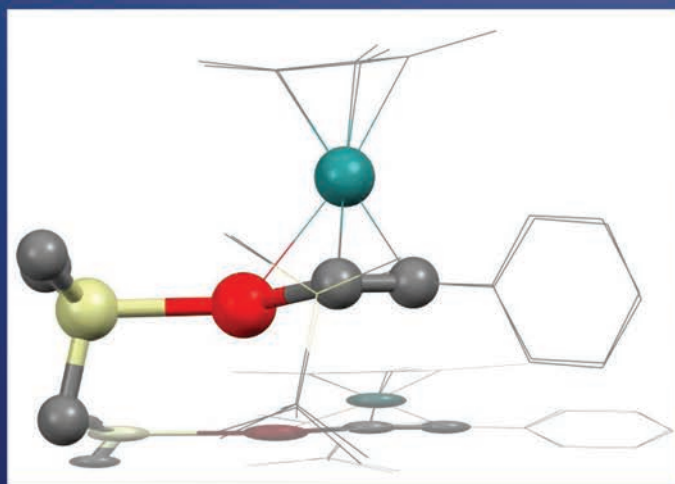
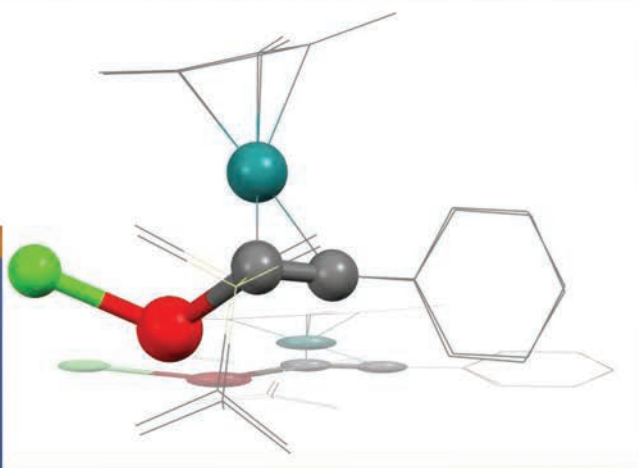


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PAPER

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Diverse coordination modes in tin analogues of a cyclopentadienyl anion depending on the substituents on the tin atom



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Diverse coordination modes in tin analogues of a cyclopentadienyl anion depending on the substituents on the tin atom†‡

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Reactions of an anionic heavy ruthenocene with CCl_4 , MeI, EtBr and Me_3SiCl afforded the first stannole monoanion complexes. Surprisingly, coordination modes of the stannole rings are highly dependent on the substituents on the tin atom. The chloro derivative exhibits a η^4 -fashion-like coordination mode with a bent stannole ring, whereas the trimethylsilyl derivative adopts the conventional η^5 -coordination mode. Coordination modes of the alkyl derivatives are in between the two types. Cyclic voltammograms for these complexes reveal that the electron-donating character of the stannole ligand becomes stronger as the stannole ring becomes planar. Theoretical calculations elucidate that the different coordination modes originate from both electronegativity of an adjacent atom to the tin atom and bulkiness of a substituent on the tin atom.

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Introduction

Substitution of skeletal carbon atoms in organic molecules by heavy group 14 elements has been one of the main issues in organometallic and heteroatom chemistry since the first synthesis of a heavier analogue of ethylene, disilene, by West and co-workers.¹ This heavy element chemistry always surprises both experimental and theoretical chemists because the structures and reactivity of carbon-based compounds and their heavier analogues are drastically different.² For example, double and triple bonds between C–C are planar and linear, respectively, whereas the corresponding bonds between E–E (E = Si, Ge, Sn, and Pb) are non-planar/linear and *trans*-bent (Fig. 1).

The investigation on heavy analogues of cyclopentadienyl anions (Cp^-), one of the most important ligands in organometallic chemistry, reveals that heavy Cp^- s also exhibit remarkable different characteristics (Fig. 2).³ First, metallole monoanions (EC_4R_5^- , E = Si, Ge, Sn, and Pb) have highly pyramidalized metal centers because of their non-aromatic

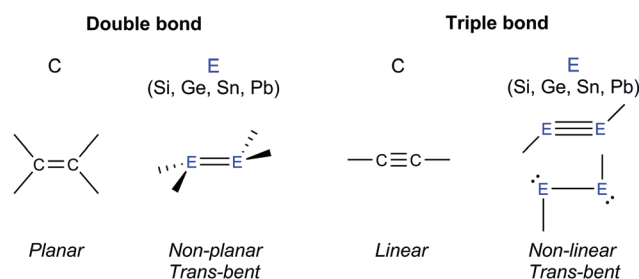


Fig. 1 Differences of double- and triple bonds between carbon-based compounds and their heavy analogues. Substituents were abbreviated for clarity.

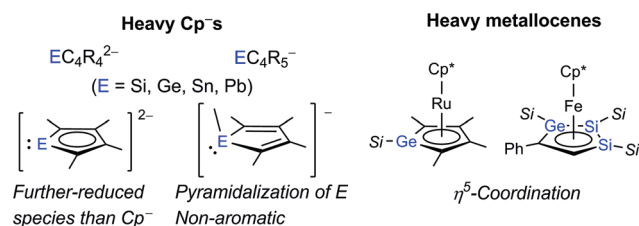


Fig. 2 Chemistry of heavy Cp^- s and selected examples of their transition-metal complexes.

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†This paper is dedicated to Professor Keiji Morokuma on the occasion of his 80th birthday.

‡Electronic supplementary information (ESI) available. CCDC 1049295, 1049297 and 1049354. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02202a

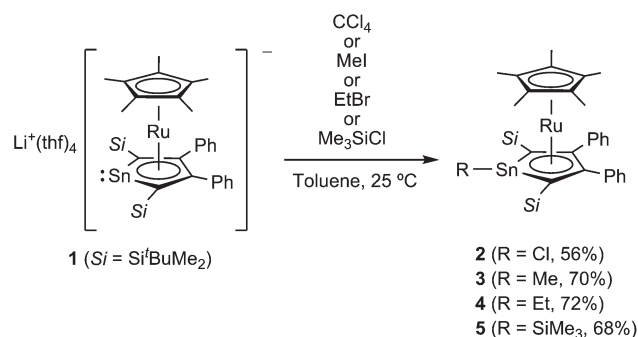
nature,⁴ in sharp contrast to the aromatic Cp^- , and the degree of the pyramidalization depends on the substituent on the metal.^{4b,c} Secondly, metalloles can form further-reduced species than Cp^- , metallole dianions ($\text{EC}_4\text{R}_4^{2-}$, E = Si,^{4b,5} Ge,⁶

Sn,⁷ and Pb⁸), in which the anionic charges delocalize over the metallole ring, leading to their aromatic nature. On the other hand, coordination chemistry of heavy Cp[−]s is similar to that of the lighter analogues (Cp[−]s).⁹ In other words, it is believed that heavy Cp[−]s always coordinate transition metals in η^5 -fashion, as do Cp[−]s, clarified by Tilley and Sekiguchi's pioneering research on this field. However, our findings reported here defy this common knowledge: coordination modes of tin analogues of Cp[−] are highly dependent on the substituent on the tin atom.

Results and discussion

Synthesis and structures

Since an anionic heavy ruthenocene bearing stannole dianion ligand **1** is expected to be a good precursor for neutral stannole complexes, the reactions of anionic heavy ruthenocene **1** with various organic halides (CCl₄, MeI, EtBr and Me₃SiCl) were examined (Scheme 1).¹⁰ Each of the reactions gave a single product, as judged from the ¹H NMR spectrum of the crude product. Chloro derivative **2** was isolated as green crystals, while alkyl and silyl derivatives **3–5** were obtained as red crystals. The reason why the chlorine atom was introduced in the reaction with CCl₄ might be explained by a steric effect: the bulkiness of the CCl₃ group could induce the reaction of stannole and chlorine moieties instead of a CCl₃ group. The solid-state structures of **2**, **4** and **5** were determined by X-ray diffraction analysis (Fig. 3, S1† and Table 1).¹⁰ Surprisingly, the coordination modes of the stannole rings are highly dependent on the substituents on the tin atom. The stannole ring in **2** deviates from planarity with the bent angle of 41.2°, and the tin atom is remarkably pyramidalized with the sum of the angles around the tin atom being 306.31°. The distance between Sn and Ru is 2.9323(5) Å, larger than those found in η^5 -stannole dianion complexes (approximately 2.73 Å),¹² suggesting that the interaction between Sn and Ru in complex **2** is weak. Thus the coordination mode in **2** is not the conventional η^5 -fashion but a η^4 -like fashion. A similar coordination mode was reported in the complexes bearing P₅ ligands.¹³ This is in



Scheme 1 Reactions of anionic heavy ruthenocene **1** with organohalogen compounds.

sharp contrast to the fact that all the metallole rings in the Si and Ge analogues of Cp[−] reported to date are almost planar and coordinate the transition metals in η^5 -fashion. We hypothesized that there is a borderline between Ge and Sn: Si and Ge congeners of Cp[−] coordinate transition metals in η^5 -fashion, while the corresponding tin analogue induces a different coordination mode. However, the molecular structure of trimethylsilyl derivative **5** reveals that the tin congener can also exhibit a similar structure: the stannole ring is nearly planar with the sum of the internal angles being 538.26° and no pyramidalization was found on the tin atom (Fig. 3), which is opposed to the highly pyramidalized tin center found in a lithium salt of a silyl-substituted stannole anion.^{4c} The Sn–Ru bond length is 2.6903(5) Å, shorter than those in η^5 -stannole dianion complexes.¹² These structural features suggest that the stannole ring in **5** coordinates the ruthenium atom in a η^5 -fashion. Interestingly, the molecular structure of ethyl derivative **4** has structural similarities to both **2** and **5**: the stannole ring is bent (24.4°) and the distance between Sn and Ru is slightly larger but much smaller than those in **1** and **2**, respectively (2.7969(6), 2.7361(5) and 2.9323(5) Å for **4**, **1** and **2**, respectively). The Sn–C bonds in **2** (av. 2.255 Å) are longer than those in other stannole complexes **1**, **4** and **5** (about 2.15 Å), suggesting that s-character of the Sn–C bonds in **2** are small. The degree of C–C bond alternation in the stannole ring in **2** (0.06 Å) is slightly larger than those in **4** and **5** (0.03 Å). The Cp* ring and the stannole ring in these complexes are oriented in staggered forms (Fig. S1†), which is in the same trend as other heavy ruthenocenes.^{9d,g,12}

NMR study

The ¹³C NMR signals for C_α and C_β, and the ¹¹⁹Sn NMR signals of **1–5** are summarized in Table 2. The signals derived from C_β are found in a similar region, while those assigned to C_α are in a different area: the C_α signals of **2** and **5** were found in the lowest and the highest field, respectively, and those of alkyl derivatives **3** and **4** are observed between those of **2** and **5**. The ¹¹⁹Sn nucleus in chloro derivative **2** resonates in a high-field region of −697.5 ppm, which suggests that the tin atom in **2** is also pyramidalized in solution.¹⁴ The ¹¹⁹Sn NMR signal

§ Crystal data for **2**: Formula, C₃₈H₅₅ClRuSi₂Sn, FW = 823.21, crystal dimension 0.20 × 0.15 × 0.10, monoclinic, space group P2₁/n, *a* = 9.6555(12) Å, *b* = 18.470(2) Å, *c* = 21.490(3) Å, β = 95.698(3)°, *V* = 3813.7(8) Å³, *D_c* = 1.434 g cm^{−3}, 100 K, Mo-K_α radiation (λ = 0.71073 Å) for *Z* = 4. Least-squares refinement based on 6400 reflections with *I* > 2.0σ(*I*) (out of 7894 unique reflections) led to a final value of *R*(w*R*₂) = 0.045 (0.101). CCDC 1049297. Crystal data for **4**: Formula, C₄₀H₆₀RuSi₂Sn, FW = 816.84, crystal dimension 0.20 × 0.20 × 0.15, orthorhombic, space group Pnma, *a* = 17.7751(13) Å, *b* = 21.1737(16) Å, *c* = 10.5846(8) Å, *V* = 3983.7(5) Å³, *D_c* = 1.362 g cm^{−3}, 100 K, Mo-K_α radiation (λ = 0.71073 Å) for *Z* = 4. Least-squares refinement based on 3959 reflections with *I* > 2.0σ(*I*) (out of 4013 unique reflections) led to a final value of *R*(w*R*₂) = 0.050 (0.123). CCDC 1049354. Crystal data for **5**: Formula, C₄₁H₆₄RuSi₃Sn, FW = 860.97, crystal dimension 0.10 × 0.10 × 0.10, monoclinic, space group P2₁/n, *a* = 11.8804(14) Å, *b* = 21.679(3) Å, *c* = 16.7980(18) Å, β = 103.113(3)°, *V* = 4213.6(8) Å³, *D_c* = 1.357 g cm^{−3}, 100 K, Mo-K_α radiation (λ = 0.71073 Å) for *Z* = 4. Least-squares refinement based on 7789 reflections with *I* > 2.0σ(*I*) (out of 9198 unique reflections) led to a final value of *R*(w*R*₂) = 0.047 (0.103). CCDC 1049295.

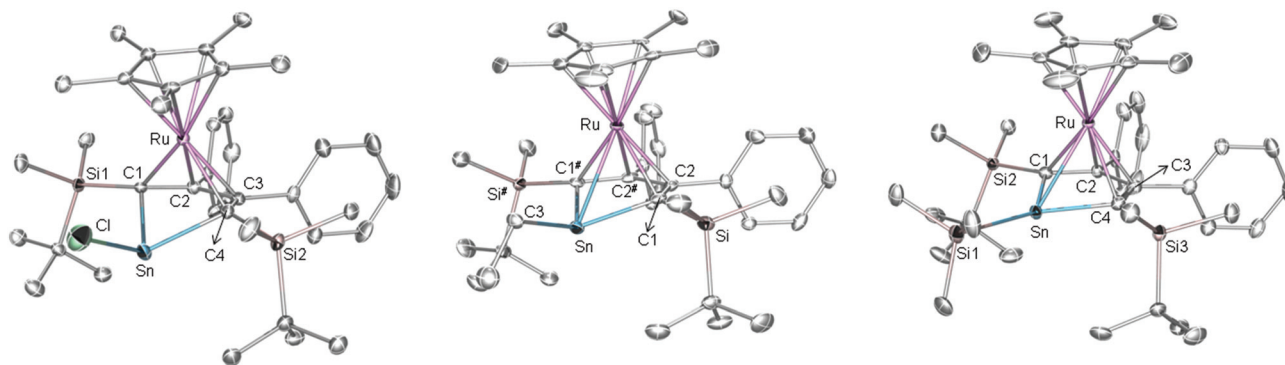


Fig. 3 Solid state structures of **2** (left), **4** (center) and **5** (right) (50% probability). All hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths and angles for **1**–**5**

| | 2 | 4 | 5 |
|----------------------------------------------------|--------------------|-----------|--------------------|
| Ru–Sn (Å) | 2.9323(5) | 2.7969(6) | 2.6903(5) |
| Sn–C _α (Å) | 2.255(4), 2.254(4) | 2.155(5) | 2.125(3), 2.123(4) |
| C _α –C _β (Å) | 1.412(5), 1.419(6) | 1.429(6) | 1.422(5), 1.430(5) |
| C _β –C _β (Å) | 1.474(6) | 1.458(9) | 1.453(5) |
| Sum of the internal angles of SnC ₄ (°) | 520.21 | 533.09 | 538.26 |
| Sum of the angles around Sn atom (°) | 306.31 | 332.15 | 357.49 |

Table 2 Comparison of the NMR data for **1**–**5**

| | 1 | 2 | 3 | 4 | 5 |
|--------------------------------------------|----------|----------|----------|----------|----------|
| $\delta(^{13}\text{C})$ for C _α | 110.32 | 140.78 | 112.18 | 109.98 | 91.28 |
| $\delta(^{13}\text{C})$ for C _β | 113.38 | 108.25 | 107.24 | 107.29 | 109.82 |
| $\delta(^{119}\text{Sn})$ | 83.8 | −697.5 | −372.3 | −343.3 | −170.7 |

of silyl derivative **5** was observed in a region lower than those of **3** and **4** bearing carbon substituents, which is an opposite trend in the case of the lithium salts of the stannole anions.^{4c} The ^{119}Sn NMR chemical shifts for complexes **2**–**5** are closely related to the coordination mode of the stannole ligands: as the bent angle of the stannole ligand becomes smaller, the ^{119}Sn signal shifts to the downfield.

Electrochemical study

Cyclic voltammograms were next measured to estimate the electron-donating ability of the stannole anion ligands. Irreversible oxidation waves (E_{pa} vs. Fc/Fc^+ [$[\text{Bu}_4\text{N}]\text{ClO}_4/\text{THF}$]) were observed at 0.48, 0.04, and -0.04 V for **2**, **4**, and **5**, respectively, revealing that silyl derivative **5** is easily oxidized, while Cl derivative **2** is the most difficult to oxidize. The different oxidation potentials of these complexes are reasonably explained by considering the difference of Ru–Sn distances in the complexes. In complex **5**, because of the shortest Ru–Sn bond, the stannole anion ligand donates its electrons on the tin atom to

the ruthenium atom most effectively, which causes the most easily oxidizable character of **5**. In contrast, the corresponding bond in **2** is the longest, leading to a weak interaction between Ru and Sn. The oxidation wave ($E_{1/2}$) of decamethylruthenocene (Cp_2^*Ru) was found at 0.25 V under the same conditions. Comparison of the difference of the oxidation potentials between heavy ruthenocenes and $(\eta^5\text{-Cp}^*)_2\text{Ru}$ ($\Delta(E) = [E_{1/2} \text{ of } (\eta^5\text{-Cp}^*)_2\text{Ru}] - [E_{\text{pa}} \text{ of heavy ruthenocene}]$) is worthy of note because this value is a good index for the electron-donating ability of heavier Cp^- ligands. The $\Delta(E)$ for Tilley's heavy ruthenocene bearing a germole ligand is 0.17 V,^{9a} while those for **2**, **4** and **5** are -0.24 , 0.21 and 0.29 V, respectively, indicating that the stannole anions (SnC_4^-) in **4** and **5** are more electron-donating ligands than the germole anion (GeC_4^-), whereas that in **2** is no longer a strong electron-donating ligand, which is supported by the following theoretical calculations.

Theoretical study

To understand the coordination modes in these stannole complexes, theoretical calculations were performed using the Gaussian 03 program.¹⁵ The molecular geometries of **2**, **4** and **5** were optimized with hybrid density functional theory at the B3PW91 level using the [4333111/433111/43] basis set augmented by two d polarization functions (d exponents 0.253 and 0.078) for Sn,¹⁶ the LANL2DZ¹⁷ basis set augmented by an f polarization function (f exponent 1.235) for Ru, and 6-31G(d) for Si, C, H, and Cl.¹⁸ The optimized structures are in good agreement with the experimental data (Table S1†). The molecular orbital mainly composed of a lone pair on the tin atom in **2** is HOMO–1, while those in **4** and **5** are HOMOs (Fig. 4). These MOs clearly show the difference of the coordination modes among these complexes. In compound **2**, the lone pair is found at the side opposite to the ruthenium atom with high s -character, which implies that the lone pair on the tin atom cannot interact with the ruthenium atom. In contrast, the lone pair in **5** has p -character and an interaction between Sn and Ru is clearly observed. Although a lone pair similar to that in the chloro derivative **2** is found in the HOMO of **4**, Sn–Ru interaction was also observed. It is therefore considered that

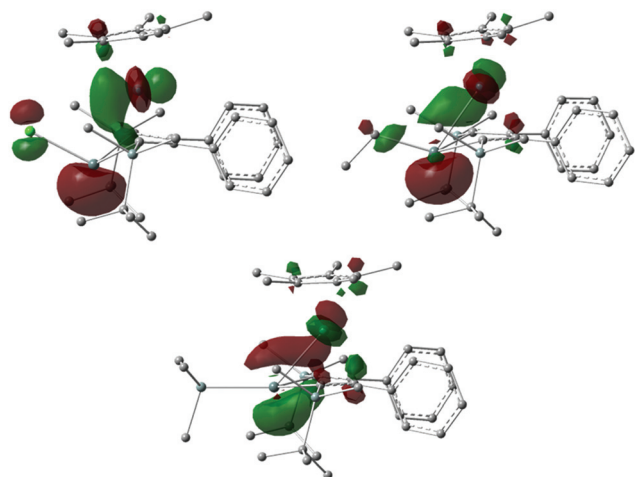


Fig. 4 HOMO-1 for 2 (upper left), HOMOs for 4 and 5 (upper right and lower, respectively) (isovalue = 0.05).

the HOMO in 4 has both the nature of HOMO-1 in 2 and HOMO in 5. Notably, the HOMO levels of 4 (−4.8 eV) and 5 (−4.7 eV) are higher than HOMO-1 (−5.44 eV) and even HOMO (−5.40 eV) levels in 2, these being in good agreement with the results of the cyclic voltammetry. Natural charges of the ruthenium atoms were calculated to be −0.22, −0.32 and −0.37 for 2, 4 and 5, respectively. The least negatively charged Ru in 2 indicates weak electron-donating character of the bent stannole ligand, whereas the most negatively charged Ru in 5 indicates that the planar stannole is the strongest electron-donating ligand among these three complexes. Wiberg bond indices¹⁹ for Ru–Sn in these complexes were next calculated. As expected, the index for 5 was calculated to be the largest (0.45) among the three, while that for chloro derivative 2 was the smallest (0.31). The index for 4 is in between the two (0.38) and the same as that of the triple-decker type ruthenocene bearing a $\mu\text{-}\eta^5\text{:}\eta^5\text{-stannole}$ dianion ligand reported by us (0.38).¹²

To gain further insight into the origin of different coordination modes, the structures of model complexes bearing H, ^tBu and SiH₃ on the tin atom were optimized. Bent angles (°) and Sn–Ru distances (Å) for each case are summarized in Table 3. The stannole ring in the H derivative is less bent than

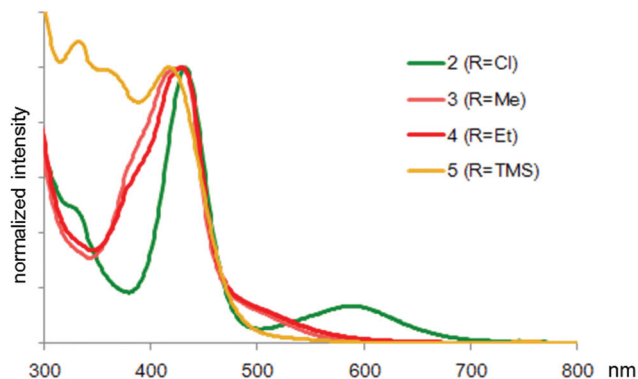


Fig. 5 UV-vis spectra for 2–5 in hexane.

that in Cl derivative 2 (24.1° vs. 36.8°), whereas the bent angle of the stannole ring in the SiH₃ derivative (18.3°) is larger than those in ^tBu (12.3°) and SiMe₃ (9.7°) derivatives. It is therefore concluded that the bent angle of a stannole ring is dependent on not only electronegativity of an adjacent atom to the tin atom but also the bulkiness of the substituent on the tin atom.

Photophysical study

The results of UV-vis absorption measurements for 2–5 in hexane were shown in Fig. 5 and Table S2.† A characteristic absorption at 590 nm was found only for 2, which causes the difference in colour of these complexes (2: green, 3–5: red). Absorptions at around 430 nm were commonly observed for 2–5, as was found in the triple decker ruthenocene bearing a stannole dianion ligand.¹² To understand the origins of these absorptions, TD-DFT calculations were performed at the same level as that for optimization. For chloro derivative 2, the calculated absorption at 586 and 430 nm (experimental: 590 and 432 nm) can be mainly assigned to HOMO → LUMO and HOMO-1 → LUMO transitions, respectively (Chart S1†). For alkyl derivative 4, the absorption maximum was calculated to be 409 nm (experimental: 429 nm), which mainly originate from HOMO → LUMO and HOMO-2 → LUMO transitions (Chart S2†). A similar trend was found in the silyl derivative, as shown in Chart S3.†

Conclusions

In conclusion, the reactions of anionic heavy ruthenocene 1 with various halides yielded chloro, alkyl, and silyl derivatives 2–5. It is a great surprise that the coordination mode of stannole monoanion ligand is highly dependent on the types of substituents on the tin atom. In contrast to the conventional η^5 coordination mode in silyl derivative 5, different coordination modes, which are between η^4 and η^5 with the bent stannole rings, were adopted for chloro and alkyl derivatives 2–4. The cyclic voltammetry revealed that the oxidation potentials of the heavy ruthenocenes become higher as the stannole

Table 3 Relationship between bent angles of the stannole ring, Sn–Ru bond lengths and substituents on the tin atom

| R | Bent angle (°) | | Sn–Ru (Å) | |
|-------------------|----------------|-------|-----------|-------|
| | Exp. | Calc. | Exp. | Calc. |
| Cl | 41.2 | 36.8 | 2.932 | 2.929 |
| H | — | 24.1 | — | 2.820 |
| Et | 24.4 | 20.0 | 2.797 | 2.794 |
| SiH ₃ | — | 18.3 | — | 2.774 |
| ^t Bu | — | 12.3 | — | 2.738 |
| SiMe ₃ | 12.0 | 9.7 | 2.690 | 2.713 |

rings are bent. The theoretical calculations elucidated that the lone pair on the tin atom in chloro derivative **2** has high s-character, which causes less effective interaction between Sn and Ru. On the other hand, the corresponding lone pair in **5** has more p-character, leading to an efficient Sn–Ru interaction. The reason for the different coordination modes of stannole anions is attributed to both electronegativity of an adjacent atom to the tin atom and bulkiness of the substituent on the tin atom, as evidenced by the theoretical calculations. The stannole ring intrinsically favours a bent structure with a η^4 -like coordination mode. However, as a substituent on the tin atom becomes larger, η^5 -coordination is more preferable because of steric repulsion between the substituent and the Cp* ligand. These findings, which defy the common knowledge that heavy Cp[−]s coordinate transition metals in a η^5 -fashion, as do Cp[−]s, are of fundamental importance to give deep insight into coordination chemistry.

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