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

Holger Braunschweig, Alexander Damme, Jan Mies, and Marius Schäfer
Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
Reprint requests to Prof. Dr. Holger Braunschweig. Fax: (+49) (0)931/888-4623. E-mail: h.braunschweig@mail.uni-wuerzburg.de

Received September 14, 2012 / published online November 8, 2012

The previously synthesized strained distannadiyl-ansa half-sandwich complex [{κ\(^1\)-Sn\(_{tBu}\)\(_2\)\(\cdot\)Sn\(_{tBu}\)\(_2\)-\(\eta^5\)-C\(_5\)H\(_5\)}Ru(CO)] was investigated with respect to its reactivity toward group 16 elements and bis(tert-butylinonitrile)palladium(0). All products were analyzed by multinuclear NMR spectroscopy, IR spectroscopy and elemental analysis. [{κ\(^1\)-Sn\(_{tBu}\)\(_2\)\(\cdot\)Sn\(_{tBu}\)\(_2\)-\(\eta^5\)-C\(_5\)H\(_5\)}Ru(CO)] 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 heteroligating 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 disilyl group at the metal center. The two-step protocol includes a metatation at the cyclopentadienyl ring, followed by a silatropic shift of the disilyl 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 bimetallated 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 [Pd(NC\(_{tBu}\)\(_2\)] into the distanna bridge of [{κ\(^1\)-Sn\(_{tBu}\)\(_2\)\(\cdot\)Sn\(_{tBu}\)\(_2\)-\(\eta^5\)-C\(_5\)H\(_5\)}Ru(CO)] [40].

Results and Discussion

The relief of ring strain in [{κ\(^1\)-Sn\(_{tBu}\)\(_2\)\(\cdot\)Sn\(_{tBu}\)\(_2\)-\(\eta^5\)-C\(_5\)H\(_5\)}Ru(CO)] (I) can be considered as the driving force for the insertion of chalcogens. In a general synthetic protocol, I was treated with the corresponding chalcogen (O\(_2\), S\(_8\), Se\(_\infty\)) 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, I was stirred for two days under dry air to ensure complete reaction. After work-up, all compounds were obtained as analytically pure solids...
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 $^{119}$Sn$^1$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 $1$ [40] and an analogous iron ansa half-sandwich complex bearing a sulfur atom in the bridging moiety [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 8 metals [37, 39]. Indeed, complex $1$ readily undergoes an oxidative addition reaction with [Pd(NC$t$Bu)$_2$]. The $^{119}$Sn$^1$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.

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].

<table>
<thead>
<tr>
<th>M$^a$</th>
<th>Sn1</th>
<th>C1–Sn2</th>
<th>M$^a$–Sn1</th>
<th>C1–Sn2–M$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_5\text{H}_5\text{Ru(CO)}_2</td>
<td>\text{SnBu}_2\text{SnBu}_2\text{SnBu}_2\text{SnBu}_2(\eta^5\text{C}_5\text{H}_5)$</td>
<td>2.687(1)</td>
<td>2.655(1)</td>
<td>2.571(1)</td>
</tr>
<tr>
<td>$\text{C}_5\text{H}_5\text{Sn}(\eta^5\text{C}_5\text{H}_5)\text{Ru(CO)}_2</td>
<td>\text{SnBu}_2\text{SnBu}_2\text{SnBu}_2\text{SnBu}_2$</td>
<td>2.207(2)</td>
<td>2.161(2)</td>
<td>2.153(2)</td>
</tr>
</tbody>
</table>

$^a$ $M = \text{Ru (1, 3), Fe;}$ $^b$ $E = \text{Sn (1), S.}$
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 (NaK alloy and sodium/benzophenone) under dry argon immediately prior to use. C₄D₆ 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 a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded in CDCl₃ or CD₂Cl₂ using tetramethylsilane as internal standard. Mass spectra were recorded on an Spectromass equipment. High-resolution mass spectra were obtained from a Micromass ZAB-2F spectrometer. – C.H. NMR (125.8 MHz, C₄D₆); δ = 203.0 (s, CO), 104.6 (s, C₅, C₆H₄), 90.3 (s, CH, C₆H₄), 89.4 (s, 2 × CH, C₅H₄), 37.8 (s, 2 C₅, tBu), 34.8 (s, C₂, tBu), 31.4 (s, CH₃, tBu), 31.4 (s, CH₃, tBu). – ¹¹⁹Sn [¹H] NMR (186.5 MHz, C₄D₆): δ = 306 (s, 3JSnSn = 417, 398 Hz), 40 (s, 2JSnSn = 417, 398 Hz). – IR: νC=O = 1992, 1937 cm⁻¹, νC₃H₅O₂RuSn₂O₄ (804.13): calcld. C 39.29, H 5.73; found C 39.40, H 5.78.

A solution of [κ¹-SnBu₂-SnBu₂(η⁵-C₅H₅)]Ru(CO)₂ (1) (100 mg, 0.13 mmol) in benzene (3 mL) was treated with Sb₅ (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, 2H, C₆H₄), 4.84 (m, 2H, C₆H₄), 1.53 (s, 18H, tBu), 1.28 (s, 18H, J_SnH = 80.1, 78.3 Hz, tBu). – ¹³C [¹H] NMR (125.8 MHz, C₆D₆): δ = 204.5 (s, CO), 99.9 (s, C₅, C₆H₄), 93.6 (s, CH, C₆H₄), 88.4 (s, CH, C₅H₄), 36.2 (s, C₅, tBu), 33.8 (s, C₂, tBu), 31.4 (s, CH₂,tBu), 31.0 (s, CH₃,tBu). – ¹¹⁹Sn [¹H] NMR (186.5 MHz, C₆D₆): δ = 299 (s, 3JSnSn = 209, 200 Hz), 43 (s, 1JSnSn = 210, 201 Hz). – IR: νC=O = 1994, 1950, 1928 cm⁻¹. – C₃H₅O₂RuSn₂O₄ (804.13): calcld. C 38.41, H 5.61; found C 38.46, H 5.64.

A solution of [κ¹-SnBu₂-SnBu₂(η⁵-C₅H₅)]Ru(CO)₂ (1) (100 mg, 0.13 mmol) in benzene (2 mL) was treated with grey selenium (30 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, 2H, C₆H₄), 4.83 (m, 2H, C₆H₄), 1.52 (s, 18H, J_SnH = 76.0, 72.5 Hz, tBu), 1.28 (s, 18H, J_SnH = 80.0, 77.0 Hz, tBu). – ¹³C [¹H] NMR (125.8 MHz, C₆D₆): δ = 203.0 (s, CO), 100.4 (s, C₅, C₆H₄), 95.5 (s, CH, C₆H₄), 88.4 (s, CH, C₅H₄), 35.7 (s, C₂, tBu), 34.0 (s, C₅, tBu), 31.9 (s, CH₃,tBu), 31.5 (s, CH₃,tBu). – ¹¹⁹Sn [¹H] NMR (186.5 MHz, C₆D₆): δ = 282 (s), 35 (s, 1JSnSn = 189, 181 Hz). – IR: νC=O = 1995, 1952.
A solution of [{κ-SnBu2-SnBu2(η²-C₅H₄)}Ru(CO)₂] (100 mg, 0.13 mmol) in benzene (4 mL) was treated with {[Pd(CN)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.

X-Ray structure determination

The diffraction data of 3 were collected on a Bruker X8APEX diffractometer with a CCD area detector and multilayer mirror-monochromatized MoKα 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: SHELX-97 [45, 46]; structure refinement: SHELXL-97 [47, 48].

Crystal data for 3: C₂H₄₀O₂RuSn₂, Mᵣ = 719.06, colorless block, 0.50 × 0.34 × 0.15 mm³, orthorhombic space group Pdd2, a = 18.253(7), b = 65.618(16), c = 9.394(2) Å, V = 11252(6) Å³, Z = 16, dcalc = 1.70 g cm⁻³, 2.4 mm⁻¹, F(000) = 5664 e, T = 100(2) K, R₁ = 0.0154, wR₂ = 0.0571, 5711 independent reflections [2θ ≤ 52.74°] 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.

Acknowledgement

Financial support by the DFG is gratefully acknowledged.

Reactions of \([\kappa^1-{\text{Sn}}_{\text{Bu}_2}{\text{Sn}}_{\text{Bu}_2}(\eta^5-\text{C}_5\text{H}_5)]\text{Ru(CO)}_2\]