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Dehydrogenative Sn–E (E = S, Se) Bond Formation Catalyzed by an Iron Complex

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ABSTRACT

Iron complex-catalyzed dehydrogenative Sn–E (E = S, Se) bond formation of hydrostannane with thiol and selenol was achieved. All new compounds were fully characterized using ^{1}H, $^{13}C\{^{1}H\}$, $^{77}Se\{^{1}H\}$, and $^{119}Sn\{^{1}H\}$ NMR measurements and elemental analyses. The structure of 1,1'-(1,3-dithia-2,2-dibutylstanyl)-[3]ferrocenophane was confirmed by single crystal X-ray diffraction.

Keywords Iron; Thiol; Selenol; Hydrostannane; Dehydrogenative Coupling

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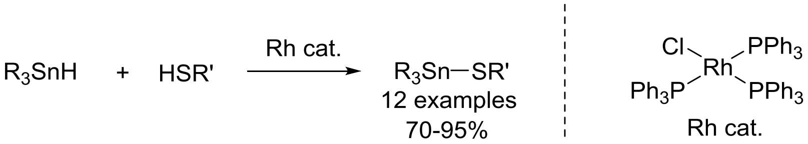
Dedicated to 82nd birthday of Professor Furukawa

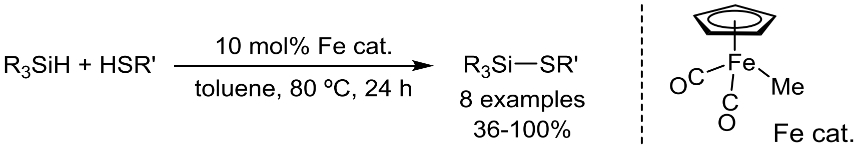
1 INTRODUCTION

Compounds having an Sn–E (E = S, Se) bond have attracted considerable attention because these compounds act as convenient reagents for the preparation of thiol esters from acid chloride[1] and for regioselective ring opening reaction of epoxides.[2] Dehydrogenative coupling of hydrostannane with thiol and selenol catalyzed by a transition metal complex is one of effective methods for Sn–E (E = S, Se) bond formation because it does not involve any by-products (except easily removable H_2) such as unnecessary inorganic salts. However, organic sulfides are generally known to serve as a catalyst poison. Actually, only one example of catalytic dehydrogenative Sn–S coupling reaction has been reported by Talley and Colley in 1981 (Scheme 1) in which a Rh complex catalyst was used.[3]



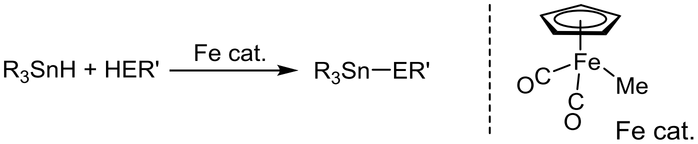
SCHEME 1

Previously, we reported dehydrogenative coupling of thiol with hydrosilane catalyzed by an iron complex (Scheme 2),[4] in which the corresponding Si–S coupling products were obtained in low to excellent yields.



SCHEME 2

This Si–S bond formation promoted by an iron complex stimulated us to challenge dehydrogenative Sn–S coupling catalyzed by a transition metal complex. Herein, we report the first example of dehydrogenative Sn–E (E = S, Se) bond formation catalyzed by a very simple, piano-stool type iron complex [$CpFe(CO)_2(Me)$] (Cp stands for η^5-C_5H_5) (Scheme 3).



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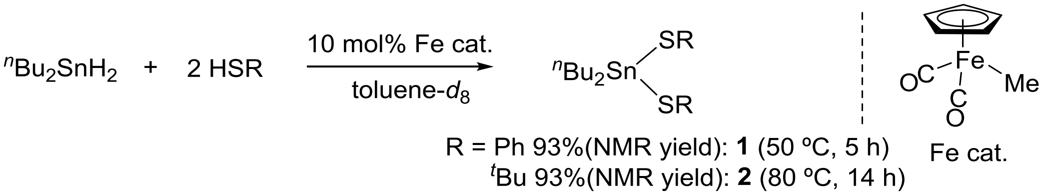
SCHEME 3

2 RESULTS AND DISCUSSION

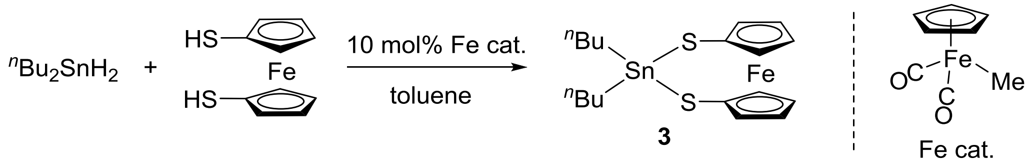
A toluene-d_8 solution containing ^{n}Bu$_2$SnH$_2$, 2 equiv. of HSPh, and 10 mol% (vs ^{n}Bu$_2$SnH$_2$) of [CpFe(CO)$_2$(Me)] was heated at 50 °C for 5 h. After the reaction, the toluene-d_8 solution was subjected to the ^{1}H NMR measurement, revealing the formation of the corresponding Sn–S coupling product ^{n}Bu$_2$Sn(SPh)$_2$ (**1**), in 93% yield (Scheme 4). When HS^{t}Bu was used, a higher reaction temperature (80 °C) and a longer reaction time (14 h) were required, but the corresponding ^{n}Bu$_2$Sn(S^{t}Bu)$_2$ was formed in 93% yield.



R = Ph 93%(NMR yield): **1** (50 °C, 5 h)
^{t}Bu 93%(NMR yield): **2** (80 °C, 14 h)

SCHEME 4

Next, we examined the reaction of 1,1'-ferrocenedithiol with secondary hydrostannane in our catalytic system with the hope of selective formation of an *ansa*-type compound such as a [3]ferrocenophane. 1,1'-Ferrocenedithiol [(HSCp)$_2$Fe] reacted with ^{n}Bu$_2$SnH$_2$ in a 1:1 molar ratio at 80 °C for 1 h in the presence of [CpFe(CO)$_2$(Me)] to give the desired 1,1'-(1,3-dithia-2,2-dibutylstanyl)-[3]ferrocenophane **3** in 88% yield (Scheme 5). Without the catalyst the reaction underwent very slowly. Therefore, it was thought that the iron complex acted as a catalyst. In addition, this reaction also took place under mild conditions (50 °C, 4 h).



88% (80 °C, 1 h)
24% (80 °C, 1 h, without a catalyst)
78% (50 °C, 4 h)

SCHEME 5

The molecular structure of **3** was determined using single crystal X-ray diffraction. Two independent molecules of **3** crystallized in the unit cell. As these are basically the same, the ORTEP drawing of **3** (Fe1 molecule) is shown in Fig. 1 and the crystal data are listed in Table 1. The Sn center adopts a typical tetrahedral geometry and has two ^{n}Bu substituents and a ferrocene-1,1'-dithiolato ligand. The Sn–S bond distances (2.4297(13), 2.4364(13) Å for Fe1 molecule, 2.4313(13), 2.4378(13) for Fe2 molecule) in **3** are longer than those of previously reported analogous bis(ferrocene-1,1′-dithiolato)stannane (2.39, 2.41 Å).[5]

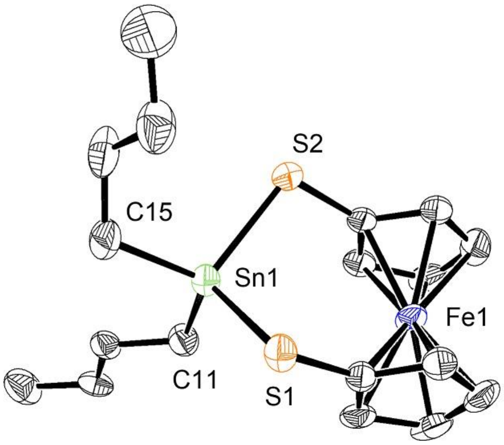
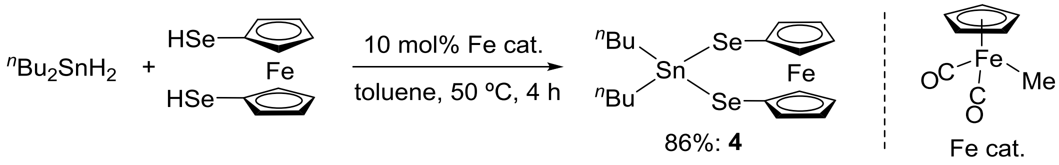


Fig. 1. ORTEP drawing of **3** (Fe1 molecule). Selected bond lengths (Å) and angles (°): Sn(1)–S(1) 2.4297(13), Sn(1)–S(2) 2.4364(13), S(1)–Sn(1)–S(2) 100.52(5), C(11)–Sn(1)–C(15) 114.16(16) for Fe1 molecule, Sn(2)–S(3) 2.4378(13), Sn(2)–S(4) 2.4313(13), S(3)–Sn(2)–S(4) 100.52(5), C(29)–Sn(2)–C(33) 116.53(16) for Fe2 molecule.

Table 1. Crystal data of **3**

Empirical formula	$C_{18}H_{26}S_2SnFe$	Volume (Å^3)	1910.6(12)
Formula weight	481.05	Z	4
T (K)	200(2)	ρ_{calcd} (g cm^{-3})	1.672
Crystal system	Triclinic	F(000)	968
Space group	P-1	Crystal size (mm^3)	0.48 × 0.020 × 0.010
a (Å)	10.622(4)	Reflections collected	19827
b (Å)	10.649(4)	Independent reflections (R(int))	8594 (0.0489)
c (Å)	18.020(7)	Final R_1 ($I > 2\sigma(I)$)	0.0388
α (°)	89.309(11)	Final R_1/wR_2 (all data)	0.0752/0.0729
β (°)	86.954(10)°	Goodness of fit	1.011
γ (°)	69.842(7)	Volume (Å^3)	1910.6(12)

The corresponding 1,1'-(1,3-diseleno-2,2-dibutylstanyl)-[3]ferrocenophane **4** was also obtained by the reaction of l,l'-ferrocenediselenol instead of 1,1'-ferrocenedithiol with $^{n}Bu_2SnH_2$ (Scheme 6).



SCHEME 6

In the ^{1}H NMR spectrum of **4**, a signal attributable to H–Sn was not observed. The $^{77}Se\{^{1}H\}$ NMR spectrum showed a signal at δ –210.10 flanked by both ^{117}Sn and ^{119}Sn satellites ($^{1}J(^{117}Sn\text{-}^{77}Se)$ = 1270 Hz, $^{1}J(^{119}Sn\text{-}^{77}Se)$ = 1331 Hz) (Fig. 2) and a singlet at δ 161.56 ($^{1}J(^{77}Se\text{-}^{119}Sn)$ = 1331 Hz) was observed in $^{119}Sn\{^{1}H\}$ NMR spectrum. These results showed that two equivariant Sn–Se bonds in **4** were formed by the dehydrogenative coupling reaction.

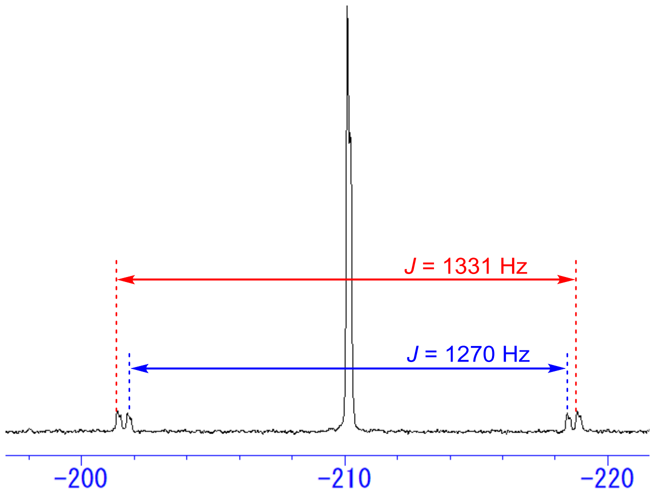
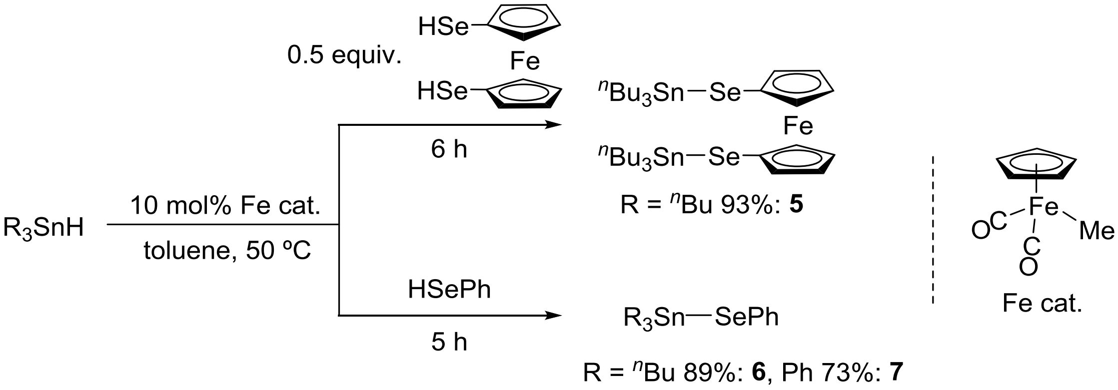


Fig. 2. $^{77}Se\{^{1}H\}$ NMR spectrum (76 MHz, C_6D_6, r.t.) of **4**.

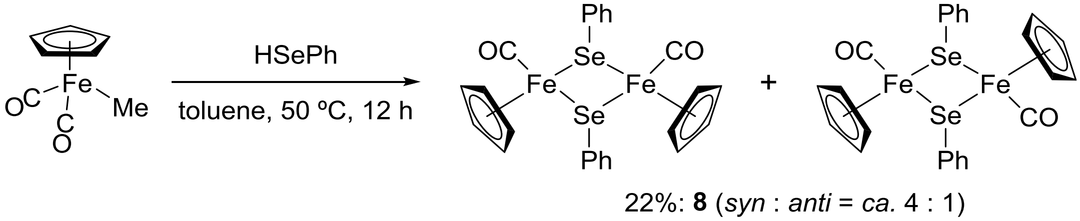
We also checked the reaction of tertiary hydrostannane with selenol. In our system, the reaction of $^{n}Bu_3SnH$ with l,l'-ferrocenediselenol $[(HSeCp)_2Fe]$ in a 2:1 molar ratio at 50 °C for 6 h in the presence of $[CpFe(CO)_2(Me)]$ afforded the desired 1,1'-bis(tributylstanylseleno)ferrocene

[(${}^{n}Bu_3SnSeCp)_2Fe$] **5**. Furthermore, the desired coupling products $R_3Sn–SePh$ (R = ^{n}Bu: **6**, Ph: **7**) were obtained by the reaction of tertiary hydrostannane R_3SnH with benzeneselenol HSePh (Scheme 7). This paper shows the first example of catalytic Sn–Se bond formation.



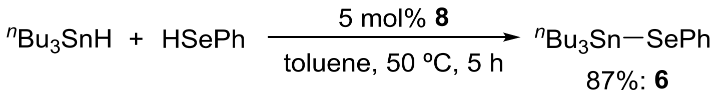
SCHEME 7

In order to obtain insight into the reaction pathway of dehydrogenative Sn–E (E = S, Se) bond formation, the stoichiometric reaction of [$CpFe(CO)_2(Me)$] with HSePh was examined. The reaction afforded the Se-bridged iron dimer complex [$CpFe(CO)(\mu\text{-}SePh)]_2$ **8** (*syn* : *anti* = *ca.* 4 : 1) in 22% yield (Scheme 8).



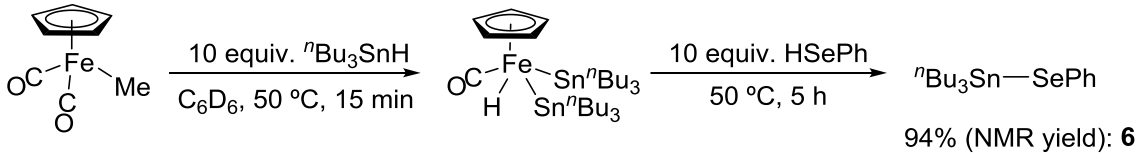
SCHEME 8

We checked the catalytic activity of **8** for dehydrogenative Sn–Se bond formation. The reaction of ${}^{n}Bu_3SnH$ with HSePh in the presence of 5 mol% of **8** at 50 °C for 5 h yielded the desired coupling product ${}^{n}Bu_3Sn–SePh$ in 87% yield (Scheme 9).



SCHEME 9

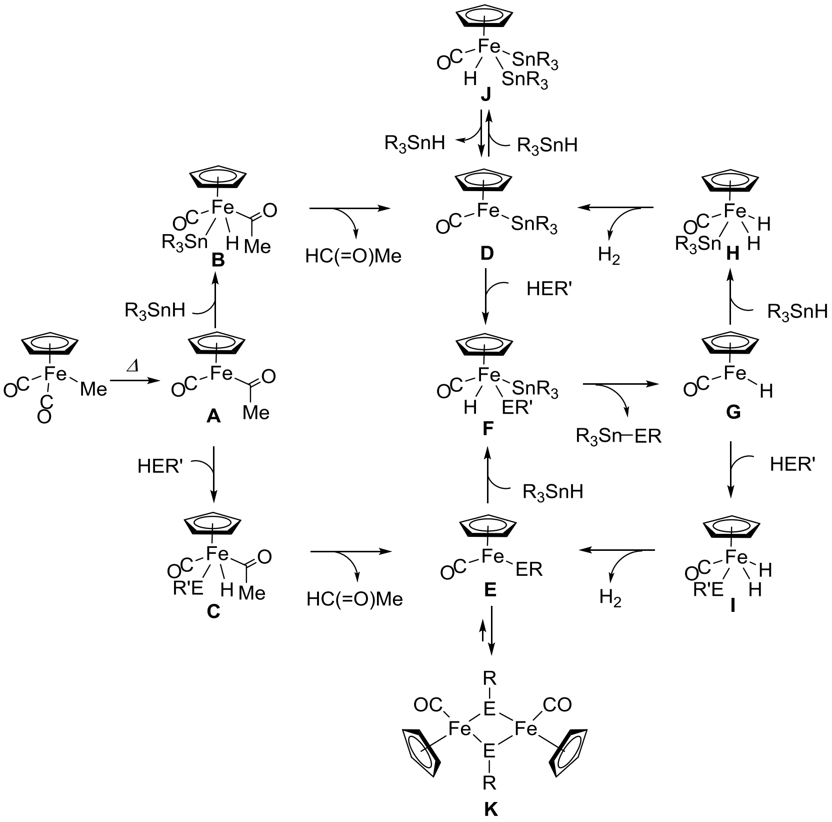
In addition, the hydrido signal (δ –13.17) of CpFe(CO)(H)(Sn^{n}Bu$_3$)$_2$ [6] was observed by the reaction of [CpFe(CO)$_2$(Me)] with 10 equiv. of ^{n}Bu$_3$SnH at 50 °C for 15 min in C_6D_6. Then, 10 equiv. of HSePh was added. After 5 h at 50 °C, the corresponding coupling compound ^{n}Bu$_3$Sn–SePh was obtained in 94% yield (Scheme 10).



SCHEME 10

These results show that **8** and CpFe(CO)(H)(SnR$_3$)$_2$ are important catalytic intermediates in this system.

A plausible reaction pathway for the dehydrogenative Sn–E (E = S, Se) bond formation is exhibited in Scheme 11. A methyl migration in the precursor [CpFe(CO)$_2$(Me)] forms an acyl complex CpFe(CO){C(=O)Me} **A**, which reacts with R$_3$SnH (or HER') to give CpFe(CO)(H){C(=O)Me}(SnR$_3$) **B** (or CpFe(CO)(H){C(=O)Me}(ER') **C**). Reductive elimination of acetoaldehyde produces CpFe(CO)(SnR$_3$) **D** (or CpFe(CO)(ER') **E**). Both the reaction of **D** with HER’ and that of **E** with R$_3$SnH produce CpFe(CO)(H)(SnR$_3$)(ER') **F**. The subsequent reductive elimination yields the corresponding coupling product R$_3$Sn–ER' and hydrido complex CpFe(CO)(H) **G**. Oxidative addition of R$_3$SnH (or HER') toward the Fe center gives a dihydrido complex CpFe(CO)(H)$_2$(SnR$_3$) **H** (or CpFe(CO)(H)$_2$(SnR$_3$)(ER') **I**). Reductive elimination of H$_2$ reproduces **D** (or **E**) to complete the catalytic cycle. A 16e stannyl complex **D** has a possibility to react with R_3SnH present in solution to give a bis(stannyl)hydridoiron complex, $CpFe(CO)(H)(SnR_3)_2$, through Sn–H oxidative addition. These types of addition of hydrosilane and hydrostannane to form bis(silyl)hydridoiron and bis(stannyl)hydridoiron complexes have been reported.[7,8] Unsaturated **E** having an ER ligand tends to dimerize to produce saturated **K**, and they are in equilibrium. This type of equiribrium and the related catalytic cycle for Si-S bond formation have been reported.[4] Therefore, the catalytic pathway to form an Sn–S and Sn–Se bond shown in Scheme 11 seems to be reasonable.



SCHEME 11

3. CONCLUSION

We found that the first examples of iron-catalyzed formation of Sn–S and Sn–Se bond in the dehydrogenation of thiol and selenol with hydrostannane, respectively. We proposed a catalytic cycle, and it was revealed that [CpFe(CO)(μ-SePh)]$_2$ **8** and CpFe(CO)(H)(SnR$_3$)$_2$ were important catalytic intermediates in this system.

4 EXPERIMENTAL

4.1 Instrumentation and Chemicals

All manipulations were carried out using standard Schlenk techniques under a dry nitrogen atmosphere. Iron complex CpFe(CO)$_2$(Me) [9] was prepared according to the literature method. The other chemicals were commercially available. Spectroscopic data of the products obtained in this work, **1** [10], **2** [11], **6** [12], **7** [13], **8** [14] agreed with those in the literatures. Solvents were purified employing a two-column solid-state purification system or were distilled from appropriate drying agents under N$_2$. NMR spectra (^{1}H, ^{13}C{^{1}H}, ^{77}Se{^{1}H} and ^{119}Sn{^{1}H}) were recorded on a JNM AL-400 spectrometer. ^{1}H and ^{13}C{^{1}H} NMR data were referred to residual peaks of solvent as an internal standard, and ^{77}Se{^{1}H} and ^{119}Sn{^{1}H} NMR chemical shifts were referenced to external SeMe$_2$ (0 ppm) and SnMe$_4$ (0 ppm) samples. Elemental analysis data were obtained on a Perkin-Elmer 2400 CHN elemental analyzer.

4.2 Preparation and NMR experiment

Preparation of ^{n}Bu$_2$Sn(SPh)$_2$ (**1**) *and* ^{n}*Bu*$_2$*Sn(S*^{t}*Bu)*$_2$ (**2**)

A toluene-*d*$_8$ solution (400 μL) containing ^{n}Bu$_2$SnH$_2$ (21 μL, 0.10 mmol) and thiol (0.20 mmol, HSPh and HS^{t}Bu) in the presence of CpFe(CO)$_2$ (Me) (1.9 mg, 0.01 mmol) was heated at 50 °C for 5 h for HSPh and at 80 °C for 14 h for HS^{t}Bu. Compounds **1** and **2** formed were identified by comparing their ^{1}H NMR data with those previously reported.[10,11] The yields of **1** and **2** were determined by ^{1}H NMR measurement using 1,4-dioxane as an internal standard (8.5 μL, 0.10 mmol).

Preparation of 1,1'-(1,3-dithia-2,2-dibutylstanyl)-[3]ferrocenophane (**3**). A toluene solution (250 μL) containing $CpFe(CO)_2(Me)$ (5.8 mg, 0.03 mmol), $[(HSCp)_2Fe]$ (75.0 mg, 0.30 mmol), and $^{n}Bu_2SnH_2$ (65 μL, 0.30 mmol) was stirred at 80 °C. After 5 h, volatile materials in the resulting solution were removed under reduced pressure. The residue was purified directly by flash chromatography (alumina, hexane). Evaporation of volatile materials from the eluate led to the formation of **3** as a yellow powder (128 mg, 88%). Single-crystals of **3** were obtained by slow evaporation of ether containing **3**. NMR spectroscopic analysis: ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 0.83 (t, *J*(H-H) = 7.4 Hz, 6H, CH_3), 1.24-1.44 (m, 8H, $CH_3C\mathit{H}_2CH_2C\mathit{H}_2Sn$), 1.64 (quintet, *J*(H-H) = 7.4 Hz, 4H, $CH_3CH_2C\mathit{H}_2CH_2Sn$), 3.84 (br, 4H, Cp), 4.05 (br, 4H, Cp); $^{13}C\{^{1}H\}$ NMR (100.4 MHz, C_6D_6, δ, ppm): 13.76 (s, Bu), 21.03 (s, Bu), 26.98 (s, Bu), 28.71 (s, Bu), 68.72 (s, Cp), 74.61 (s, Cp), 86.23 (s, Cp-*ipso*). Elemental Analysis: Calcd. For $C_{18}H_{26}SnS_2Fe$: C, 44.94; H, 5.45%; Found: C, 44.98; H, 5.55%.

Preparation of 1,1'-(1,3-diselena-2,2-dibutylstanyl)-[3]ferrocenophane (**4**). A toluene solution (250 μL) containing $CpFe(CO)_2(Me)$ (5.8 mg, 0.03 mmol), $[(HSeCp)_2Fe]$ (104.0 mg, 0.30 mmol), and $^{n}Bu_2SnH_2$ (65 μL, 0.30 mmol) was stirred at 50 °C. After 4 h, volatile materials in the resulting solution were removed under reduced pressure. To this reaction mixture was added hexane (2 mL), $MgSO_4$, and Na_2SO_4 and then the entire mixture was stirred for 1 h. The mixture was filtered to remove insoluble materials and then teh filtrate was evaporated to remove volatile materials, resulting in the formation of **4** as an orange-yellow powder (149 mg, 86%). NMR spectroscopic analysis: ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 0.84 (t, *J*(H-H) = 7.2 Hz, 6H, CH_3), 1.31 (sext, *J*(H-H) = 7.2 Hz, 4H, $CH_3C\mathit{H}_2CH_2CH_2$), 1.39 (t, *J*(H-H) = 7.2 Hz, 4H,$SnCH_2$), 1.64 (quin, *J*(H-H) = 7.2 Hz, 4H, $CH_3CH_2C\mathit{H}_2CH_2$), 3.85 (t, *J*(H-H) = 2.0 Hz, 4H, Cp), 4.05 (t, *J*(H-H) = 2.0 Hz, 4H, Cp); $^{13}C\{^{1}H\}$ NMR (100.4 MHz, C_6D_6, δ, ppm): 113.81 (s, $SnCH_2$), 20.62 (s, CH_3), 26.95 (s, $CH_3\mathit{C}H_2CH_2CH_2$), 29.39 (s, $CH_3CH_2CH_2CH_2$), 69.09 (s, Cp), 75.88 (s, Cp), 79.26 (s, Cp-*ipso*); $^{77}Se\{^{1}H\}$ NMR (76.1 MHz, C_6D_6, ppm): δ –210.10 (s, *J*(^{117}Sn-^{77}Se) = 1270 Hz, *J*(^{119}Sn-^{77}Se) = 1331 Hz, $SnSeC_5H_4$); $^{119}Sn\{^{1}H\}$ NMR (148.9 MHz, C_6D_6, ppm): δ 161.56 (s,

$J(^{77}Se-^{119}Sn)$ = 1331 Hz). Elemental Analysis: Calcd. For $C_{18}H_{26}Se_2SnFe$: C, 37.61; H, 4.56%; Found: C, 37.66; H, 4.80%.

Preparation of 1,1'-bis(tributylstanylseleno)ferrocene (**5**). A toluene solution (250 μL) containing $CpFe(CO)_2(Me)$ (5.8 mg, 0.03 mmol), $[(HSCp)_2Fe]$ (75.0 mg, 0.30 mmol), and $^nBu_3SnH$ (156 μL, 0.60 mmol) was stirred at 50 °C. After 6 h, volatile materials in the resulting solution were removed under reduced pressure. To this reaction mixture was added hexane (2 mL), $MgSO_4$, and Na_2SO_4 and then the entire mixture was stirred for 1 h. The mixture was filtered to remove insoluble materials and then the filtrate was evaporated to remove volatile materials, resulting in the formation of **5** as a yellow oil (274 mg, 93%). NMR spectroscopic analysis: ^1H NMR (400 MHz, C_6D_6, δ, ppm): 0.89 (t, J(H-H) = 7.3 Hz, 18H, CH_3), 1.07 (t, J(H-H) = 7.3 Hz, 12H, $CH_3CH_2CH_2CH_2$), 1.30 (sext, J(H-H) = 7.3 Hz, 12H, $CH_3CH_2CH_2CH_2$), 1.56 (quin, J(H-H) = 8.3 Hz, 12H, $CH_3CH_2CH_2CH_2$), 4.11 (s, 4H, Cp), 4.42 (s, 4H, Cp); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, δ, ppm): 13.92 (s, $SnCH_2$), 14.04 (s, CH_3), 27.45 (s, $CH_3CH_2CH_2CH_2$), 29.36 (s, $CH_3CH_2CH_2CH_2$), 70.02 (s, Cp), 71.43 (s, Cp), 77.88(s, Cp-*ipso*). Elemental Analysis: Calcd. For $C_{34}H_{64}Se_2Sn_2Fe$: C, 44.29; H, 6.78%; Found: C, 44.70; H, 7.00%.

Preparation of $^nBu_3SnSePh$ (**6**) *and* $Ph_3SnSePh$ (**7**)

Benzeneselenol (11 μL, 0.10 mmol) was treated with $^nBu_3SnH$ for **6** and Ph_3SnH for **7** (0.10 mmol) in the presence of $CpFe(CO)_2$ (Me) (1.9 mg, 0.01 mmol) in toluene-d_8 (400 μL). at 50 °C for 5. Compounds **6** and **7** were identified by comparing their ^1H NMR data with those previously reported.[11,12] The yields of **6** and **7** were determined by ^1H NMR measurement using 1,4-dioxane as an internalstandard (8.5 μL, 0.10 mmol).

Preparation of $[CpFe(CO)(\mu\text{-}SePh)]_2$ ***8***

An acetonitrile solution (5 mL) containing $CpFe(CO)_2(Me)$ (192 mg, 1.0 mmol) and benzeneselenol (106 μL, 1.0 mmol) was stirred at 50 °C. After 12 h, volatile materials in the resulting solution were removed under reduced pressure. To this reaction mixture was purified by reprecipitation from dichloromethane (1 mL) by hexane (10 mL). The obtained precipitate was filtered and dried to give **8** (*syn* : *anti* = *ca.* 4 : 1) as a brown powder (66 mg, 22%). Complex **8** was identified by comparing their ^{1}H NMR data with those previously reported.[14]

NMR experiment

A C_6D_6 solution (500 μL) containing $CpFe(CO)_2(Me)$ (3.8 mg, 0.02 mmol), $^{n}Bu_3SnH$ (53.8 μL, 0.2 mmol) and 1,4-dioxane (17.1 μL, 0.2 mmol) as an internal standard was placed in an NMR tube with a Teflon cap. The sample was heated at 50 °C. After 15 min, the hydrido signal (δ –13.17) of $CpFe(CO)(H)(Sn^{n}Bu_3)_2$ was observed by the ^{1}H NMR spectrum and then benzeneselenol (21.2 μL, 0.2 mmol) was added in the reaction mixture. The sample was heated at 50 °C for 5 h. The yield (94%) of formed $^{n}Bu_3Sn–SePh$ was determined by ^{1}H NMR.

4.3 Crystal structure determination and refinement

X-ray intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation. Calculations were performed with the CrystalClear software package of Molecular Structure Corporation. The structure was solved by direct methods and expanded using Fourier techniques. The structure was refined by full matrix least-squares technique using the program SHELXL-2014.[15] The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Complex **3** has been deposited with the Cambridge Crystallographic Data Centre under CCDC 1871153. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Tel.; +44 1223 336408; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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