46 (m, 4H, cyclopentadienyl H), 7.13 (m, 8H, cyclopentadienyl H), 0.40 (s, 72H, $\mathrm{Si}Me_3$). IR: 2950w, 2890w, 1441w, 1399w, 1319w, 1242s, 1204w sh, 1078s, 917m, 824s, 796m, 747s, 692s cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.4c00412.

Spectra (NMR, IR) and crystallographic data (PDF)

Accession Codes

CCDC 2368437, 2368438, 2369786, 2372340, 2373975, 2376407, and 2386151 contain the supplementary crystallographic data for the paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U. K.; Fax: + 44-1223-336033. Crystal data, full bond lengths and angle tables, and structure refinement information can be found in the Supporting Information.

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Notes

The authors declare no competing financial interest.

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