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Synthesis and Structure of Distanna and Tristanna Ansa Half-Sandwich Complexes of Ruthenium and Nickel

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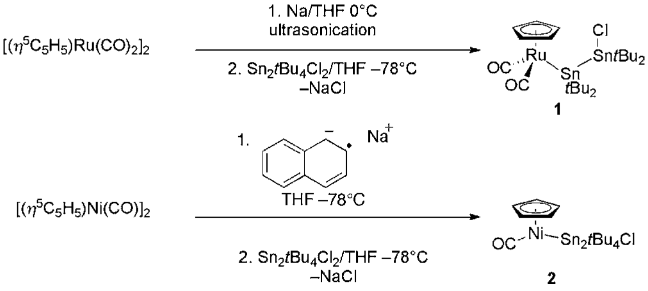
Supporting Information

ABSTRACT: The synthesis and structural characterization of the first tin-bridged ansa half-sandwich complexes via a two-step protocol from Na[η^5-C_5H_5Ru$(CO)_2$] and in situ generated Na[η^5-C_5H_5Ni(CO)] are presented. Both compounds are characterized by multinuclear NMR spectroscopy and single-crystal diffraction.

[*n*]Metallocenophanes and related [*n*]metalloarenophanes have been intensively studied over the past decades,[1] disclosing a broad spectrum of structural motifs particularly with respect to variations of the central metal and the bridging unit between the two carbocyclic ligands.[2] The propensity of strained [*n*]metallocenophanes to undergo ring-opening polymerization (ROP) to furnish metallopolymers is of special interest.[1b,c,e,f] In this respect, ferrocenophanes with bridging silanediyl moietys are the prominent examples.[1a] Recently, we and others focused on metallocenophanes with different transition metals and bridging elements, introducing e.g., early transition metals such as titanium or vanadium.[2] Ansa half-sandwich complexes constitute a particular subclass of [*n*]metallocenophanes, which have also proven their potential as possible precursors for metal-containing polymers. Their propensity to establish highly strained bridging motifs in combination with a sterically accessible coordination sphere renders these species particularly well-suited precursors for ROP.[3] In contrast to the aforementioned [*n*]metallocenophanes and [*n*]metalloarenophanes, however, their structural diversity is far less developed. Thus, mostly carbon[4] and, to a lesser extent, its higher homologues silicon[3,5a,d] and tin[5b,c,e,f] have been reported as bridging elements. Likewise, variations of the central metal are focused on the heavier group 6 elements[5b−f] rhenium[5a] and iron.[3] To the best of our knowledge, ruthenium-based ansa half-sandwich complexes are hitherto unknown, and for the corresponding nickel species, no direct synthetic route nor a fully characterized complex has been reported yet, despite the fact that [1]- and [2]metallocenophanes are known for both metals.[2c,u] Here, we present the synthesis and structural characterization of the first examples of tin-bridged ansa half-sandwich complexes with ruthenium and nickel as metal centers.

In the case of ansa half-sandwich complexes of molybdenum and tungsten, we achieved their synthesis by an efficient one-step protocol via the corresponding dilithiated complex precursors[5b−d] Because the corresponding bimetalated group 8 half-sandwich complexes are hitherto unknown, we followed a different protocol[3,5a] for the synthesis of the targeted ruthenium and nickel complexes. By the treatment of Sn_2tBu$_4$Cl$_2$[6a] with freshly prepared Na[(η^5-C_5H_5)Ru$(CO)_2$] derived from $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$[6b] in tetrahydrofuran (THF) at 0 °C, **1** (Scheme 1) was obtained in 57% yield after crystallization from pentane at −30 °C. Because of the thermal instability of the corresponding Na[(η^5-C_5H_5)Ni(CO)],[7] $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$[6c] was treated with 2 equiv of a freshly prepared sodium naphthalene solution at −78 °C, followed by a quick transfer into a solution of Sn_2tBu$_4$Cl$_2$ in THF. The nickel distannyl complex **2** was obtained as deep-red crystals after crystallization from pentane at −30 °C in yields of 25−30%.

Scheme 1. Syntheses of 1 and 2



Both compounds were characterized by IR and multinuclear NMR spectroscopy, which are in full agreement with the proposed structures. The ^{1}H NMR spectra of **1** and **2** show two singlets at δ 4.99 and 5.49, respectively, which can be assigned to the cyclopentadienyl ligand. The signals associated with the *tert*-butyl groups are detected as two singlets, which are accompanied by $^{117/119}$Sn satellites indicative of the $^3J_{HSn}$ couplings. In addition, ^{119}Sn NMR spectra exhibit two distinct resonances each [δ 194 and 116 (**1**) and δ 218 and 117 (**2**)], resulting from the expected chemical inequivalence of the tin atoms. Both signals show a direct $^1J_{SnSn}$ coupling of 1627 and 1556 Hz for **1**, as well as 1735 and 1652 Hz in the case of **2**.

Compounds **1** and **2** were subjected to single-crystal X-ray diffraction analysis (Figure 1). Two different molecules are present in the asymmetric unit of **2**, for which the structural parameters are almost identical. Thus, in the following, we confine our discussion to one molecule for compound **2**. The M−Sn bond lengths of 2.6769(3) and 2.5244(6) Å for **1** and **2**

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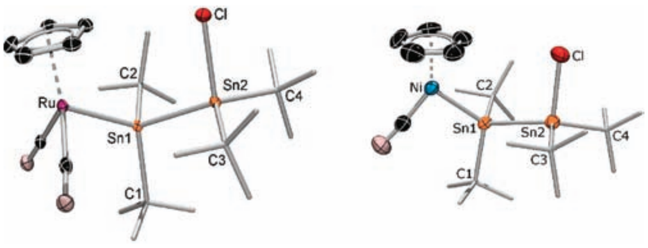
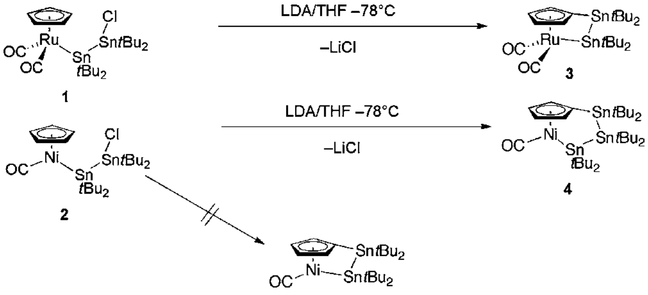


Figure 1. Molecular structures of **1** (left) and **2** (right) in the solid state. Hydrogen and carbon atoms at the *tert*-butyl groups are omitted for clarity. Thermal ellipsoids are at 50% probability. Relevant bond lengths (Å) and angles (deg) for **1**: Ru−Sn1 2.6769(2), Sn1−Sn2 2.8501(2); C1−Sn1−C2 108.01(6), Sn1−Sn2−Cl 104.25(1), C3−Sn2−Cl 100.71(4), C4−Sn2−Cl 98.19(4), C3−Sn2−C4 111.95(6). Relevant bond lengths (Å) and angles (deg) for **2** (only one molecule of the asymmetric unit is presented): Ni−Sn1 2.5244(6), Sn1−Sn2 2.8621(4),C1−Sn1−C2 109.81(1), Sn1−Sn2−Cl 103.55(3), C3−Sn2−Cl 100.3(1), C4−Sn2−Cl 98.3(1), C3−Sn2−C4 113.03(8).

are slightly longer than the average Ru−Sn and Ni−Sn bonds, respectively,[8] which might be attributed to the sterically demanding *tert*-butyl groups. The tin−tin distances of 2.8501(3) Å (**1**) and 2.8621(4) Å (**2**) are longer than those in the starting material *t*Bu$_4$Sn$_2$Cl$_2$ [2.8299(5) Å] and can be compared with similar half-sandwich complexes containing the *t*Bu$_4$Sn$_2$ moiety.[5b,9] The tetrahedral geometry at Sn1 with angles between 107.99(8)° and 115.32(6)° (**1**) and between 105.64(1)° and 115.4(1)° (**2**) indicates the influence of the bulky metal fragments in contrast to the geometry of Sn2, in which the bulky *tert*-butyl groups lead to acute Cl−Sn−C and wide *t*Bu−Sn−*t*Bu angles.[9]

The treatment of **1** with lithiumdiisopropylamide (LDA) at −78 °C leads to the desired ansa half-sandwich complex **3** (Scheme 2) in 67% yield after crystallization from pentane at −30 °C. Using the same protocol for **2** to achieve the desired distanna-bridged nickel half-sandwich complex leads to a complex mixture, which after chromatographic workup yielded the tristannanediyl-bridged nickel half-sandwich complex **4** in 50% yield.

Scheme 2. Synthesis of the Ansa Half-Sandwich Complexes 3 and 4 by Intramolecular Salt Elimination



The presence of a tristannanediyl bridge in the case of **4** is certainly somewhat unexpected. However, we recently reported a corresponding tungsten ansa half-sandwich complex, where the formation of a tristannanediyl bridge was attributed to the insertion of a stannylene moiety, which was generated under reductive reaction conditions.[5b] Likewise, the formation of **4** may be explained by the subsequent insertion of Sn*t*Bu$_2$ into the Sn−Sn bond of a [2]stanna half-sandwich complex. Both compounds were fully characterized by IR and multinuclear NMR spectroscopy in solution. The products exhibit two pseudotriplets for the ring protons in the ^{1}H NMR spectra at δ 5.13 and 4.96 for **3** and at δ 5.63 and 5.34 for **4**. The *tert*-butyl groups of **3** show two signals at δ 1.56 and 1.32, which are accompanied by $^{119/117}$Sn satellites arising from the $^3J_{\text{HSn}}$ coupling. In the case of **4**, singlets at δ 1.58, 1.51, and 1.42 can be found for the three chemical inequivalent sets of *tert*-butyl groups, which are also accompanied by $^{119/117}$Sn satellites. In addition, ^{119}Sn NMR spectroscopy exhibits two signals at δ −58 and −59 for **3**, with large high-field shifts of 242 and 164 ppm in comparison to those of the starting material **1**, which are typical for this class of ansa half-sandwich complexes.[5a] For **4**, three signals at δ 249, 73, and −48 are found, which further substantiates the presence of a tristanna moiety. For both compounds, single-crystal X-ray diffraction analysis was employed to confirm the proposed structures (Figure 2). The Ru−Sn bond length of 2.6868(2) Å in **3** is slightly longer than that in **1**, while the Sn−Sn bond length is 3 pm shorter than that in the starting material. The tin bridge together with the metal center and the cyclopentadienyl *ipso*-carbon atom forms a four-membered metallacycle. The endocyclic angles Ru−Sn2−Sn1 = 84.35(1)° and Sn2−Sn1−C1 = 81.15(5)° deviate significantly from the tetrahedral angle expected for an sp^3-hybridized tin atom, indicating high strain within the molecule. These endocyclic angles can be compared with those of analogous compounds of group 6 ansa complexes, which lie in the same range.[5a] The torsion angle Sn2−Ru−C1−Sn1 of 10.73(6)° is small.

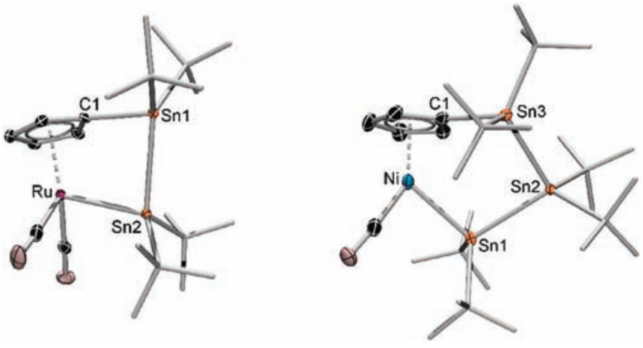


Figure 2. Molecular structures of **3** (left) and **4** (right) in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability. Relevant bond lengths (Å) and angles (deg) for **3**: Ru−Sn2 2.6866(2), Sn1−Sn2 2.8202(2); Ru−Sn2−Sn1 84.35(1), Sn2−Sn1−C1 81.13(4). Relevant bond lengths (Å) and angles (deg) for **4**: Ni−Sn2 2.5513(4), Sn1−Sn2 2.8788(2), Sn2−Sn3 2.8344(3); Ni−Sn1−Sn2 101.34(1), Sn1−Sn2−Sn3 96.6(1), Sn1−Ni−C1−Sn3 40.4(1).

In the case of **4**, the metal−tin bond length of 2.5513(4) Å is even longer than that in **2**. Likewise, the Sn1−Sn2 and Sn2−Sn3 separations of 2.8788(2) and 2.8344(3) Å, respectively, follow this trend, which can be assigned to steric demands of the *tert*-butyl groups. The endocylic ring angles of the metallacycle Ni−C1−Sn3−Sn2−Sn1 are smaller than those for the average tetrahedral sp^3-hybridized tin atoms [Ni−Sn1−Sn2 101.34(1)°, Sn1−Sn2−Sn3 96.60(1)°, and Sn2−Sn3−C1 97.68(6)°], indicating only small ring strain within the ansa bridge. The torsion angle Sn1−Ni−C1−Sn3 of 40.4(1)° is moderate and can be compared with analogous trisila-bridged ansa half-sandwich complexes of group 6 metals.[5c]

In conclusion, we have reported the first fully characterized ansa half-sandwich complexes of ruthenium and nickel. Both compounds were obtained via a two-step protocol starting from the distannane $\mathrm{ClSn}t\mathrm{Bu}_2\text{-}\mathrm{Sn}t\mathrm{Bu}_2\mathrm{Cl}$. However, the major product obtained in the case of nickel comprised of a tristannanediyl bridge presumably formed upon stannylene insertion.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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