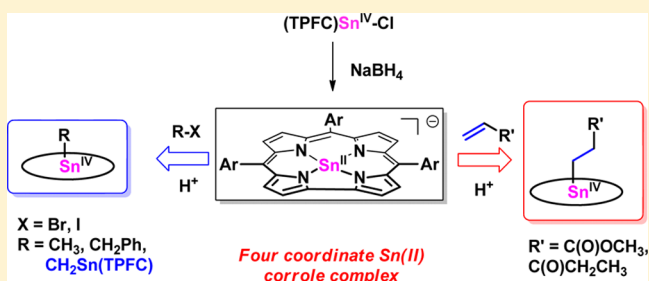


## Synthesis and Reactivity Studies of a Tin(II) Corrole Complex

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## Supporting Information

**ABSTRACT:** A series of tris(pentafluorophenyl)corrole (TPFC) tin(IV) and tin(II) complexes were prepared and studied by various characterization techniques including <sup>1</sup>H, <sup>19</sup>F, and <sup>119</sup>Sn NMR and UV–vis spectroscopy, mass spectrometry, and single-crystal X-ray diffraction. The unusual 4-coordinate, monomeric, divalent tin(II) complex [(TPFC)-Sn<sup>II</sup>]<sup>-</sup> (**2a**) showed highly efficient reactivity toward alkenes and alkyl halides via a nucleophilic addition pathway leading to the quantitative formation of alkyl stannyl corrole compounds. DFT calculations confirmed the divalent nature of the tin center in **2a**, and an NBO analysis showed about 99.99% Sn lone pair character, of which 83.6% was Sn 5s and 16.35% was Sn 5p character.



## INTRODUCTION

Corrole was first discovered by Johnson and Kay as early as 1964 in an attempt to synthesize vitamin-B<sub>12</sub>.<sup>1</sup> However, corrole chemistry was slow to develop until 1999 when Gross reported a facile synthesis of meso-aryl substituted corroles.<sup>2</sup> Capable of forming trianions upon full deprotonation, corrole is well-known for stabilizing metals in apparently high oxidation states. A variety of metallo-corrole complexes were synthesized,<sup>3,4</sup> and some of them displayed similar or even superior properties to the related porphyrin complexes.<sup>4</sup> Despite this, compared with porphyrins, the reactivity of metallo-corroles remained only partially developed, especially for main group element corrole complexes.

The heavier group 14 complexes are receiving increasing attention,<sup>5</sup> and in some cases these main group compounds display reactivities as rich as transition metal complexes, for example in the activation of small molecules.<sup>6</sup> In a major breakthrough, Power and co-workers recently reported room temperature activation of H<sub>2</sub> by germanium and tin analogues of ethylene<sup>7</sup> and the reversible reaction of distannynes with ethylene under ambient conditions.<sup>8</sup> Roesky and co-workers reported activation of small molecules using low valent group 14 elements stabilized by sterically appropriate ligands.<sup>5d</sup> Recently, we reported synthesis of a pentacoordinate germanium corrole hydride complex which exhibited reactivity toward a variety of substrates.<sup>9</sup> However, tin corrole chemistry was still limited to synthetic and spectroscopic studies.<sup>10</sup> Moreover, reports of low-valent tin corrole complexes are very limited,<sup>11</sup> possibly due to the instability caused by coordination

of a strongly electron-donating corrole ligand. Herein, we report a facile method to prepare the tris(pentafluorophenyl)corrole (TPFC) tin(II) anion [(TPFC)Sn<sup>II</sup>]<sup>-</sup>, and its highly efficient reactivity toward alkenes and alkyl halides.

## RESULTS AND DISCUSSION

In this Article we focus on the chemistry deriving from corrolato tin(IV) chloride (TPFC)Sn<sup>IV</sup>Cl (**1a**) initially prepared by Gross and co-workers.<sup>2,10b</sup> The tin corrole complexes reported to date contain tetraalkylcorrole ligands,<sup>3a,10a</sup> and the only tin triarylcorrole contains the electron-withdrawing TPFC.<sup>2,10b</sup> We have prepared two further examples, (TPC)Sn<sup>IV</sup>Cl (**1b**) and (TTC)Sn<sup>IV</sup>Cl (**1d**) (TPC = 5,10,15-triphenylcorrole, TTC = 5,10,15-tritolylicorrole), from the reaction of SnCl<sub>2</sub> with the free base corroles in refluxing DMF. This result demonstrates that tin triarylcorrole complexes can be readily prepared, although, as with the other reported examples, the syntheses are successful beginning with SnCl<sub>2</sub> but not with SnCl<sub>4</sub>, despite the Sn(IV) products. The molecular structure of (TTC)Sn<sup>IV</sup>Cl shows the expected features: a 5-coordinate tin atom displaced 0.635 Å from the mean N<sub>4</sub> plane toward the chloro ligand, and a domed corrole ligand (see Figure S1, Supporting Information).

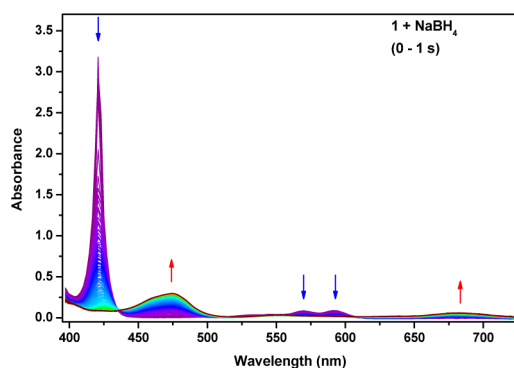
In our previous report, NaBH<sub>4</sub> reduction of the germanium complexes (TPFC)GeX (X = Cl or OH) generated a germanium hydride complex (TPFC)GeH in which the hydride

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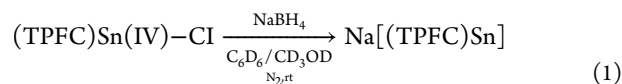
resonance was clearly observed at  $-2.14$  ppm in the  $^1\text{H}$  NMR. The vibrational absorption band  $\nu(\text{Ge}-\text{H})$  at  $2085\text{ cm}^{-1}$  was also measured by IR spectroscopy.<sup>9</sup> In a similar fashion, mixing excess  $\text{NaBH}_4$  with **1a** under a  $\text{N}_2$  atmosphere at room temperature resulted in a new set of  $^1\text{H}$  NMR resonances accompanied by an immediate color change from deep wine-red to deep brown-green. The slightly shifted pyrrole-H resonances indicated quantitative conversion of **1a** to a new corrolato tin complex **2a**. However, no  $\nu(\text{Sn}-\text{H})$  vibration in the IR spectrum nor tin hydride resonance in the  $^1\text{H}$  NMR spectrum was found, even at low temperature. The absence of a Sn-H proton signal indicated that **2a** was not a corrolato tin hydride complex. It is worth noting that the shift of the  $^{119}\text{Sn}$  NMR resonance of **1a** from  $-350$  ppm to higher field at  $-576$  ppm for **2a** lies in the range  $\delta -550$  to  $-600$  generally observed for four-coordinate Sn(II) species.<sup>11d,12</sup>

The stopped-flow technique was used to track the UV-vis spectral changes during reduction of **1a** (Figure 1). Upon



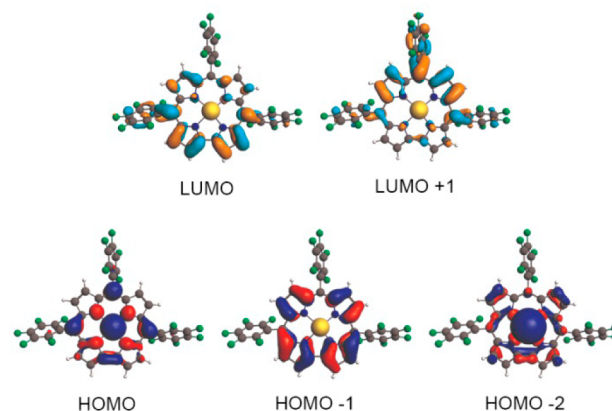
**Figure 1.** Reduction of **1a** in toluene with excess  $\text{NaBH}_4$  monitored by stopped-flow UV-vis absorption spectroscopy (optical path = 2 mm).

mixing a toluene solution of **1a** with  $\text{NaBH}_4/\text{CH}_3\text{OH}$  a large red shift in the Soret band from 414 to 472 nm with a well-defined isosbestic point at 435 nm was observed within 1 s, along with a significant wine-red to brown-green color change. Kadish et al. reported electroreduction of  $(\text{OEC})\text{SnCl}$  ( $\text{OEC}$  = octaethylcorrole) by cyclic voltammetry and reported that the Soret band shifted from 411 to 475 nm. Two-electron reduction from Sn(IV) to Sn(II) was proposed to account for these observations.<sup>10a</sup> These observations suggested that compound **2a** could be formulated as an anion  $[(\text{TPFC})\text{Sn}]^-$  prepared through reduction of  $(\text{TPFC})\text{Sn}^{\text{IV}}\text{Cl}$  by  $\text{NaBH}_4$  (eq 1).



A number of porphyrin and phthalocyanine complexes of the lighter group 14 elements have recently been shown to have ligand noninnocent character.  $(\text{TPP})\text{Si}(\text{THF})_2$ ,  $(\text{TPP})\text{Si}(\text{py})_2$ ,  $(\text{TPP})\text{Ge}(\text{py})_2$ ,  $(\text{Pc})\text{Ge}(\text{py})_2$ , and  $(\text{Pc})\text{Si}(\text{py})_2$  ( $\text{TPP}$  = tetraphenylporphyrin;  $\text{Pc}$  = phthalocyanine,  $\text{py}$  = pyridine) appear from their formulations to contain M(II) centers, but in fact contain M(IV) centers and reduced, 20-electron, antiaromatic porphyrin or phthalocyanine ligands.<sup>13</sup> In order to further characterize this reduced tin corrole species we undertook a DFT study (OLYP/STO-TZ2P) for both  $(\text{Cor})\text{SnCl}$  ( $\text{Cor}$  = TPFC **1a**, TPC **1b**, unsubstituted corrole **1c**) and  $[(\text{Cor})\text{Sn}]^-$  ( $\text{Cor}$  = TPFC **2a**, TPC **2b**, unsubstituted

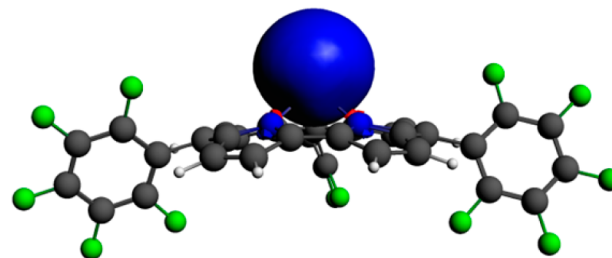
corrole **2c**). According to the calculations, the ground states of **2a-c** are unambiguously closed-shell. The frontier molecular orbitals of **2a**, depicted in Figure 2, show that a tin lone pair



**Figure 2.** Molecular orbitals from HOMO - 2 to LUMO + 1 for  $[(\text{TPFC})\text{Sn}]^-$  (**2a**).

contributes primarily to the HOMO - 2 (44.9%) and to a much lesser degree to the HOMO (12.9%). Accordingly, the lowest triplet state is derived via a  $\pi-\pi^*$  excitation and not via an excitation out of the Sn lone pair; for **2c**, the lowest triplet state was found to be at 1.287 eV above the ground state.

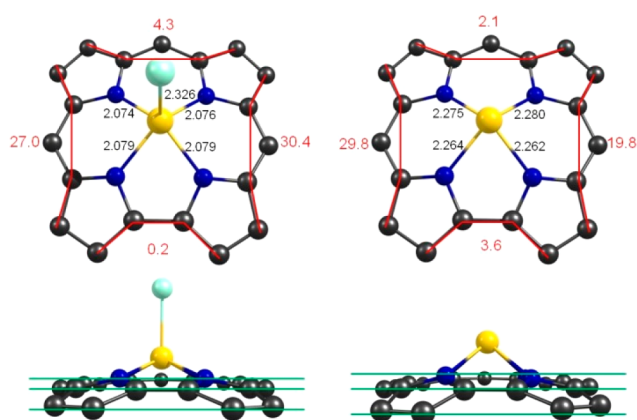
NBO analysis confirmed the divalent nature of the Sn center of **2a**,  $[(\text{TPFC})\text{Sn}^{\text{II}}]^-$ . Thus, an NBO was found with about 99.99% Sn lone pair character, of which 83.6% was Sn 5s and 16.35% was Sn 5p character (Figure 3).



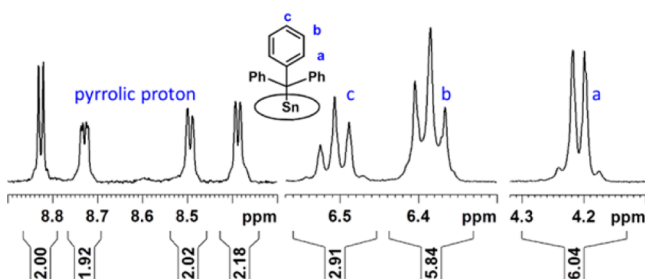
**Figure 3.** NBO for **2a** corresponding to the Sn lone pair.

The optimized geometries of both  $(\text{TPFC})\text{Sn}^{\text{IV}}\text{Cl}$  (**1a**) and  $[(\text{TPFC})\text{Sn}^{\text{II}}]^-$  (**2a**) exhibit domed structures with metal-nitrogen distances over 2.0 Å, which are long for typical metallocorroles (Figure 4).<sup>14</sup> For the  $(\text{Cor})\text{SnCl}$  derivatives, the Sn-N bond lengths are in the range 2.07–2.08 Å and the Sn atom lies 0.70, 0.92, and 1.17 Å above the  $\text{N}_4$ ,  $(\text{C}_\alpha)_4$ , and  $(\text{C}_\beta)_8$  planes, respectively. For the  $[(\text{Cor})\text{Sn}^{\text{II}}]^-$  derivatives, the Sn-N bonds are longer, averaging about 2.27 Å, and the metallocorrole unit as a whole is substantially more domed; the Sn atom in **2a** is only 1.17, 1.45, and 1.81 Å above the  $\text{N}_4$ ,  $(\text{C}_\alpha)_4$ , and  $(\text{C}_\beta)_8$  planes, respectively.

Complex **2a** was quite sensitive to air; therefore, all the following reactions were performed in the glovebox or using Schlenk line techniques and spectra measured in a J. Young NMR tube. In an attempt to trap the  $[(\text{TPFC})\text{Sn}^{\text{II}}]^-$  anion, treatment of a benzene- $d_6$  solution of **2a** with excess  $\text{Ph}_3\text{C}^+\text{BF}_4^-$  immediately afforded a blue-violet solution which was assigned to the formation of  $(\text{TPFC})\text{Sn}(\text{CPh}_3)$  (**3**, yield 81%) (Figure 5, Scheme 1). The  $^1\text{H}$  NMR spectrum displayed

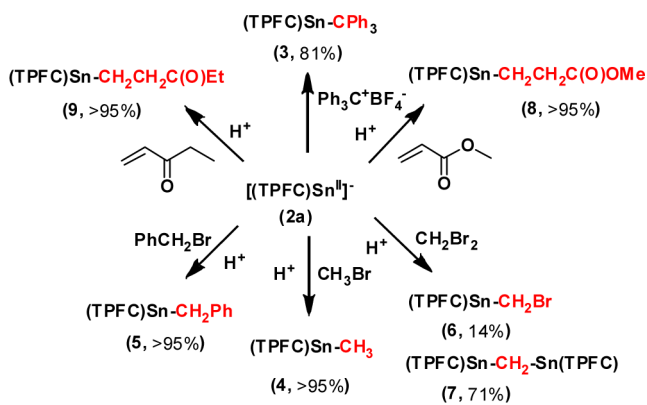


**Figure 4.** Selected distances (Å) and dihedral angles (deg) for **1a** (left) and **2a** (right). The planes shown in the lower views are calculated for the  $N_4$ ,  $(C_\alpha)_4$ , and  $(C_\beta)_8$  sets of atoms.



**Figure 5.**  $^1\text{H}$  NMR spectrum (benzene- $d_6$ ) of the pyrrolic and phenyl proton signals for  $[(\text{TPFC})\text{SnC}(\text{C}_6\text{H}_5)_3]$  (**3**).

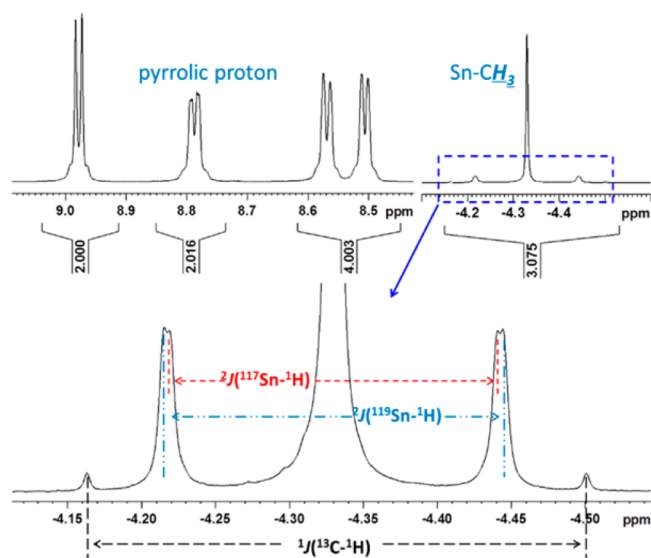
### Scheme 1. Chemical Reactivity of the $[(\text{TPFC})\text{Sn}^{\text{II}}]^-$ Anion **2a**



three sets of aromatic signals with the total integral ratio of 15:8 relative to the corrole ligand. The phenyl proton signals assigned to the axial trityl group (integral ratio 2:2:1) were shifted to high field due to the ring current effect of the corrole ligand.

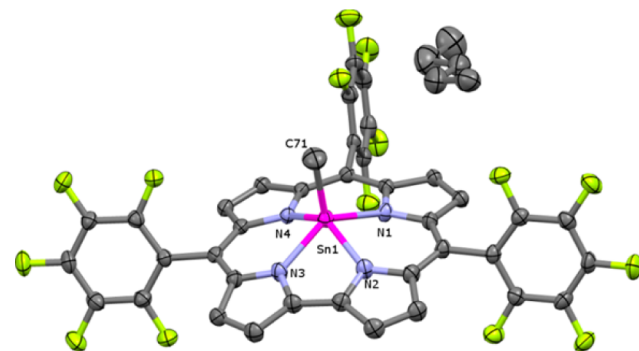
Alkyl stannyl corrole complexes were previously prepared by Kadish et al. from the reaction of Grignard reagents with (corrole) $\text{SnCl}$ .<sup>10a,e</sup> Here, we report a straightforward one-pot method for the preparation of alkyl stannyl corroles in high yield. Mixing  $\text{NaBH}_4$  and excess  $\text{CH}_3\text{I}$  or  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$  with a methanol solution of **1a** resulted in immediate and quantitative formation of  $(\text{TPFC})\text{SnR}$  ( $\text{R} = \text{CH}_3$  (**4**) or  $\text{CH}_2\text{C}_6\text{H}_5$  (**5**), Scheme 1). The  $^1\text{H}$  NMR spectrum of complex **4** exhibited a singlet at  $-4.33$  ppm with diagnostic  $^{117}\text{Sn}$ ,  $^{119}\text{Sn}$ , and  $^{13}\text{C}$

coupling  $^2J(^{117}\text{Sn}-^1\text{H}) = 89$  Hz,  $^2J(^{119}\text{Sn}-^1\text{H}) = 92$  Hz which was assigned to the axial methyl protons (Figure 6). The



**Figure 6.**  $^1\text{H}$  NMR spectrum (benzene- $d_6$ ) of  $(\text{TPFC})\text{SnCH}_3$  (**3**).

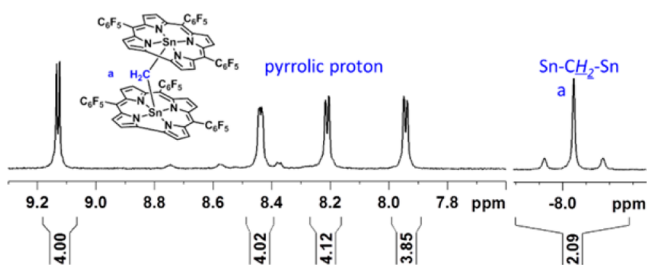
molecular structure of **4** was determined by a single-crystal diffraction study, which, to the best of our knowledge, is the first reported alkyl- $\text{Sn}(\text{IV})$  corrole crystal structure (Figure 7).



**Figure 7.** Structure of **4-n-pentane** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

The tin atom is displaced  $0.78$  Å from the corrole  $N_4$  mean plane toward the methyl ligand, and the corrole ligand adopts a domed conformation. The  $\text{Sn}-\text{C}$  bond length of complex **4** ( $2.114$  Å) is slightly longer than that in  $(\text{OEC})\text{SnC}_6\text{H}_5$  ( $2.105$  Å).<sup>10a</sup>

The reaction of the  $[(\text{TPFC})\text{Sn}^{\text{II}}]^-$  anion **2a** with  $\text{CH}_2\text{Br}_2$  produced  $(\text{TPFC})\text{SnCH}_2\text{Br}$  (**6**) and the methylene-bridged bimetallic complex  $(\text{TPFC})\text{SnCH}_2\text{Sn}(\text{TPFC})$  (**7**), identified by  $^1\text{H}$  and  $^{119}\text{Sn}$  NMR spectrometry (Figure 8, Scheme 1). The one-carbon-bridged  $\text{Sn}^{\text{IV}}-\text{CH}_2-\text{Sn}^{\text{IV}}$  dimer (**7**) is readily identified in solution by comparison of its distinctive pyrrolic proton resonances with the previously reported  $^1\text{H}$  NMR spectra for the  $\mu$ -oxo dimers  $[(\text{TPFC})\text{Fe}]_2\text{O}^{10b}$  and  $[(\text{TPFC})\text{Ge}]_2\text{O}$ .<sup>15</sup> The four sets of pyrrolic hydrogens in the monocorrole  $(\text{TPFC})\text{SnCH}_3$  (**4**) occur within a  $0.5$  ppm range, but in the dinuclear complex **7** they occur over a wider range of  $1.2$  ppm ( $\delta = 9.13-7.93$  ppm) (Figure 8) due to the local magnetic field from the combined ring currents of adjacent corrole rings. The methylene protons of **7** which lie

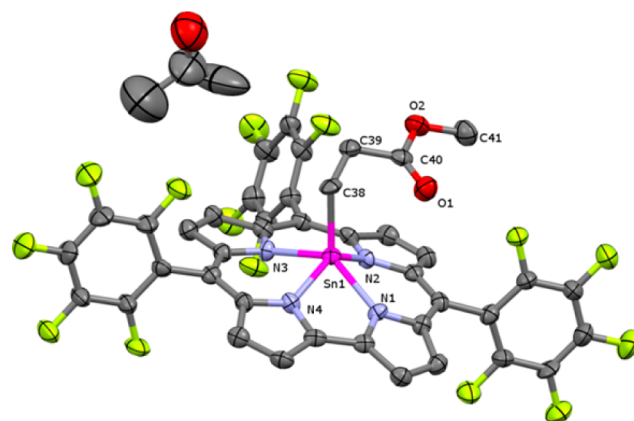


**Figure 8.**  $^1\text{H}$  NMR spectrum (benzene- $d_6$ ) of **7** (pyrrolic and methylene protons).

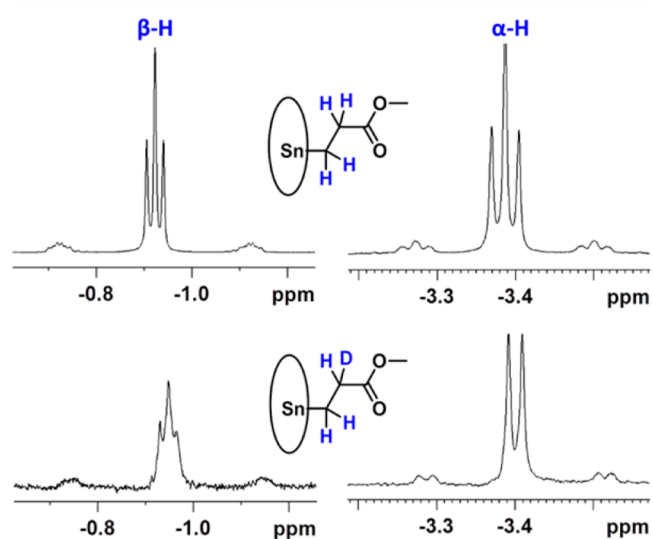
between the two corrole planes experience the combined shielding ring current effects associated with two aromatic rings. The resonance for the  $\text{CH}_2$  hydrogens at  $-8.04$  ppm ( $^2J_{\text{Sn-H}} = 50.2$  Hz) in the  $^1\text{H}$  NMR spectrum arises from coupling with the two magnetically equivalent tin atoms, an unmistakable signature for a methylene-bridged dicorrole structure (Figure 8). The UV-vis spectra exhibited a 13 nm shift of the Soret band to shorter wavelength compared with **4**. Significant broadening of both the Soret and Q bands was also observed, similar to that reported for  $[(\text{TPFC})\text{Ge}]_2\text{O}$ .<sup>15</sup> HRMS (ESI) spectra revealed  $M^+$  signals within acceptable limits of error ( $-1.6$  ppm). The product ratio of **6** and **7** can be modulated by the number of equivalents of  $\text{CH}_2\text{Br}_2$  added. Complex **7** is the first reported bimetallic tin corrole species and can be compared to the structurally characterized complex  $[\{\text{Sn}(\text{tmtaa})\}_2(\mu\text{-CH}_2)]\text{I}_2$  prepared by oxidative addition of  $\text{CH}_2\text{I}_2$  to the tin(II) precursor  $\text{Sn}(\text{tmtaa})$ .<sup>16</sup> The tmtaa ligand (tmtaa = dianion of 6,8,15,17-tetramethyl-5,9,14,18-tetraazadibenzo[14]-annulene dianion) can be considered to be a porphyrin and corrole analogue, comprising a macrocycle containing four nitrogen donors in a square planar arrangement. For  $[\{\text{Sn}(\text{tmtaa})\}_2(\mu\text{-CH}_2)]\text{I}_2$  the  $\text{SnCH}_2\text{Sn}$  protons appear in the  $^1\text{H}$  NMR spectrum at  $0.58$  ppm ( $^2J_{\text{Sn-H}} = 93$  Hz), and in the molecular structure the  $\text{Sn}-\text{CH}_2-\text{Sn}$  bridging angle is  $122.5^\circ$ .<sup>16</sup>

Previously, we reported the reactivity of alkenes with  $(\text{TPFC})\text{GeH}$ . No Ge-alkyl was formed in the reaction of Ge-H with methyl acrylate (MA) until a catalytic amount of KOH was added.<sup>9a</sup> On the basis of these observations, the  $[(\text{TPFC})\text{Ge}^{\text{II}}]^-$  anion was proposed as the intermediate, followed by reaction with alkenes to form germanium alkyls. To investigate the corresponding reactivity of **2a**, excess MA was added to a  $\text{C}_6\text{D}_6$  solution of **2a**. The brown-green solution turned to wine-red immediately, and the newly formed species was identified as  $(\text{TPFC})\text{SnCH}_2\text{CH}_2\text{COOCH}_3$  (**8**, yield >95%). The triplet at  $-3.39$  ppm ( $^3J_{\text{H-H}} = 7.0$  Hz,  $^2J_{\text{H-Sn}} = 91.2$  Hz) in the  $^1\text{H}$  NMR spectrum was attributed to the  $\alpha\text{-CH}_2$  protons adjacent to tin. Complex **8** was also characterized by an X-ray crystal structure determination, and its molecular structure is illustrated in Figure 9.

A control reaction was performed to shed light on the mechanism of the reaction of **2a** with MA. Preparation of complex **2a** by  $\text{NaBH}_4$  reduction of **1a** in  $\text{C}_6\text{D}_6/\text{CH}_3\text{OD}$  followed by addition of MA generated the  $\beta$ -deuterated alkyl tin complex  $(\text{TPFC})\text{SnCH}_2\text{CHD}\text{COOCH}_3$  (**8-D**), indicating that one of the  $\beta$ -protons came from the hydroxyl proton of methanol (Figure 10). The reaction was proposed to proceed by formation of a nucleophilic-addition reaction intermediate followed by protonation by methanol. The anti-Markovnikov selectivity probably resulted from both the steric hindrance of the planar ligand and the electron-positive terminal olefinic



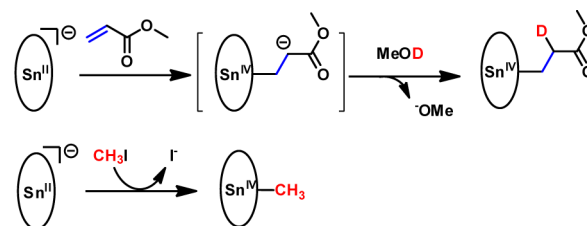
**Figure 9.** Structure of **8-acetone** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.



**Figure 10.**  $^1\text{H}$  NMR spectra (benzene- $d_6$ ) of the alkyl protons of  $(\text{TPFC})\text{SnCH}_2\text{CH}_2\text{C}(\text{O})\text{OMe}$  (**10**) and  $(\text{TPFC})\text{SnCH}_2\text{CHDC}(\text{O})\text{OMe}$ .

carbon. Reaction of **2a** with excess ethyl vinyl ketone (EVK) at room temperature also quantitatively produced  $(\text{TPFC})\text{SnCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_3$  (**9**). When excess  $\text{NaBH}_4$  was added, complex **9** was further reduced to the  $\gamma$ -hydroxy stannyl alkyl compound  $(\text{TPFC})\text{SnCH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$  (**10**). However, using pentene as the substrate only gave trace amounts of tin alkyls due to the less electropositive terminal carbon. The difference in reactivity was in good accord with the generation of a carbanion intermediate stabilized by the electron-withdrawing substituents in MA and EVK (Scheme 2). Ogoshi and co-workers reported reduction of  $(\text{OEP})\text{Rh}^{\text{III}}\text{Cl}$  by  $\text{NaBH}_4$

#### Scheme 2. Proposed Reaction Pathway of $[(\text{TPFC})\text{Sn}^{\text{II}}]^-$ Anion with MA and $\text{CH}_3\text{I}$



to give [(OEP)Rh<sup>I</sup>]<sup>-</sup> and its subsequent reaction with alkenes to form alkyl rhodium(III) porphyrins.<sup>17</sup> The reaction mechanism involved nucleophilic attack of the Rh(I) anion on the alkene substrates to generate  $\beta$ -carbanion rhodium alkyls followed by protonation. Formation of alkyl stannyl corrole complexes from the [(TPFC)Sn<sup>II</sup>]<sup>-</sup> anion and alkyl halides was proposed to proceed through a similar classical S<sub>N</sub>2 pathway (Scheme 2).

Activation of alkyl halides by divalent tin(II) is not unusual. Most reports discuss the reactions of dicoordinate L<sub>2</sub>Sn(II) with alkyl halides RX via oxidative addition to give L<sub>2</sub>Sn<sup>IV</sup>(R)X species.<sup>18</sup> Kadish et al. reported oxidative addition of CH<sub>3</sub>I to several divalent Sn(II) porphyrin complexes (Por)Sn(II) with immediate generation of (Por)Sn<sup>IV</sup>(CH<sub>3</sub>)I.<sup>18c</sup> The different reactivity compared with nucleophilic attack by the [(TPFC)Sn<sup>II</sup>]<sup>-</sup> anion reveals the unique features of corrole ligand: (i) the preference for five-coordinate over six-coordinate geometry facilitates the S<sub>N</sub>2 pathway;<sup>4</sup> (ii) the Sn(II) metal center combined with the trianionic corrole ligand gives an anionic complex [(TPFC)Sn<sup>II</sup>]<sup>-</sup> which favors a nucleophilic displacement reaction to form a neutral Sn(IV) complex as the product, rather than the conventional oxidative addition observed for the porphyrin complex where both Sn–C and Sn–X bond are formed with coordination number increased by 2.

Monomeric L<sub>2</sub>Sn(II): can be considered to be a heavy element carbene analogue; however, it is less reactive toward multiple bonds than its lighter group 14 congeners. For the activation of triple bonds, only strained cycloalkynes were reported to react with stannylenes.<sup>19</sup> 1,3-Dienes were the only alkenes that formed 1,4-adducts with stannylenes.<sup>20</sup> Although there are reports of Sn(II) hydride species that activated multiple bonds such as alkynes, ketones, and CO<sub>2</sub>, these reactions essentially display metal hydride reactivities that generate further functionalized Sn(II) species.<sup>5g</sup> Thus, the Sn(II) corrole system offers a novel reaction pattern with alkenes via a nucleophilic addition pathway.

In summary, we have reported the synthesis of a novel four-coordinate, divalent tin corrole complex [(TPFC)Sn<sup>II</sup>]<sup>-</sup> (**2a**) by facile reduction of (TPFC)Sn<sup>IV</sup>Cl (**1a**) using NaBH<sub>4</sub>. The anion **2a** was characterized on the basis of UV–vis data observed in the course of the stopped flow reduction experiment and DFT calculations. The divalent tin complex **2a** showed highly nucleophilic chemical reactivity toward alkyl halides and olefins to produce quantitatively alkyl stannyl corrole complexes through a nucleophilic attack pathway. An unprecedented one-carbon bridged dimetallic (TPFC)Sn–CH<sub>2</sub>Sn(TPFC) was obtained.

## EXPERIMENTAL SECTION

**Materials and Physical Measurements.** C<sub>6</sub>D<sub>6</sub> and CDCl<sub>3</sub> were purchased from Cambridge Isotope Laboratory Inc. Other solvents were distilled before use. Aldehydes and olefins were purchased from Aldrich or Alfa Aesar and were distilled before use, and all other chemicals were purchased from Aldrich or Alfa Aesar unless otherwise noted and used as received. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker AVII<sup>+</sup>-400 spectrometer, Bruker AM 300 MHz spectrometer, or a Bruker AM 400 MHz spectrometer at ambient temperature. <sup>19</sup>F NMR and <sup>119</sup>Sn NMR spectra were recorded on a Bruker AVII<sup>+</sup>-500 spectrometer with reference to CF<sub>3</sub>COOH and SnMe<sub>4</sub>, respectively. IR spectroscopy was performed either on a PerkinElmer Spectrum 100 FT-IR spectrometer or on a PerkinElmer Paragon 1000 PC FT-IR spectrometer. Mass spectra were taken on a Bruker Apex IV FTMS or on a VG-7070 mass spectrometer using the FAB+ ionization method and *m*-nitrobenzyl alcohol as matrix. UV–vis

spectra were recorded on a SHIMADZU UV-3100 UV–vis–NIR spectrophotometer or on a PerkinElmer Instrument Lambda 35 UV–vis spectrometer. The single-crystal X-ray diffraction data were collected on a Rigaku MM007HF Saturn724+ diffractometer or on a Siemens SMART CCD diffractometer with a Mo K $\alpha$  radiation source. Stopped-flow data were obtained using a SX20 stopped-flow spectroscopy purchased from the Applied Photophysics Ltd.

**Computational Methods.** All calculations were carried out with the program ADF 2013<sup>21</sup> program using the OLYP<sup>22</sup> functional and ZORA STO-TZ2P basis sets. Scalar relativistic effects were taken into account with the ZORA Hamiltonian and the ZORA basis sets. Grimme's D3 correction was employed to take dispersion effects into account.<sup>23</sup> The optimized geometries of **1a** and **2a** were verified as true minima using vibrational analyses.

5,10,15-Tris(pentafluorophenyl)corrole H<sub>3</sub>(TPFC),<sup>2</sup> 5,10,15-triphenylcorrole (H<sub>3</sub>TPC),<sup>24</sup> 5,10,15-tritylcorrole (H<sub>3</sub>TTC),<sup>24</sup> and (TPFC)SnCl (**1a**)<sup>30b</sup> were prepared by literature procedures.

(TPP)SnCl (**1b**). H<sub>3</sub>(TPC) (138 mg, 0.26 mmol) and SnCl<sub>2</sub> (493 mg, 2.6 mmol) were added to a 25 mL round-bottom flask with a Schlenk-type side arm. The flask was heated several times under vacuum and flushed with nitrogen. Dry pyridine (10 mL) was added by syringe through a rubber septum. The mixture was refluxed for 10 min during which time the color changed from dark-green to dark-blue. After cooling to room temperature the solvent was evaporated under reduced pressure, and the resulting bright violet residue was dissolved in dichloromethane. Insoluble salts were removed by filtration, and the filtrate was passed through a silica column with dichloromethane/methanol (19:1) as eluent. A dark blue band was collected and the solvent removed from this fraction under reduced pressure to give Sn(TPP)Cl as dark blue-purple crystals (yield 80 mg, 45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 9.23 (d, <sup>3</sup>J(H,H) = 4.19 Hz, 2H; H $\beta$ ), 9.15 (2 H, d, <sup>3</sup>J(H,H) = 4.80 Hz, 2H; H $\beta$ ), 8.86 (d, <sup>3</sup>J(H,H) = 2.4 Hz, 2H; H $\beta$ ), 8.84 (d, <sup>3</sup>J(H,H) = 1.9 Hz, 2H; H $\beta$ ), 8.42 (d, <sup>3</sup>J(H,H) = 7.9 Hz, 2H; *ortho*-H), 7.97 (d, <sup>3</sup>J(H,H) = 7.5 Hz, 4H; *ortho*-H), 7.76 (m, 7H; *meta,para*-H), 7.59 (m, 2H; *meta*-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 144.01, 141.01, 140.23, 138.74, 134.80, 134.74, 134.57, 134.55, 134.51, 134.43, 133.88, 129.57, 127.80, 127.67, 127.48, 127.06, 125.72, 118.63, 118.58, 117.23, 111.09, 104.50, 103.47. IR:  $\nu$  (cm<sup>-1</sup>) 3035 (w), 2921 (w), 2851 (w), 1889 (w), 1814 (w), 1770 (w), 1724 (w), 1597 (w), 1575 (w), 1496 (w), 1456 (m), 1440 (w), 1430 (m), 1373 (w), 1312 (m), 1261 (m), 1220 (w), 1192 (w), 1175 (w), 1155 (w), 1077 (m), 1062 (s), 1036 (s), 1025 (s), 1010 (m), 996 (s), 903 (m), 842 (w), 790 (s), 775 (s), 750 (s), 730 (m), 709 (s), 698 (vs), 677 (m), 663 (s), 647 (m), 632 (m), 620 (m), 592 (w). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$  (nm) ( $\epsilon$ ): 419 (1.008 42), 530 (0.040 42), 567 (0.062 86), 603 (0.1439). MS (FAB, *m*-nitrobenzyl alcohol): *m/z* (%) [M]<sup>+</sup> 678 (13), [M – Cl]<sup>+</sup> 643 (10), [M – C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> 565 (1). HRMS (FAB) Calcd for C<sub>37</sub>H<sub>23</sub><sup>35</sup>ClN<sub>4</sub><sup>120</sup>Sn: 678.06332, Found: 678.06277.

(TTC)SnCl (**1d**). Anhydrous SnCl<sub>2</sub> (152 mg, 0.802 mmol) and H<sub>3</sub>(TTC) (50.0 mg, 0.088 mmol) were dissolved in DMF (8 mL) under N<sub>2</sub>. After 40 min of heating under reflux the solvent was evaporated, and the bright violet residue was dissolved in ethyl acetate. The subsequent chromatography on silica using ethyl acetate as eluent afforded SnCl(TTC) as a purple solid (60 mg, 95%). Crystals suitable for crystallography were obtained from a solution of benzene/*n*-heptanes. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 9.19 ppm (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2H,  $\beta$ -pyrrole), 9.15 (d, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz, 2H; H $\beta$ ), 8.85 (d, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz, 2H; H $\beta$ ), 8.83 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2H; H $\beta$ ), 8.27 (d, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 2H; *meta*-H), 7.84 (d, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 2H; *meta*-H), 7.56–7.65 (m, 6H; *meta,para*-H), 7.51 (d, <sup>3</sup>J<sub>H,H</sub> = 7.7 Hz, 2H; *ortho*-H), 2.69 (s, 9 H; CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 21.8, 113.4, 115.5, 117.3, 118.9, 126.0, 127.3, 128.7, 128.8, 129.9, 135.0, 137.6, 137.9, 139.1, 140.6, 144.5 ppm. IR:  $\nu$  (cm<sup>-1</sup>) 3022.1 (w), 2954.0 (w), 2920.1 (m), 2854.3 (w), 2105.1 (w), 1908 (w), 1803.8 (w), 1645.8 (w), 1608.9 (w), 1566.8 (w), 1510.3 (m), 1455.3 (m), 1428.8 (w), 1372.6 (w), 1330.6 (w), 1313.1 (s), 1279.7 (w), 1221.8 (w), 1180.6 (m), 1107.5 (w), 1060.8 (s), 1044.9 (w), 1032.6 (s), 1020.7 (m), 997.1 (m), 905.6 (w), 880.2 (w), 855.5 (w), 841.2 (w), 789.1 (s), 773.8 (s), 719.2 (m), 704.7 (w), 677.6 cm<sup>-1</sup> (m). UV–vis (2):  $\lambda_{\max}$  ( $E_{\text{rel}}$ ) = 420.0

(1.00), 533.0 (0.04), 569.5 (0.05), 609.0 nm (0.15). MS (TOF/ESI)  $m/z$  (%):  $[M]^+$  720.1 (45),  $[M^+ - Cl]$  685.1 (100), 595.3 (9), 443.3 (3), 150.1 (2), 102.1 (9). HRMS Calcd for  $(C_{40}H_{29}N_4ClSn)$  720.1103. Found: 720.1092;  $\Delta = -0.0011$ .

**Na[(TPFC)Sn<sup>II</sup>] (2a).** To a benzene/methanol ( $v/v = 30:1$ ) solution of (TPFC)Sn–Cl (**1a**) was added  $NaBH_4$  in an inert atmosphere, and product  $Na[(TPFC)Sn^{II}]$  (**2a**) was formed immediately. Excess  $NaBH_4$  was removed by filtration of benzene or toluene solution of  $Na[(TPFC)Sn^{II}]$  (**2a**, yield >95%)  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  (ppm) 9.07 (d,  $^3J(H,H) = 3.7$  Hz, 2H;  $H_\beta$ ), 8.91 (d,  $^3J(H,H) = 4.2$  Hz, 2H;  $H_\beta$ ), 8.65 (m, 4H;  $H_\beta$ ).  $^{19}F$  NMR (376 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –137.0 (dd,  $^3J(F,F) = 24.3$  Hz,  $^4J(F,F) = 7.9$  Hz, 2F; *ortho-F*), –137.4 (m, 2F; *ortho-F*), –137.6 (dd,  $^3J(F,F) = 24.3$  Hz,  $^4J(F,F) = 7.7$  Hz, 2F; *ortho-F*), –152.6 (t,  $^3J(F,F) = 20.9$  Hz, 2F; *para-F*), –152.8 (t,  $^3J(F,F) = 20.8$  Hz, 1F; *para-F*), –161.8 (m, 6F; *meta-F*).  $^{119}Sn$  NMR (186 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –57.6.

**(TPFC)SnC(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> (3, 81%).**  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  (ppm) 8.83 (d,  $^3J(H,H) = 4.1$  Hz, 2H;  $H_\beta$ ), 8.73 (dd,  $^3J(H,H) = 4.7$  Hz, 2H;  $H_\beta$ ), 8.50 (d,  $^3J(H,H) = 4.6$  Hz, 2H;  $H_\beta$ ), 8.39 (d,  $^3J(H,H) = 4.2$  Hz, 2H;  $H_\beta$ ), 6.51 (t,  $^3J(H,H) = 7.4$  Hz, 3H; *para-H*), 6.39 (t,  $^3J(H,H) = 7.7$  Hz, 6H; *meta-H*), 4.21 (d,  $^3J(H,H) = 9.3$  Hz, 6H; *ortho-H*).  $^{19}F$  NMR (376 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –136.5 (2F; *ortho-F*), –136.9 (1F; *ortho-F*), –137.3 (1F; *ortho-F*), –137.8 (1F; *ortho-F*), –152.5 (m, 3F; *para-F*), –161.6 (m, 6F; *meta-F*).  $^{119}Sn$  NMR (186 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –464. HRMS (ESI) Calcd  $[M]^+$ : 1156.071 20. Found: 1156.072 85. Calcd  $[M + H]^+$ : 1157.079 02. Found: 1157.079 71.

**General Procedures for Preparation of (TPFC)SnR (R = Alkyl) Complexes.** Excess alkyl halides or alkenes were added into benzene solution of **2** in an inert atmosphere. (TPFC)SnR (R = alkyl) complexes was formed immediately in high yields. Column chromatography (silica, PE:CH<sub>2</sub>Cl<sub>2</sub> = 1:3) afforded pure compounds. One-pot synthesis by mixing complex **1**, substrates, and  $NaBH_4$  in benzene/methanol solution under an inert atmosphere also produced (TPFC)SnR (R = alkyl) complexes.

**(TPFC)SnCH<sub>3</sub> (4, Yield >95%).**  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  (ppm) 8.98 (d,  $^3J(H,H) = 4.1$  Hz, 2H;  $H_\beta$ ), 8.79 (d,  $^3J(H,H) = 4.7$  Hz, 2H;  $H_\beta$ ), 8.57 (d,  $^3J(H,H) = 4.5$  Hz, 2H;  $H_\beta$ ), 8.63 (m, 2H;  $H_\beta$ ), –4.33 (s,  $^2J(^1H, ^{117}Sn) = 88.9$  Hz,  $^2J(^1H, ^{119}Sn) = 91.6$  Hz,  $^1J(^1H, ^{13}C) = 135.3$  Hz; 2H).  $^{19}F$  NMR (376 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –137.8 (m, 3F; *ortho-F*), –138.3 (dd,  $^3J(F,F) = 24.1$  Hz,  $^4J(F,F) = 7.1$  Hz, 2F; *ortho-F*), –138.4 (dd,  $^3J(F,F) = 24.9$  Hz,  $^4J(F,F) = 7.4$  Hz, 1F; *ortho-F*), –152.3 (t,  $^3J(F,F) = 22.3$  Hz, 1F; *para-F*), –152.4 (t,  $^3J(F,F) = 22.1$  Hz, 2F; *para-F*), –161.9 (m, 6F; *meta-F*).  $^{119}Sn$  NMR (186 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –355. UV–vis (MeOH)  $\lambda_{max}$  (nm): 397, 418, 530, 570, 599. HRMS (ESI) Calcd  $[M + H]^+$ : 928.984 61. Found: 928.987 08. The complex was crystallized from slow evaporation of hexane solution.

**(TPFC)SnCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (5, >95%).**  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  (ppm) 8.95 (d,  $^3J(H,H) = 4.1$  Hz, 2H;  $H_\beta$ ), 8.72 (d,  $^3J(H,H) = 4.5$  Hz, 2H;  $H_\beta$ ), 8.50 (d,  $^3J(H,H) = 4.5$  Hz, 2H;  $H_\beta$ ), 8.46 (d,  $^3J(H,H) = 4.1$  Hz, 2H;  $H_\beta$ ), 6.41 (t,  $^3J(H,H) = 7.3$  Hz, 1H; *para-H*), 6.29 (t,  $^3J(H,H) = 7.4$  Hz, 2H; *meta-H*), 4.12 (d,  $^3J(H,H) = 7.5$  Hz, 2H; *ortho-H*). –2.12 (s,  $^2J(^1H, ^{119}Sn) = 110.4$  Hz, 2H; CH<sub>2</sub>).  $^{19}F$  NMR (376 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –137.6 (dd,  $^3J(F,F) = 25.0$  Hz,  $^4J(F,F) = 6.9$  Hz, 2F; *ortho-F*), –137.7 (dd,  $^3J(F,F) = 25.2$  Hz,  $^4J(F,F) = 7.7$  Hz, 1F; *ortho-F*), –138.1 (dd,  $^3J(F,F) = 23.9$  Hz,  $^4J(F,F) = 7.1$  Hz, 1F; *ortho-F*), –138.2 (dd,  $^3J(F,F) = 25.3$  Hz,  $^4J(F,F) = 7.5$  Hz, 2F; *ortho-F*), –152.6 (t,  $^3J(F,F) = 18.6$  Hz, 1F; *para-F*), –152.7 (t,  $^3J(F,F) = 20.1$  Hz, 2F; *para-F*), –162.0 (m, 6F; *meta-F*).  $^{119}Sn$  NMR (186 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –368. UV–vis (MeOH)  $\lambda_{max}$  (nm): 400, 421, 532, 572, 602. HRMS (ESI) Calcd  $[M]^+$ : 1004.008 27. Found: 1004.007 25.

**(TPFC)SnCH<sub>2</sub>Br (6).**  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  (ppm) 8.99 (d,  $^3J(H,H) = 4.2$  Hz, 2H;  $H_\beta$ ), 8.81 (d,  $^3J(H,H) = 4.6$  Hz;  $H_\beta$ ), 8.60 (m,  $^3J(H,H) = 4.7$  Hz, 2H;  $H_\beta$ ), 8.53 (d,  $^3J(H,H) = 4.2$  Hz, 2H;  $H_\beta$ ), –2.31 (s,  $^2J(^1H, ^{119}Sn) = 27.1$  Hz, 2H).  $^{19}F$  NMR (376 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –137.1 (dd,  $^3J(F,F) = 25.2$  Hz,  $^4J(F,F) = 8.0$  Hz, 1F; *ortho-F*), –138.5 (dd,  $^3J(F,F) = 25.2$  Hz,  $^4J(F,F) = 7.2$  Hz, 2F; *ortho-F*), –139.1 (dd,  $^3J(F,F) = 25.2$  Hz,  $^4J(F,F) = 7.2$  Hz, 1F; *ortho-F*), –138.2 (dd,  $^3J(F,F) = 25.2$  Hz,  $^4J(F,F) = 7.5$  Hz, 1F; *ortho-F*), –153.2 (m, 3F; *para-F*), –162.6 (m, 6F; *meta-F*).  $^{119}Sn$  NMR (186 MHz,  $C_6D_6$ ):  $\delta$

(ppm) –420. UV–vis (MeOH)  $\lambda_{max}$  (nm): 397, 418, 530, 569, 595. HRMS (ESI) Calcd  $[M]^+$ : 1005.886 23. Found: 1005.887 41.

**(TPFC)SnCH<sub>2</sub>Sn(TPFC) (7).**  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  (ppm) 9.13 (d,  $^3J(H,H) = 4.1$  Hz, 4H;  $H_\beta$ ), 8.43 (m, 4H;  $H_\beta$ ), 8.21 (m,  $^3J(H,H) = 4.6$  Hz, 4H;  $H_\beta$ ), 7.94 (d,  $^3J(H,H) = 4.5$  Hz, 4H;  $H_\beta$ ), –8.04 (s,  $^3J(^1H, ^{119}Sn) = 98.7$  Hz, 2H).  $^{19}F$  NMR (376 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –135.9 (m, 4F; *ortho-F*), –136.8 (dd,  $^3J(F,F) = 25.0$  Hz,  $^4J(F,F) = 7.2$  Hz, 2F; *ortho-F*), –138.4 (dd,  $^3J(F,F) = 25.4$  Hz,  $^4J(F,F) = 7.4$  Hz, 4F; *ortho-F*), –138.5 (dd,  $^3J(F,F) = 25.1$  Hz,  $^4J(F,F) = 6.7$  Hz, 2F; *ortho-F*), –152.4 (t,  $^3J(F,F) = 21.6$  Hz, 2F; *para-F*), –152.5 (t,  $^3J(F,F) = 21.2$  Hz, 4F; *para-F*), –162.6 (m, 12F; *meta-F*).  $^{119}Sn$  NMR (186 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –339. UV–vis (MeOH)  $\lambda_{max}$  (nm): 405, 534, 576, 601. HRMS (ESI) Calcd  $[M]^+$ : 1839.921 73. Found: 1837.928 66.

**(TPFC)SnCH<sub>2</sub>CH<sub>2</sub>C(O)OMe (8, >95%).**  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  (ppm) 8.98 (d,  $^3J(H,H) = 4.1$  Hz, 2H;  $H_\beta$ ), 8.90 (m, 2H;  $H_\beta$ ), 8.68 (m, 2H;  $H_\beta$ ), 8.52 (d,  $^3J(H,H) = 4.1$  Hz, 2H;  $H_\beta$ ), 2.59 (s, 3H), –0.92 (t,  $^3J(H,H) = 6.8$  Hz,  $^3J(^1H, ^{119}Sn) = 160.1$  Hz, 2H), –3.39 (t,  $^3J(H,H) = 7.0$  Hz,  $^2J(^1H, ^{119}Sn) = 91.2$  Hz, 2H).  $^{19}F$  NMR (376 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –137.6 (dd,  $^3J(F,F) = 24.5$  Hz,  $^4J(F,F) = 7.4$  Hz, 1F; *ortho-F*), –138.1 (m, 2F; *ortho-F*), –138.3 (m, 2F; *ortho-F*), –138.7 (dd,  $^3J(F,F) = 25.4$  Hz,  $^4J(F,F) = 7.8$  Hz, 1F; *ortho-F*), –152.5 (m, 3F; *para-F*), –161.9 (m, 6F; *meta-F*).  $^{119}Sn$  NMR (186 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –368. UV–vis (MeOH)  $\lambda_{max}$  (nm): 397, 418, 531, 570, 598. HRMS (ESI) Calcd  $[M]^+$ : 999.997 99. Found: 1000.002 17. The complex was crystallized from hexane/acetone solution.

**(TPFC)SnCH<sub>2</sub>CHDC(O)OMe (8-D, >95%).**  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  (ppm) 8.98 (d,  $^3J(H,H) = 4.1$  Hz, 2H;  $H_\beta$ ), 8.78 (m, 2H;  $H_\beta$ ), 8.56 (d,  $^3J(H,H) = 4.4$  Hz;  $H_\beta$ ), 8.51 (d,  $^3J(H,H) = 4.2$  Hz, 2H;  $\beta$ -pyrrole H), 2.58 (s, 3H), –0.95 (t,  $^3J(H,H) = 6.9$  Hz,  $^3J(^1H, ^{119}Sn) = 158$  Hz, 1H), –3.40 (d,  $^3J(H,H) = 7.0$  Hz,  $^2J(^1H, ^{119}Sn) = 91.8$  Hz, 2H). UV–vis (MeOH)  $\lambda_{max}$  (nm): 397, 418, 530, 570, 599. HRMS (ESI) Calcd  $[M]^+$ : 1001.004 27. Found: 1001.005 69.

**(TPFC)SnCH<sub>2</sub>CH<sub>2</sub>COCH<sub>2</sub>CH<sub>3</sub> (9, >95%).** Reaction with EVK to give **9** was performed separately instead of one-pot synthesis. Excess of  $NaBH_4$  should be removed before addition of EVK.  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  (ppm) 9.02 (dd,  $^3J(H,H) = 1$  Hz, 2H,  $H_\beta$ ), 8.81 (d,  $^3J(H,H) = 4.5$  Hz, 2H;  $H_\beta$ ), 8.58 (d,  $^3J(H,H) = 4.5$  Hz, 2H;  $H_\beta$ ), 8.54 (d,  $^3J(H,H) = 4.0$  Hz, 2H;  $H_\beta$ ), 0.58 (q,  $^3J(H,H) = 7.3$  Hz, 2H;  $\delta$ -CH<sub>2</sub>), –0.16 (t,  $^3J(H,H) = 7.3$  Hz, 3H;  $\epsilon$ -CH<sub>3</sub>), –0.93 (t,  $^3J(H,H) = 6.6$  Hz,  $^3J(Sn,H) = 166$  Hz, 2H;  $\beta$ -CH<sub>2</sub>), –3.43 (t,  $^3J(H,H) = 6.6$  Hz,  $^3J(Sn,H) = 94$  Hz, 2H;  $\alpha$ -CH<sub>2</sub>).  $^{19}F$  NMR (376 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –137.5 (dd,  $^3J(F,F) = 24.0$  Hz,  $^4J(F,F) = 7.3$  Hz, 1F; *ortho-F*), –137.7 (dd,  $^3J(F,F) = 25.5$  Hz,  $^4J(F,F) = 7.7$  Hz, 2F; *ortho-F*), –138.1 (dd,  $^3J(F,F) = 25.7$  Hz,  $^4J(F,F) = 7.6$  Hz, 2F; *ortho-F*), –138.5 (dd,  $^3J(F,F) = 26.2$  Hz,  $^4J(F,F) = 7.3$  Hz, 1F; *ortho-F*), –152.6 (t,  $^3J(F,F) = 21.8$  Hz, 1F; *para-F*), 152.7 (t,  $^3J(F,F) = 22.9$  Hz, 2F; *para-F*), –162.1 (m, 6F; *meta-F*). UV–vis (MeOH)  $\lambda_{max}$  (nm): 399, 420, 532, 572, 601. HRMS (ESI) Calcd  $[M + H]^+$ : 999.026 58. Found: 999.028 25.

**(TPFC)SnCH<sub>2</sub>CH<sub>2</sub>C(OH)HCH<sub>2</sub>CH<sub>3</sub> (10).** One-pot reaction of EVK generated further reduced complex **10**.  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  (ppm) 8.99 (dd,  $^3J(H,H) = 4.1$  Hz, 2H;  $\beta$ -pyrrole H), 8.78 (m, 2H; 2H,  $H_\beta$ ), 8.57 (t,  $^3J(H,H) = 5.0$  Hz, 2H; 2H,  $H_\beta$ ), 8.52 (d,  $^3J(H,H) = 3.9$  Hz, 2H; 2H,  $H_\beta$ ), 1.01 (m, 1H;  $\gamma$ -OH), –0.11 (t,  $^3J(H,H) = 7.4$  Hz, 3H;  $\epsilon$ -CH<sub>3</sub>), –0.27 (m, 2H;  $\delta$ -CH<sub>2</sub>), –1.16 (d,  $^3J(H,H) = 4.4$  Hz, 1H;  $\gamma$ -CH), –1.61 (m, 1H;  $\beta$ -CH), –1.94 (m, 1H;  $\beta$ -CH), –3.31 (m, 2H,  $\alpha$ -CH<sub>2</sub>).  $^{19}F$  NMR (376 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –137.4 (dd,  $^3J(F,F) = 25.7$  Hz,  $^4J(F,F) = 7.3$  Hz, 2F; *ortho-F*), –137.6 (dd,  $^3J(F,F) = 25.0$  Hz,  $^4J(F,F) = 8.0$  Hz, 1F; *ortho-F*), –137.8 (dd,  $^3J(F,F) = 25.4$  Hz,  $^4J(F,F) = 7.7$  Hz, 1F; *ortho-F*), –138.2 (dd,  $^3J(F,F) = 24.2$  Hz,  $^4J(F,F) = 7.0$  Hz, 2F; *ortho-F*), –152.5 (t,  $^3J(F,F) = 21.5$  Hz, 3F; *para-F*), –161.9 (m, 6F; *meta-F*).  $^{119}Sn$  NMR (186 MHz,  $C_6D_6$ ):  $\delta$  (ppm) –380.  $\lambda_{max}$  (nm): 400, 420, 532, 572, 601. UV–vis (MeOH)  $\lambda_{max}$  (nm): 399, 420, 532, 572, 601. HRMS (ESI) Calcd  $[M + H]^+$ : 1001.042 23. Found: 1001.039 69.

## ■ ASSOCIATED CONTENT

## ■ Supporting Information

Details of the synthetic procedures and spectral data for complexes 2–10. X-ray crystallographic data in CIF format for compounds 1d, 4, and 8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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