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Synthesis, Structures, and Electronic Properties of Triple- and Double-Decker Ruthenocenes Incorporated by a Group 14 Metallole Dianion Ligand

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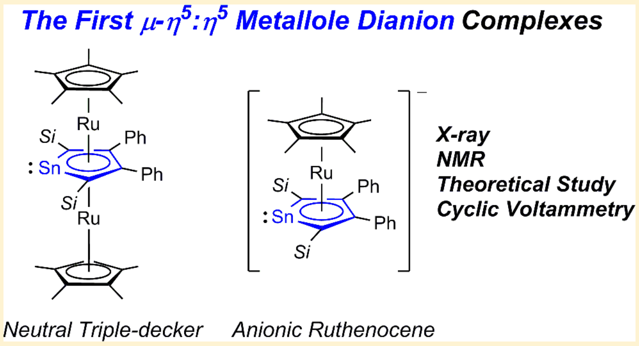
Supporting Information



ABSTRACT: The neutral triple-decker ruthenocenes and anionic ruthenocene bearing a stannole dianion were successfully synthesized by the reactions of dilithiostannoles with $[Cp^*RuCl]_4$. This is the first example of a transition-metal complex bearing a group 14 metallole dianion with $\mu{-}\eta^5{:}\eta^5$ coordination mode. These complexes were fully characterized by NMR spectroscopy and single-crystal X-ray diffraction analysis. In the complexes, each of the ruthenium atoms is coordinated by the stannole ring in an η^5-fashion. The aromaticity of the stannole dianion moieties is retained judging from no C−C bond alternation in the stannole rings. CH/π interaction was found in the packing structure of the $SiMe_3$ derivative, which leads to a well-ordered column-like structure. The oxidation wave of the triple-decker complex was observed at −0.43 V (vs ferrocene), which reveals that the triple-decker type heavy ruthenocene is oxidized more easily than the ferrocene. Comparison of the oxidation potential between the triple-decker complex and decamethylruthenocene (Cp^*_2Ru, $Cp^* = \eta^5\text{-}C_5Me_5$) reveals that a stannole ligand functions as an electron-donating ligand much stronger than the conventional electron-rich Cp* ligand.

INTRODUCTION

Cyclopentadienyl anions ($C_5H_5^-$; Cp^-) have been one of the most important ligands for transition-metal complexes since the structural elucidation of ferrocene (Cp_2Fe) in 1952.[1] A number of transition-metal complexes bearing Cp ligands as ancillary ligands are widely used as catalysts and materials in a wide variety of areas such as synthetic chemistry, polymer chemistry, and materials science.[2] In general, substituents on the cyclopentadienyl rings such as electron-donating alkyl and silyl groups, and electron-withdrawing carboxyl groups perturb electronic states as well as steric environments of the original Cp complexes, and the resulting complexes exhibit new catalytic activity and selectivity.[3] On the other hand, replacing carbon atoms of Cp rings by heteroatoms has also attracted considerable attention because such conversion would produce new coordination modes, and their electron-donating and -accepting properties would be drastically changed. For example, C_3B_2,[4] CB_2N_2,[5] PC_4,[6] P_5,[7] SbC_4,[8] and BiC_4[9] rings behave as η^5-ligands toward transition metals and it was proved that the CB_2N_2 and P_5 rings function as strong electron-donor and -acceptor, respectively. In contrast, transition-metal complexes bearing heavier group 14 analogues of Cp^- ($EC_4R_5^-$ or $E_2C_3R_5^-$, where E = Si, Ge, Sn, Pb and R = substituents) as η^5-coordinating ligands have much less been explored, even though such heavier Cp^- ligands would function as rather strong electron-donating ligands because of their high HOMO level derived from heavy atoms. In fact, η^5-sila-, germa-, trisila-, and disilagerma-cyclopentadienyl (SiC_4,[10] GeC_4,[11] Si_3C_2,[12] and Si_2GeC_2,[13] respectively) complexes have been synthesized by Tilley and Sekiguchi's groups independently, which were summarized in Chart 1, and their electrochemical analyses revealed that these complexes are oxidized more easily than the corresponding complexes bearing a well-known electron-donating ligand, Cp* ($Cp^* = \eta^5\text{-}C_5Me_5$). The low-lying oxidation potentials of such heavy metallocenes can be attributed to strong electron-donating nature of the heavy Cp^- ligands. Notably, an η^5-germole hafnium complex exhibits a σ-bond metathesis that cannot take place using the corresponding carbon derivatives.[14] However, the research on transition-metal chemistry of heavier group 14 analogues of Cp^- is limited to Si and Ge cases and the further heavy analogues, Sn and Pb

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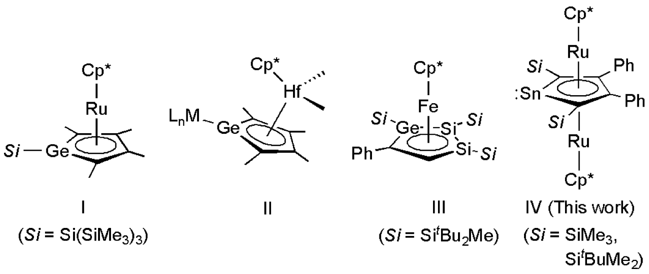
Chart 1. Selected Examples for Heavier Group 14 Derivatives of Metallocenes



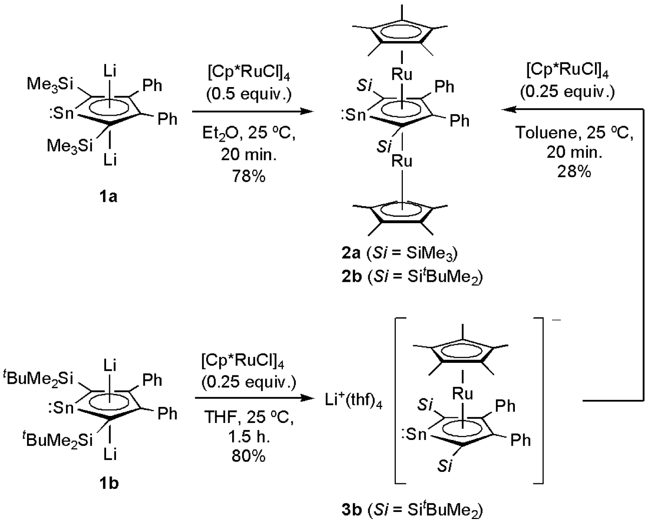
derivatives, have never been synthesized even though electron-donating ability of heavy Cp^- ligands bearing Sn and Pb is expected to surpass that of the Si and Ge analogues.

It should be noted that group 14 metalloles (EC_4, where E = Si, Ge, Sn, Pb) can form more reduced species than Cp^-, that is, metallole dianions ($EC_4R_4^{2-}$), which is in sharp contrast to the fact that such dianionic species have never been synthesized in the all-carbon cases (C_5 ring). All the family of group 14 metallole dianions (EC_4^{2-} where E = Si,[15] Ge,[16] Sn,[17] Pb[18]) have already been synthesized and structurally characterized in the last two decades. The next challenge in this field is an application of such metallole dianions as novel η^5-coordinating ligands. The two anionic charges enable the metallole dianions to coordinate two transition-metals in μ–η^5:η^5- or μ–η^1:η^5-fashions. Moreover, triple- and multidecker complexes containing such metallole dianions are expected to be neutral, which is in sharp contrast to the fact that triple-decker complexes composed of three Cp^- ligands and two transition metals $\{(\eta^5\text{-CpM})(\mu\text{–}\eta^5{:}\eta^5\text{-Cp})[M(\eta^5\text{-Cp})]\}$ are always cationic species.[19] To synthesize metallole dianion complexes, reactions of metallole dianions with transition-metal halides are the straightforward methods. Nevertheless, to the best of our knowledge, there has been only one report on such reactions, which resulted in the formation of unexpected products.[20] Tilley's group reported the first germole dianion complex, where the germole dianion coordinates to group 9 metals and hafnium in η^1- and η^5-fashions, respectively (II in Chart 1). Therefore, metallole dianion transition-metal complexes bearing μ–η^5:η^5-coordinating modes, the simplest ferrocene-type triple-decker complexes, remain elusive. We report herein the synthesis, structures and electronic analysis of the first triple-decker complex bearing a μ–η^5:η^5-metallole dianion. The synthesis and structure of an anionic sandwich complex is also demonstrated.

■ RESULTS AND DISCUSSION

Reaction of dilithiostannole **1a**[21] with 0.5 equiv of $[Cp^*RuCl]_4$ in diethyl ether provided the first η^5-stannole complex **2a**, which is also worthy of note in terms of the first example of μ–η^5:η^5-metallole dianion transition-metal complex (Scheme 1). The corresponding reaction using 0.25 equiv of $[Cp^*RuCl]_4$ was next examined to introduce only one Cp*Ru unit to the stannole. However, the reaction also gave **2a** and a half amount of **1a** remained, which suggests that introduction of the second Cp*Ru unit took place much faster than that of the first one. When another dilithiostannole **1b**[21] that bears silyl groups bulkier than those of **1a** was used as the starting material, anionic sandwich complex **3b** was successfully isolated. The bulky *tert*-butyldimethylsilyl group can suppress the introduction of the second Cp*Ru unit to **3b**, and **3b** was obtained as a stable compound. The second Cp*Ru unit can be introduced by the treatment of **3b** with $[Cp^*RuCl]_4$ in toluene. Notably, the corresponding reaction using a tetraethyl derivative resulted in the formation of not η^5-stannole complexes but bicyclic Ru_2Sn_2 complexes,[20] and choices of the substituents on metallole dianions are therefore important for the synthesis of μ–η^5:η^5-metallole dianion complexes.

Scheme 1. Synthetic Schemes for the First μ–η^5:η^5-Stannole Dianion Complexes 2 and Anionic η^5-Stannole Complex 3b, Prepared from Dilithiostannole 1



Upon complexation, the ^{13}C NMR signals derived from the stannole rings shifted to a high-field region, as summarized in Table 1. Contrary to characteristic signals assignable to C_α atoms observed at a low-field region for **1a** and **1b** (182.38 and 176.35 ppm, respectively), the corresponding signals for **3b** and **2** are found at 110.32 and about 85 ppm, respectively. Such high-field shifts were also observed in other heavier group 14 metallocenes.[11–13] The degree of the high-field shifts in triple-decker complexes **2** larger than in anionic sandwich complex **3b** indicates that back-donation from the ruthenium atoms to the stannole moiety in **2** is larger than that in **3b**. The ^{119}Sn NMR signals of **2a**, **2b**, and **3b** were observed at 324.5, 278.4, and 83.8 ppm, respectively, which are in a higher field than those of the starting materials (446.4 and 472.6 ppm for **2a** and **2b**, respectively).

Table 1. Comparison of the Selected NMR Data for 1–3

	1a	2a	
	1b	2b	3b
$\delta(^{13}C)$ for C_α	182.38	85.26	110.32
	176.53	82.97	
$\delta(^{13}C)$ for C_β	146.23	86.32	113.38
	146.98	89.36	
$\delta(^{119}Sn)$	446.4	324.5	83.8
	472.6	278.4	

The solid-state structures of **2a**, **2b**, and **3b** were established by X-ray diffraction analysis (Figure 1). The sum of the internal angles of the stannole rings are approximately 540° and the C–C bond lengths in the stannole rings of the complexes are nearly equal, suggesting that aromaticity of the stannoles is retained. Remarkably, the Sn–C and C–C bond lengths of the

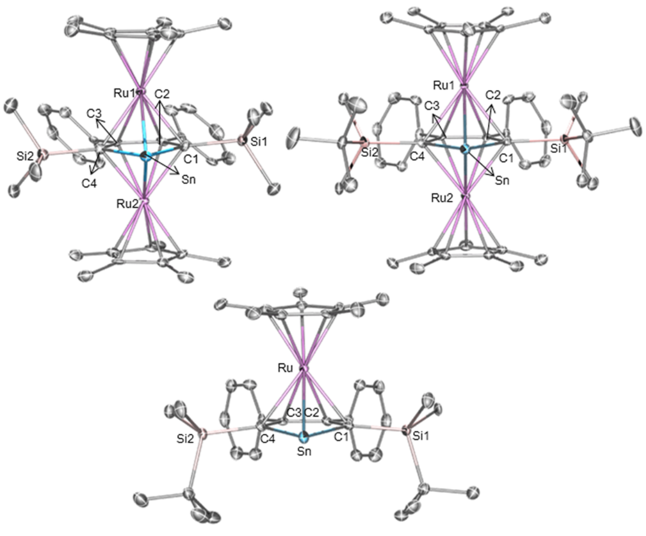


Figure 1. ORTEP drawing of **2a** (upper left), **2b** (upper right), and **3b** (lower) (50% probability). All hydrogen atoms and the cationic moiety of **3b** are omitted for clarity. Selected bond lengths: Sn−C1, 2.274(6); C1−C2, 1.464(8); C2−C3, 1.504(8); C3−C4, 1.436(8); Sn−C4, 2.286(5); Sn−Ru1, 2.7436(7); Sn−Ru2, 2.7331(7), Ru−Center of the SnC$_4$ ring, 1.804, 1.815 for **2a**; Sn−C1, 2.276(5); C1−C2, 1.453(6); C2−C3, 1.498(6); C3−C4, 1.454(6); Sn−C4, 2.264(4); Sn−Ru1, 2.7283(5); Sn−Ru2, 2.7476(5), Ru−Center of the SnC$_4$ ring, 1.822, 1.835 for **2b**; Sn−C1, 2.176(4); Sn−C4, 2.186(4); C1−C2, 1.429(5); C2−C3, 1.443(5); C3−C4, 1.437(6); Sn−Ru, 2.7361(5); Ru−Center of the SnC$_4$ ring, 1.836 for **3b**.

stannole rings in triple-decker complexes **2** are longer than those in dilithiostannole **1** and anionic sandwich complex **3b** by approximately 3−5%. The elongation seems to be caused by strong back-donation from the two ruthenium atoms to the antibonding orbitals of the stannole moiety, which is supported by the high-field shifts of ^{13}C NMR signals in the triple-decker complexes larger than those in the anionic sandwich complex as mentioned above. The distances between the ruthenium atoms and the center of the stannole rings are 1.804−1.836 Å, which are similar to those in other heavy ruthenocenes (1.81−1.823 Å).[11a,13b] The Sn−Ru distances in **2** and **3b** are about 2.73 Å, which are in the range of Ru−Sn bond lengths that have been reported (2.543−3.141 Å),[22] suggesting that the tin atoms coordinate to the ruthenium atoms. Interestingly, all the methyl groups on the Cp* ligands are bent from the C$_5$ ring planes to the opposite sides of the stannole rings by 9.7°, 12.4°, and 8.3° (average), for **2a**, **2b**, and **3b**, respectively, because of steric repulsion. The top views of **2** and **3** are shown in Figure 2. The Cp* and the stannole rings in anionic sandwich complex **3b** are arranged in a staggered form, as was found in other heavy ruthenocene.[13b] Although the difference between **2a** and **2b** is only the size of the silyl substituents, the orientation of the terminal Cp* rings in **2a** (eclipse) differs from that in **2b** (staggered). The origin of the different orientation can be reasonably explained by their packing structures. In the packing structure of **2b**, no intermolecular interaction was found. In contrast, the distances between the adjacent molecules in **2a** are close, and the nearest and the second nearest distances between carbon atoms of the Cp* ring and hydrogen atoms of the methyl groups on the Cp* ring are 2.824 and 2.979 Å. As the former value lies in the range of, and the latter slightly exceeds, the C−H distances bearing CH/π interaction (d(C−H) 2.71 ± 0.19 Å),[23] it can be concluded that CH/π interactions in the packing structure of **2a** leads to the polymeric and column-like structure, as shown in Figure 3. The eclipse conformation probably makes the CH/π interaction more effective.

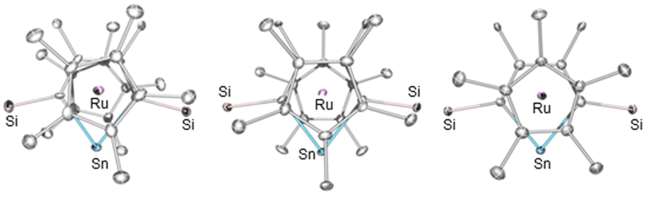


Figure 2. Top views of heavy ruthenocenes **2a** (left), **2b** (center), and **3b** (right).

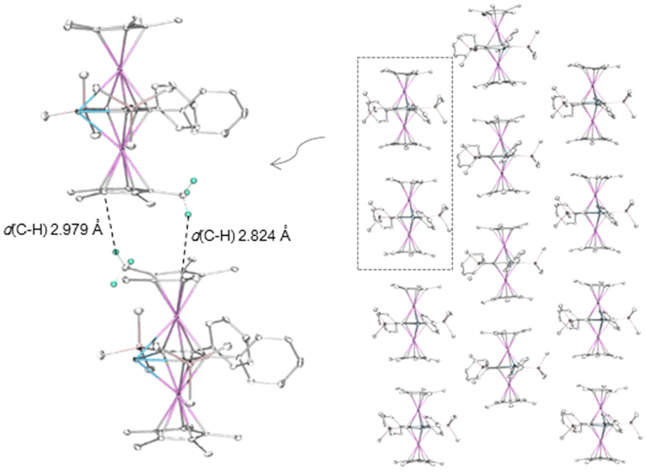


Figure 3. Column-like packing structure of **2a**.

To understand electronic structure of the stannole complexes, theoretical calculations for **2a** were performed by the *Gaussian 03* program.[24] The molecular geometry of **2a** was optimized with hybrid density functional theory at the B3PW91 level[25] using LANL2DZ[26] basis set augmented by a d polarization function (ξ = 0.186) and an f polarization function (ξ = 1.235) for Sn and Ru, respectively, and 6-31G(d) for Si, C ,and H.[27] The selected molecular orbitals of importance are shown in Figure 4. The HOMO and the HOMO-1 mainly consist of d_{yz} of the ruthenium atom and the lone pair of the tin atom, respectively. The HOMO-2 exhibits the stannole dianion moiety which coordinates the ruthenium atoms as an allyl anion, while the HOMO-7 represents an interaction between p(Sn) and d(Ru). Moreover, the Wiberg bond index (WBI)[28] of the Sn−Ru bonds is calculated to be 0.38, which strongly supports the existence of the interaction between them. The C$_4$ moiety of the stannole has an interaction with the ruthenium atoms, which is found in the HOMO-22. It is therefore concluded that the stannole moiety coordinates to the ruthenium atoms in $\mu-\eta^5:\eta^5$-fashions. The silyl groups on the alpha-carbons appear to play an important role on the formation of η^5-stannole complexes because only the silyl-substituted dilithiostannoles can form η^5-stannole complexes.[20]

The cyclic voltammetry of **2a** was measured to evaluate electron-donating ability of the stannole ligand. [Bu$_4$N]-[TPFPB] (TPFPB = tetrakis(pentafluorophenyl)borate) was used as a supporting electrolyte to stabilize the resulting cationic species formed after anticipated oxidation of **2a**.[29] The cyclic voltammogram of **2a** recorded in CH$_2$Cl$_2$ is shown in

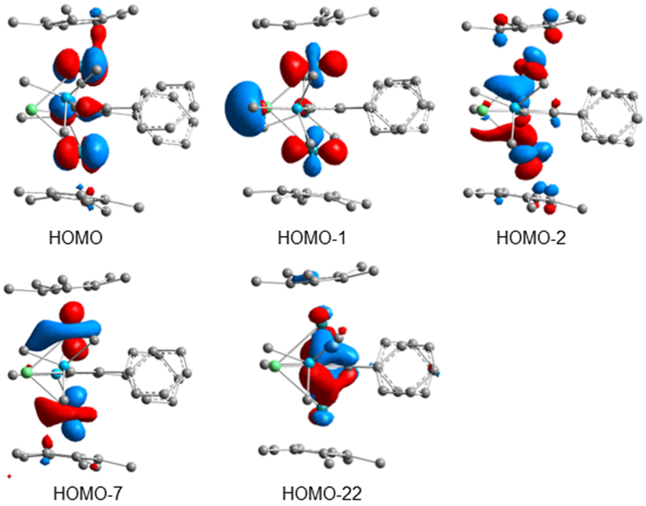


Figure 4. Molecular orbitals of **2a** (isovalue = 0.05). HOMO (d_{yz}(Ru)), HOMO-1 (d hybrid orbital and lone pair(Sn)), HOMO-2 (π(C−Sn−C)−d(Ru)), HOMO-7 (d(Ru)−p(Sn)), HOMO-22 (π-(C$_4$)−d_{xy}). Gray, carbon; lime green, Sn; bright blue, silicon; green, ruthenium.

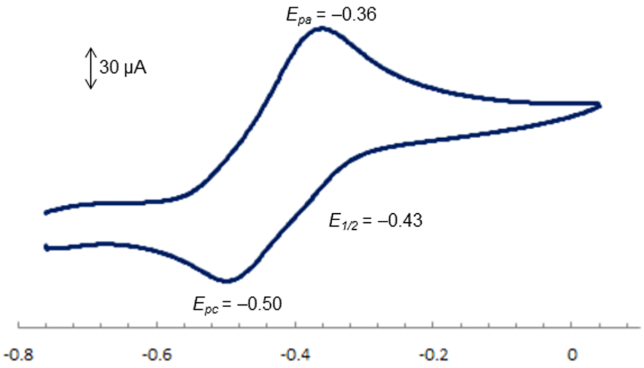


Figure 5. Cyclic voltammogram of **2a** in 1.1 mM CH$_2$Cl$_2$/0.1 M [Bu$_4$N][TPFPB] (scan rate 0.2 V s^{-1}).

Figure 5. A quasi-reversible oxidation wave was observed (E_{pa} = −0.36, E_{pc} = −0.50, $E_{1/2}$ = −0.43 V vs Fc/Fc$^+$). Notably, the oxidation waves of other metallocenes bearing heavier group 14 analogues of Cp$^-$ are irreversible,[11−13] which suggests that the cationic species of **2a** on the electrode is more stable than those of the other heavy metallocenes. Since decamethylruthenocene {(η^5-Cp*)$_2$Ru} exhibits an oxidation wave at 0.08 V (vs Fc/Fc$^+$) under similar conditions,[30] the stannole dianion ligand in **2a** functions as an electron-donating ligand stronger than the Cp* ligand, which is a widely used donating ligand.

Comparing the difference of the oxidation potentials between heavy ruthenocenes and decamethylruthenocene ($\delta(E)$ = [E_{ox} of decamethylruthenocene] − [E_{pa} of heavier ruthenocene]) is of considerable interest because these values are diagnostic of electron-donating ability of the heavier Cp$^-$ ligands. The values of $\delta(E)$ = 0.17, 0.48, and 0.49 V for heavy ruthenocenes bearing η^5-GeC$_4$,[11a] η^5-Si$_3$C$_2$,[12] and η^5-Si$_2$GeC$_2$,[13b] respectively, reveal that the E$_3$C$_2$ complex (E = Si or Ge) is oxidized more easily than the GeC$_4$ complex. In other words, the trimetallacyclopentadienide (Si$_3$C$_2^-$ and Si$_2$GeC$_2^-$) ligands are electron-donating ligands stronger than the germolyl (GeC$_4^-$) ligand, probably due to the number of heavy atoms in the five-membered ring. However, the value of $\delta(E)$ for **2a** is approximately 0.44 V, which is comparable to those of the η^5-trimetallacyclopentadienyl ruthenium complexes. It is noteworthy that introduction of only one tin atom into the carbon π-framework, leading to the stannole ligand, results in comparable electron-donating ability with the Si$_3$C$_2$ and Si$_2$GeC$_2$ ligands.

CONCLUSION

The triple- and double-decker type heavy ruthenocenes were successfully synthesized by the reactions of silyl-substituted dilithiostannoles with [Cp*RuCl]$_4$. Those complexes were characterized by NMR, elemental analysis and X-ray diffraction analysis. In the triple-decker complexes, the stannole dianion coordinates the two ruthenium atoms above and below its five-membered ring, functioning as a novel and useful substitute for the unprecedented cyclopentadienyl dianion (Cp^{2-}). It is noted that the synthesis of such a neutral triple-decker complex is impossible in the chemistry of all-carbon ligands to date. The CV measurement of **2a** revealed that the electron-donating ability of the stannole dianion surpasses that of Cp* and even the germole anion (GeC$_4^-$), and is comparable to that of trimetallacyclopentadienyl anions Si$_3$C$_2^-$ and Si$_2$GeC$_2^-$. The easily oxidized character and theoretical calculations elucidated the function of the stannole dianion as a μ−η^5:η^5-ligand. The triple-decker complexes would be new attractive candidates in catalytic and materials chemistry. Moreover, because anionic ruthenocene **3b** can be a good precursor for heterobimetallic triple-decker complexes, the reactions of **3b** with various transition-metal reagents are now under investigation.

EXPERIMENTAL SECTION

General Procedure. All experiments were performed under argon atmosphere in a glovebox or using a standard Schlenk technique. Compounds **1a** and **1b** were prepared by the literature methods.[21] Diethyl ether, toluene, and benzene-d_6 for NMR measurement were purified by potassium mirror before used. ^{1}H NMR (400 or 500 MHz), ^{13}C NMR (101 MHz), ^{7}Li NMR (194 MHz), ^{29}Si NMR (99 MHz) and ^{119}Sn NMR (187 MHz) were recorded on a Bruker DPX-400 Cryo or a AVANCE-500T. The intensity data for X-ray crystallographic analyses were collected at −173 or −198 °C on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. The structures were solved by direct methods, and refined by full-matrix least-squares method by SHELXL-97 program. UV−vis spectra of **2** were recorded on a Hitachi U-1900 spectrophotometer. Cyclic voltammetry was measured on an ALS CHI600A with a tailored glassware.[31]

Synthesis of Triple-Decker 2a. Compound **1a** (26 mg, 0.041 mmol) and [Cp*RuCl]$_4$ (22 mg, 0.021 mmol) were dissolved in Et$_2$O (2 mL), and the mixture was stirred for 20 min at room temperature. After removal of the solvent, materials insoluble in hexane were filtrated through Celite to provide **2a** as brown powder (28 mg, 73%). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from a toluene solution at −33 °C. **2a**: mp > 300 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 0.10 (s, 18H, Si*Me*$_3$), 1.72 (s, 30H, C$_5$*Me*$_5$), 6.98−7.04 (m, 2H, *Ph*), 7.05−7.10 (m, 4H, *Ph*), 7.99 (d, J = 8 Hz, 4H, *Ph*). ^{13}C NMR (101 MHz, C$_6$D$_6$): δ 6.34 (1°, Si*Me*$_3$), 12.91 (1°, C$_5$*Me*$_5$), 84.99 (4°, *C*$_5$Me$_5$), 85.26 (4°, C_α), 86.32 (4°, C_β), 126.20 (2°, *Ph*), 128.28 (2°, *Ph*), 136.18 (3°, *Ph*), 141.37 (4°, *Ph*). ^{29}Si NMR (99 MHz, C$_6$D$_6$): δ −0.6. ^{119}Sn NMR (187 MHz, C$_6$D$_6$): δ 324.5. UV−vis (hexane): λ_{max} = 435 nm. Anal. Calcd for C$_{42}$H$_{58}$Ru$_2$Si$_2$Sn: C, 53.67; H, 6.22. Found: C, 53.13; H, 6.12.

Synthesis of Anionic Sandwich 3b. Compound **1b** (177 mg, 0.25 mmol) and [Cp*RuCl]$_4$ (69 mg, 0.063 mmol) were dissolved in THF (3 mL), and the mixture was stirred for 1.5 h at room temperature. After removal of the solvent, materials insoluble in toluene were filtrated thorough Celite to provide a crude product. Recrystallization of the crude product from a 1:5 mixture of THF and toluene provided **3b** as yellow crystals (215 mg, 80%). **3b**: mp > 95 °C (decomp.). ^{1}H NMR (500 MHz, C_6D_6): δ −0.36 (s, 6H, Si^{t}Bu*Me*$_2$), 0.56 (s, 6H, Si^{t}Bu*Me*$_2$), 1.02 (s, 18H Si^t*Bu*Me$_2$), 1.32−1.38 (m, 16H, *thf*), 2.09 (s, 15H, C_5Me_5), 3.50−3.57 (m, 16H, *thf*) 6.93 (dd, J = 7, 8 Hz, 2H, *Ph*), 7.01 (dd, J = 7, 8 Hz, 4H, *Ph*), 7.45 (d, J = 7 Hz, 4H, *Ph*). ^{13}C NMR (101 MHz, C_6D_6): δ −1.96 (1°, Si^{t}Bu*Me*$_2$), 3.43 (1°, Si^{t}Bu*Me*$_2$), 13.71 (1°, C_5Me_5), 18.20 (4°, Si^t*Bu*Me$_2$), 25.55 (2°, *thf*), 29.20 (1°, Si^t*Bu*Me$_2$), 68.12 (2°, *thf*), 87.57 (4°, C_5Me$_5$), 110.32 (4°, C_α), 113.38 (4°, C_β), 125.57 (3°, *Ph*), 126.24 (3°, *Ph*), 134.55 (3°, *Ph*), 144.75 (4°, *Ph*). ^{7}Li NMR (194 MHz, C_6D_6): δ −0.3. ^{29}Si NMR (99 MHz, C_6D_6): δ 4.7. ^{119}Sn NMR (187 MHz, C_6D_6): δ 83.8.

Synthesis of 2b. Compound **3b** (63 mg, 0.058 mmol) and $[Cp^*RuCl]_4$ (16 mg, 0.015 mmol) were dissolved in toluene (2 mL), and the mixture was stirred for an hour at room temperature. After removal of the solvent, materials soluble in hexane were removed by washing with hexane (1 mL, three times). The resulting powder was extracted with toluene and filtered off through Celite. The filtrate was concentrated and stored at −30 °C to provide **2b** as red crystals (17 mg, 28%). **2b**: mp = 206−208 °C. ^{1}H NMR (500 MHz, C_6D_6): δ −0.08 (s, 12H, Si^{t}Bu*Me*$_2$), 1.38 (s, 18H, Si^t*Bu*Me$_2$), 1.64 (s, 30H, C_5Me_5), 6.98−7.08 (m, 6H, *Ph*), 8.05−8.10 (m, 4H, *Ph*). ^{13}C NMR (101 MHz, C_6D_6): δ 3.74 (1°, Si^{t}Bu*Me*$_2$), 13.19 (1°, C_5Me_5), 22.67 (4°, Si^t*Bu*Me$_2$), 30.91 (1°, J_{Sn-C} = 49 Hz, Si^t*Bu*Me$_2$), 82.97 (4°, J_{Sn-C} = 392, 407 Hz, C_α), 85.95 (4°, C_5Me$_5$), 89.36 (4°, J_{Sn-C} = 27 Hz, C_β), 125.76 (3°, *Ph*), 126.28 (3°, *Ph*), 138.06 (3°, *Ph*), 140.83 (4°, *Ph*). ^{29}Si NMR (99 MHz, C_6D_6): δ 8.7. ^{119}Sn NMR (187 MHz, C_6D_6): δ 278.4. UV−vis (hexane): λ_{max} = 442 nm. Anal. Calcd for $C_{48}H_{70}Ru_2Si_2Sn$: C, 56.29; H, 6.89. Found: C, 56.01; H, 6.86.

Crystallographic Data Deposition. Crystallographic data for compounds **2a**, **2b**, and **3b** have been deposited with the Cambridge Crystallographic Data Centre as CCDC 1009278, 1009277, and 1009279, respectively (www.ccdc.cam.ac.uk/data_request/cif).

■ ASSOCIATED CONTENT

Supporting Information

Crystal data and CIF files of **2a**, **2b**, and **3b**; ^{1}H and ^{13}C NMR spectra for **2a** and **3b**; Cartesian coordinates for **2a**. 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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