

Insertion of Chalcogens and Bis(*tert*-butylisonitrile)palladium(0) into a Strained Ruthenium Half-sandwich Complex

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The previously synthesized strained distannadiyl-*ansa* half-sandwich complex [$\{\kappa^1\text{-Sn}t\text{Bu}_2\text{-Sn}t\text{Bu}_2\text{-}(\eta^5\text{-C}_5\text{H}_5)\}\text{Ru}(\text{CO})_2$] was investigated with respect to its reactivity toward group 16 elements and bis(*tert*-butylisonitrile)palladium(0). All products were analyzed by multinuclear NMR spectroscopy, IR spectroscopy and elemental analysis. [$\{\kappa^1\text{-Sn}t\text{Bu}_2\text{SSn}t\text{Bu}_2\text{-}(\eta^5\text{-C}_5\text{H}_5)\}\text{Ru}(\text{CO})_2$] was furthermore characterized by X-ray diffraction.

Key words: Ruthenium, Tin, Chalcogens, Palladium, Oxidative Addition, X-Ray Diffraction, *ansa* Half-sandwich Complexes

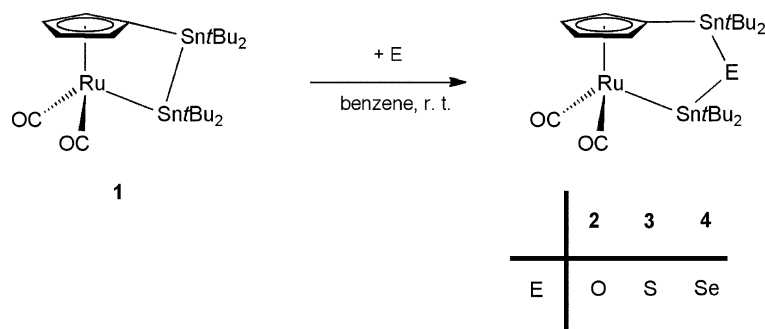
Introduction

Metallocenophanes [1–6] and the corresponding metalloarenophanes [7–18] have been in the focus of chemists and material scientists for the past 15 years, with the main emphasis lying on iron derivatives and ring-opening polymerization (ROP) reactions, to give organometallic polymers with promising properties [19–27]. In contrast to this rich field, related *ansa* half-sandwich complexes are still under-represented. While many efforts have been based on carbon as the bridging moiety [28], we and others recently focused on the synthesis of *ansa* half-sandwich complexes with heteroatomic bridging moieties in view of their use as precursors for ring-opening polymerization including a series of complexes with group 6, 8 and 10 metals and heavier group 14 elements as bridging moieties [29–40]. Synthetic strategies for such complexes generally follow two routes. The first one was introduced by Gladysz and coworkers and starts from a half-sandwich complex bearing a disilanyl group at the metal center. The two-step protocol includes a metallation at the cyclopentadienyl ring, followed by a silatropic shift of the disilanyl group to the Cp ligand and a subsequent ring closure [41]. The second route disclosed by our group is based on

a one-step synthesis starting from bimetalated half-sandwich complexes and salt metathesis with suitable bridging units [35, 38]. The resulting *ansa* half-sandwich complexes show high ring strain, which facilitates insertion reactions [35, 39] as well as ring-opening polymerization reactions, as shown by Pannell and coworkers [29, 30]. The work presented here focuses on the insertion of chalcogens and $[\text{Pd}(\text{NC}t\text{Bu})_2]$ into the distanna bridge of [$\{\kappa^1\text{-Sn}t\text{Bu}_2\text{-Sn}t\text{Bu}_2\text{-}(\eta^5\text{-C}_5\text{H}_5)\}\text{Ru}(\text{CO})_2$] [40].

Results and Discussion

The relief of ring strain in [$\{\kappa^1\text{-Sn}t\text{Bu}_2\text{-Sn}t\text{Bu}_2\text{-}(\eta^5\text{-C}_5\text{H}_5)\}\text{Ru}(\text{CO})_2$] (**1**) can be considered as the driving force for the insertion of chalcogens. In a general synthetic protocol, **1** was treated with the corresponding chalcogen (O_2 , S_8 , Se_∞) in benzene at ambient temperature, yielding the desired 1,3-distanna-2-chalcogena-*ansa* compounds in good to moderate yields. In case of sulfur and grey selenium, sonification was used for efficient mixing of the reagents, allowing reaction times of 2 h for both chalcogens (Scheme 1). In the case of oxygen, **1** was stirred for two days under dry air to ensure complete reaction. After work-up, all compounds were obtained as analytically pure solids



Scheme 1. Chalcogen insertion into the tin–tin bond.

and characterized in solution by multinuclear NMR spectroscopy. All NMR data meet our expectations and are comparable to those of previously reported related iron complexes [39].

Thus, the relaxation of the high ring strain and the resulting notable change in geometry lead to a dramatic down-field shift of the signal of the ruthenium-bound tin atom in the $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum from $\delta = -59$ to about 300 ppm (**2**: 306 ppm; **3**: 299 ppm; **4**: 282 ppm). Further insight into the molecular structures of **2–4** has been provided by an X-ray diffraction study of complex **3** (Fig. 1). As reported for analogous compounds with iron as the central metal [39], the insertion leads to an almost complete relief of ring strain, as evidenced by the tetrahedral Ru–Sn1–S1 angle of 109.6(1) (Table 1). Furthermore, the loss of rigidity causes a shortening of the Ru–Sn1 and C1–Sn2 bond lengths in comparison with those of the precursor complex **1**, a finding that is consistent with that already made for the corresponding iron compound [39].

In addition, the reactivity of **1** towards the oxidative addition of a low-valent group 10 metal complex was investigated (Scheme 2). Such complexes play an important role in catalytic transformations, for example in palladium-catalyzed cross-coupling [42] or distannylation reactions [43]. Similar reactivity patterns have already been disclosed by us in the case of other tin-bridged *ansa* half-sandwich complexes of group 6 and

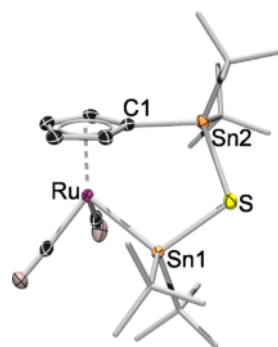


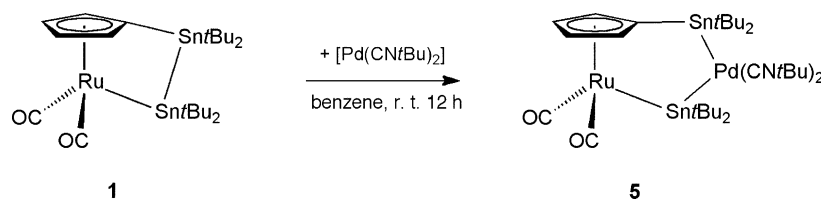
Fig. 1. Molecular structure of **3** with displacement ellipsoids at the 50% probability level. Hydrogen atoms and carbon ellipsoids of the *tert*-butyl groups were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru–Sn1 2.655(1), C1–Sn2 2.161(2), Sn1–S 2.456(1), Sn2–S1 2.401(8); Ru–Sn1–S1 109.7(1), C1–Sn1–S1 104.2(1).

8 metals [37, 39]. Indeed, complex **1** readily undergoes an oxidative addition reaction with $[\text{Pd}(\text{NC}t\text{Bu})_2]$. The $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of the product **5** shows two signals at $\delta = 250$ and 136 ppm, which represent a large down-field shift compared to the starting material, indicating larger angles at both stannyl fragments and release of ring strain. Similar to previously synthesized Pd(II) complexes of *ansa* half-sandwich complexes [37, 39] only one signal for the chemically non-equivalent *tert*-butyl isonitrile ligands is observed.

	$[\{\kappa^1\text{-Sn}t\text{Bu}_2\text{Sn}t\text{Bu}_2\text{-}(\eta^5\text{-C}_5\text{H}_5)\}\text{Ru}(\text{CO})_2]$, 1 [40]	$[\{\kappa^1\text{-Sn}t\text{Bu}_2\text{SSn}t\text{Bu}_2\text{-}(\eta^5\text{-C}_5\text{H}_5)\}\text{Ru}(\text{CO})_2]$, 3	$[\{\kappa^1\text{-Sn}t\text{Bu}_2\text{SSn}t\text{Bu}_2\text{-}(\eta^5\text{-C}_5\text{H}_5)\}\text{Fe}(\text{CO})_2]$ [39]
$M^a\text{-Sn1}$	2.687(1)	2.655(1)	2.571(1)
C1–Sn2	2.207(2)	2.161(2)	2.153(2)
$M^a\text{-Sn1-E}^b$	84.4(1)	109.7(1)	110.63(1)
C1–Sn2–E ^b	81.1(1)	104.2(1)	103.33(1)

^a $M = \text{Ru}$ (**1**, **3**), Fe; ^b $E = \text{Sn}$ (**1**), S.

Table 1. Selected bond lengths (Å) and angles (deg) of **3** in comparison with those of the precursor complex **1** [40] and an analogous iron *ansa* half-sandwich complex bearing a sulfur atom in the bridging moiety [39].

Scheme 2. Oxidative addition of **1** to $[\text{Pd}(\text{CN}t\text{Bu})_2]$.

In conclusion, we have shown that the insertion of chalcogens (O, S, Se) into a highly reactive distanna bridge of an *ansa* ruthenium half sandwich leads to expansion of the bridging moiety with a significant decrease of ring strain. Moreover, upon oxidative addition of a palladium(0) species to the Sn–Sn bond in **1** we obtained a bimetallic complex in excellent yield.

Experimental Section

All manipulations were conducted under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glove box techniques. Solvents (pentane, benzene) were purified by distillation from appropriate drying agents (NaK₃ alloy and sodium/benzophenone) under dry argon immediately prior to use. C₆D₆ was degassed by three freeze-pump-thaw cycles and stored over molecular sieves. IR spectra were recorded in solid state on a Bruker alpha FT-IR-spectrometer. Elemental analyses were obtained from an Elementar Vario MICRO cube instrument. NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer (500.1 MHz for ¹H, 186.5 MHz for ¹¹⁹Sn{¹H}), 125.8 MHz for ¹³C{¹H}). Chemical shifts are given in ppm, and are referenced against external SiMe₄ (¹H, ¹³C), and SnMe₄ (¹¹⁹Sn). Starting materials were prepared according to literature procedures: $[\{\kappa^1\text{-Sn}t\text{Bu}_2\text{-Sn}t\text{Bu}_2\text{-}(\eta^5\text{-C}_5\text{H}_5)\}\text{Ru}(\text{CO})_2]$ [**40**], and $[\text{Pd}(\text{CN}t\text{Bu})_2]$ [**44**]. All other compounds were obtained commercially and used without further purification.

$[\{\kappa^1\text{-Sn}t\text{Bu}_2\text{OSn}t\text{Bu}_2(\eta^5\text{-C}_5\text{H}_4)\}\text{Ru}(\text{CO})_2]$ (**2**)

A solution of $[\{\kappa^1\text{-Sn}t\text{Bu}_2\text{-Sn}t\text{Bu}_2(\eta^5\text{-C}_5\text{H}_4)\}\text{Ru}(\text{CO})_2]$ (**1**) (100 mg, 0.13 mmol) in benzene (3 mL) was stirred for 2 d in an apparatus sealed with a drying tube filled with P₂O₅. The solvent was evaporated under reduced pressure, and the residue was extracted with pentane (3 × 10 mL). The volume of the combined extracts was reduced to 2 mL *in vacuo*, and the product was left to crystallize at –30 °C for 12 h. Yield: 34.4 mg (0.43 mmol, 34%). Pale-grey solid. M. p.: 169 °C. – ¹H NMR (500.1 MHz, C₆D₆): δ = 4.98 (m, 2 H, C₅H₄), 4.88 (m, 2 H, C₅H₄), 1.53 (s, 18 H, ³J_{SnH} = 74.0, 71.0 Hz, *t*Bu₂), 1.27 (s, 18 H, ³J_{SnH} = 79.0, 75.5 Hz, *t*Bu₂). – ¹³C{¹H} NMR

(125.8 MHz, C₆D₆): δ = 203.0 (s, CO), 104.6 (s, C_q, C₅H₄), 90.3 (s, CH, C₅H₄), 89.4 (s, 2 × CH, C₅H₄), 37.8 (s, 2 C_q, *t*Bu₂), 34.8 (s, C_q, *t*Bu₂), 31.4 (s, CH₃, *t*Bu₂), 31.4 (s, CH₃, *t*Bu₂). – ¹¹⁹Sn{¹H} NMR (186.5 MHz, C₆D₆): δ = 306 (s, ²J_{SnSn} = 417, 398 Hz), 40 (s, ²J_{SnSn} = 417, 398 Hz). – IR: ν_{C=O} = 1992, 1937 cm^{–1}. – C₂₃H₄₀O₃RuSn₂ (804.13): calcd. C 39.29, H 5.73; found C 39.40, H 5.78.

$[\{\kappa^1\text{-Sn}t\text{Bu}_2\text{SSn}t\text{Bu}_2(\eta^5\text{-C}_5\text{H}_4)\}\text{Ru}(\text{CO})_2]$ (**3**)

A solution of $[\{\kappa^1\text{-Sn}t\text{Bu}_2\text{-Sn}t\text{Bu}_2(\eta^5\text{-C}_5\text{H}_4)\}\text{Ru}(\text{CO})_2]$ (**1**) (100 mg, 0.13 mmol) in benzene (3 mL) was treated with S₈ (4.10 mg, 15.8 μmol) and centered in an ultrasonic bath for 2 h. The work-up procedure was performed in a manner similar to that for **2**. Yield: 70.1 mg (85.0 μmol, 67%). Pale-beige solid. M. p.: 158 °C. – ¹H NMR (500.1 MHz, C₆D₆): δ = 5.10 (m, 2 H, C₅H₄), 4.84 (m, 2 H, C₅H₄), 1.53 (s, 18 H, ³J_{SnH} = 75.7, 72.3 Hz, *t*Bu₂), 1.28 (s, 18 H, ³J_{SnH} = 80.1, 78.3 Hz, *t*Bu₂). – ¹³C{¹H} NMR (125.8 MHz, C₆D₆): δ = 204.5 (s, CO), 99.9 (s, C_q, C₅H₄), 93.6 (s, CH, C₅H₄), 88.4 (s, CH, C₅H₄), 36.2 (s, C_q, *t*Bu₂), 33.8 (s, C_q, *t*Bu₂), 31.4 (s, CH₃, *t*Bu₂), 31.0 (s, CH₃, *t*Bu₂). – ¹¹⁹Sn{¹H} NMR (186.5 MHz, C₆D₆): δ = 299 (s, ¹J_{SnSn} = 209, 200 Hz), 43 (s, ¹J_{SnSn} = 210, 201 Hz). – IR: ν_{C=O} = 1994, 1950, 1928 cm^{–1}. – C₂₃H₄₀O₂RuSSn₂ (804.13): calcd. C 38.41, H 5.61; found C 38.46, H 5.64.

$[\{\kappa^1\text{-Sn}t\text{Bu}_2\text{SeSn}t\text{Bu}_2(\eta^5\text{-C}_5\text{H}_4)\}\text{Ru}(\text{CO})_2]$ (**4**)

A solution of $[\{\kappa^1\text{-Sn}t\text{Bu}_2\text{-Sn}t\text{Bu}_2(\eta^5\text{-C}_5\text{H}_4)\}\text{Ru}(\text{CO})_2]$ (**1**) (100 mg, 0.13 mmol) in benzene (2 mL) was treated with grey selenium (30.0 mg, 0.38 mmol) and placed in an ultrasonic bath for 2 d. The work-up procedure was performed similarly as described for (**2**). Yield 60.0 mg (69.2 μmol, 55%). M. p.: 148 °C. – ¹H NMR (500.1 MHz, C₆D₆): δ = 5.17 (m, 2 H, C₅H₄), 4.83 (m, 2 H, C₅H₄), 1.52 (s, 18 H, ³J_{SnH} = 76.0, 72.5 Hz, *t*Bu₂), 1.28 (s, 18 H, ³J_{SnH} = 80.0, 77.0 Hz, *t*Bu₂). – ¹³C{¹H} NMR (125.8 MHz, C₆D₆): δ = 203.0 (s, CO), 100.4 (s, C_q, C₅H₄), 95.5 (s, CH, C₅H₄), 88.4 (s, CH, C₅H₄), 35.7 (s, C_q, *t*Bu₂), 34.0 (s, C_q, *t*Bu₂), 31.9 (s, CH₃, *t*Bu₂), 31.5 (s, CH₃, *t*Bu₂). – ¹¹⁹Sn{¹H} NMR (186.5 MHz, C₆D₆): δ = 282 (s), 35 (s, ¹J_{SnSn} = 189, 181 Hz). – IR: ν_{C=O} = 1995, 1952,

1928 cm⁻¹. – C₂₃H₄₀O₂RuSeSn₂ (867.09): calcd. C 36.06 H 5.26; found C 36.82, H 5.62.

[κ^1 -Sn*t*Bu₂-{*cis*-Pd(NC*t*Bu)₂}-Sn*t*Bu₂(η^5 -C₅H₄)]Ru(CO)₂] (5)

A solution of [κ^1 -Sn*t*Bu₂-Sn*t*Bu₂(η^5 -C₅H₄)]Ru(CO)₂] (100 mg, 0.13 mmol) in benzene (4 mL) was treated with [Pd(NC*t*Bu)₂] (36.0 mg, 0.13 mmol) and stirred over night. The solvent was removed *in vacuo*, and the residue was extracted with pentane (3 × 10 mL). The volume of the combined extracts was reduced to 2 mL *in vacuo*, and the product was allowed to crystallize at –30 °C for 12 h. Yield 106 mg (0.11 mmol, 87%). Yellow solid. M. p.: 178 °C. – ¹H NMR (500.1 MHz, C₆D₆): δ = 5.65 (m, 2 H, C₅H₄), 5.15 (m, 2 H, C₅H₄), 1.73 (s, 18 H, ³J_{SnH} = 58.8, 56.3 Hz, *t*Bu₂), 1.50 (s, 18 H, ³J_{SnH} = 56.6, 54.5 Hz, *t*Bu₂) 0.97 (s, 18 H, *t*Bu). – ¹³C{¹H} NMR (125.8 MHz, C₆D₆): δ = 207.8 (s, CO), 150.7 (s, C_q, NC), 106.6 (s, C_q, C₅H₄), 96.0 (s, CH, C₅H₄), 88.7 (s, CH, C₅H₄), 56.6 (s, C_q, NC*t*Bu₂), 35.7 (s, CH₃, *t*Bu₂), 33.5 (s, CH₃, *t*Bu₂), 33.0 (s, C_q, *t*Bu₂), 31.2 (s, C_q, *t*Bu₂), 29.9 (s, CH₃, NC*t*Bu₂). – ¹¹⁹Sn{¹H} NMR (186.5 MHz, C₆D₆): δ = 250 (s), 136 (s). – IR: $\tilde{\nu}_{C=O}$ = 1994, 1971, 1952, 1913, $\nu_{N=C}$ = 2161, 2144 cm⁻¹. – C₃₃H₅₈O₂PdRuSn₂ (962.06): calcd. C 41.30, H 6.09, N 2.92; found C 41.20, H 6.18 N 2.58.

X-Ray structure determination

The diffraction data of **3** were collected on a Bruker X8APEX diffractometer with a CCD area detector and multi-layer mirror-monochromatized MoK α radiation. The structure was solved using Direct Methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were assigned to idealized geometric positions and included in the structure factor calculations. Structure solution: SHELXS-97 [45, 46]; structure refinement: SHELXL-97 [47, 48].

Crystal data for **3**: C₂₃H₄₀O₂RuSSn₂, *M*_r = 719.06, colorless block, 0.50 × 0.34 × 0.15 mm³, orthorhombic space group *Fdd*2, *a* = 18.253(7), *b* = 65.618(16), *c* = 9.394(2) Å, *V* = 11252(6) Å³, *Z* = 16, *d*_{calcd} = 1.70 g cm⁻³, 2.4 mm⁻¹, *F*(000) = 5664 e, *T* = 100(2) K, *R*₁ = 0.0154, *wR*₂ = 0.0571, 5711 independent reflections [$2\theta \leq 52.74^\circ$] and 274 refined parameters.

CCDC 901003 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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