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Unexpected Formation of Ru_2Sn_2 Bicyclic Four-Membered Ring Complexes with Butterfly and Inverse-Sandwich Structures

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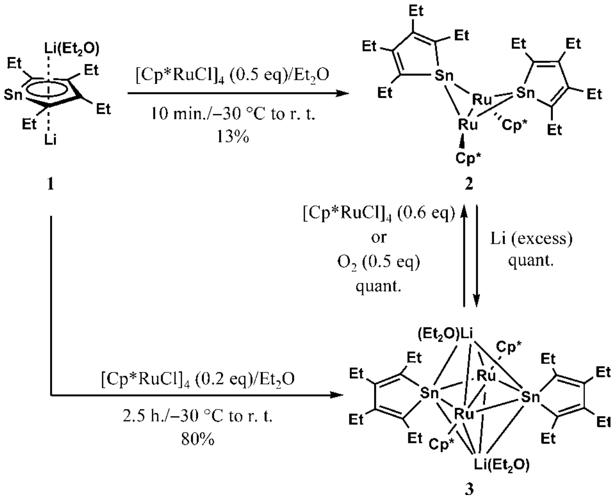
Supporting Information

ABSTRACT: Reactions of tetraethyldilithiostannole **1** with $[Cp^*RuCl]_4$ afforded not η^5-stannole dianion complexes but two novel bis(stannylene)-bridged dinuclear ruthenium complexes, which have butterfly and inverse-sandwich structures, respectively, depending on the stoichiometry of $[Cp^*RuCl]_4$ toward dilithiostannole. The redox behavior between the two complexes is found to be reversible. The molecular structures were determined by X-ray diffraction analysis. The Ru–Ru bond of the butterfly complex is 2.3428(6) Å, which is the shortest among those of dinuclear ruthenium complexes having Cp or Cp*Ru units. Theoretical calculations revealed that the very short Ru–Ru bond is due to the presence of one σ bond between the ruthenium atoms and two three-centered bonds delocalized over the two Ru_2Sn rings.

Heavier congeners of the cyclopentadienyl anion have received much attention in view of their aromaticity.[1] Dianion equivalents of what are called metalloles, such as silole,[2] germole,[3] and stannole,[4] synthesized in the last 2 decades, are concluded to be aromatic based on the structural analysis and theoretical calculations. In parallel to such synthetic approaches, systematic theoretical calculations to understand their aromaticity are also published.[5] Very recently, our group has reported that even substituting a lead atom for an aromatic-ring carbon atom does not disrupt aromatic character.[6] One of the next challenges in this field is application of these heavier cyclopentaidienyl anions as novel ligands for transition-metal complexes. From this point of view, several transition-metal complexes coordinated by heavier cyclopentadienyl ligands in a η^5 fashion have already been reported[7] that were synthesized by reactions of monoanion equivalents of metalloles with transition-metal reagents. Reactions of the corresponding dianion equivalents with transition metals are therefore the most straightforward to synthesize η^5-metallole dianion complexes. However, such reactions have not been reported thus far, even though Dysard and Tilley succeeded in the unexpected synthesis of a η^5-germole dianion complex from a monoanion equivalent.[7d] We therefore examined reactions of a dianion equivalent of stannole, dilithiostannole **1**, with $[Cp^*RuCl]_4$ ($Cp^* = \eta^5$-C_5Me_5).[8]

Scheme 1. Reactions of Dilithiostannole 1 with $[Cp^*RuCl]_4$ and a Reversible Redox Reaction between Complexes 2 and 3



After the addition of diethyl ether to a mixture of tetraethyldilithiostannole **1**[4b] and $[Cp^*RuCl]_4$ (0.5 equiv), the color of the solution changed from yellow brown to dark brown via deep blue during the first few minutes (Scheme 1). A ^1H NMR spectrum of the crude product revealed the quantitative formation of a novel compound, and not a η^5-stannole dianion complex but $Cp^*Ru(\mu$-$SnC_4Et_4)_2RuCp^*$ (**2**) was isolated as air- and moisture-sensitive dark-brown crystals in 13% yield.[9] To investigate the mechanism for the formation of **2**, the reaction of **1** with 0.2 equiv of $[Cp^*RuCl]_4$ was examined (Scheme 1). In this reaction, the deep-blue color intermediately observed in the former reaction did not change even after stirring for 1 h, and $[Li(Et_2O)]_2[Cp^*Ru(\mu$-$SnC_4Et_4)_2RuCp^*]$ (**3**) was isolated as air- and moisture-sensitive dark-blue crystals in 80% yield.[9] Compound **3** is of interest as a rare example of compounds with Ru–Li bonds.[10] It is noted that the reaction of **3** with $[Cp^*RuCl]_4$ or O_2 resulted in the clean formation of **2**, indicating that complex **3** is oxidized to complex **2** by ruthenium(II) in the reaction of **1** with $[Cp^*RuCl]_4$. On the other hand, reduction of **2** with lithium afforded **3** quantitatively. It is therefore concluded that the redox behavior between complex **2** and **3** is reversible.

The molecular structures of **2** and **3** were finally determined by X-ray diffraction analyses, as shown in Figures 1 and 2,

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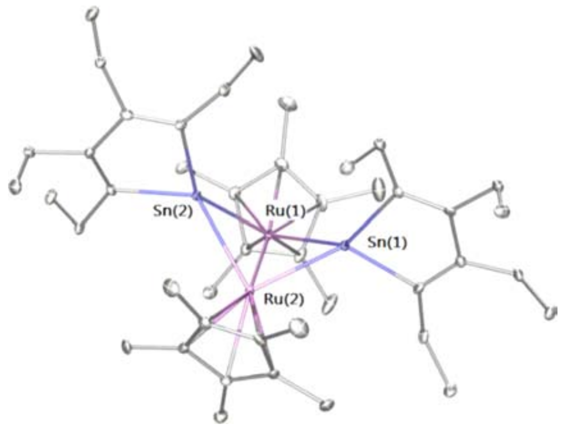

Figure 1. Molecular structure of **2** (30% probability). All hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Ru(1)–Ru(2), 2.3428(6); Ru(1)–Sn(1), 2.6162(6); Sn(1)–Ru(2), 2.5903(6); Ru(2)–Sn(2), 2.6092(6); Sn(2)–Ru(1), 2.6096(6).

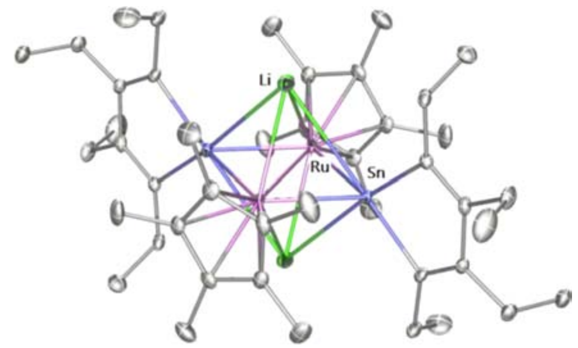

Figure 2. Molecular structure of one of the two independent molecules of **3** (30% probability). All hydrogen atoms and diethyl ether molecules are omitted for clarity. Selected bond lengths [Å]: Ru(1)–Ru(1)$^{\#}$, 2.7919(6); Ru(1)–Sn(1), 2.5781(4); Sn(1)–Ru(1)$^{\#}$, 2.5949(5); Ru(1)–Li(1), 2.696(7); Ru(1)–Li(1)$^{\#}$, 2.811(7); Sn(1)–Li(1), 3.234(7); Sn(1)–Li(1)$^{\#}$, 3.209(7).

respectively.[11] The bicyclic four-membered ring of **2** has a butterfly structure with a small dihedral angle of 112.80(2)°. According to the EAN rule, the Ru–Ru bond in complex **2** should have triple-bond character. In fact, the Ru–Ru bond length of **2** is 2.3428(6) Å, which is remarkably shorter than those of silylene-bridged dinuclear ruthenium complexes with Ru–Ru triple bonds [2.4686(5) and 2.4492(9) Å].[12] To the best of our knowledge, the Ru–Ru bond of **2** is the shortest among those of complexes with Cp or Cp*Ru units.

Although two independent half-moieties of the molecule were found in a unit cell of **3**, these two molecules have quite similar structures, and only one is therefore discussed here. In contrast to the butterfly structure of **2**, the Ru_2Sn_2 bicyclic four-membered ring of **3** is planar. Each lithium atom is coordinated by a diethyl ether molecule and the four-membered ring in η^1 and η^4 fashion, respectively. Although organic rings sandwiched by alkali metals are commonly reported,[13] inorganic rings containing transition metals with such inverse-sandwich structures are quite rare.[14] According to the EAN rule, the Ru–Ru bond in **3** should have double-bond character. However, the Ru–Ru bond length of **3** is 2.7916(6) Å, which is slightly longer than the upper limit for the Ru=Ru double bond length (2.257–2.767 Å).[15] The Ru–Sn bond lengths of **3** [2.5781(4) and 2.5945(9) Å] lie in the shortest range of reported Ru–Sn^{II} bond lengths (2.574–2.721 Å).[16] The Ru–Li bond lengths of **3** are 2.696(7) and 2.811(7) Å, comparable to those of compounds bearing Ru–Li bonds [2.777(5) and 2.837(5) Å].[10] The Sn–Li distances of **3** [3.209(7) and 3.234(7) Å] are slightly longer than the longest Sn–Li bond [3.141(7) Å] that was ever reported[17] but are much shorter than the sum of their van der Waals radii (3.87 Å).[18]

In the ^{13}C NMR spectrum of **2**, the four Et groups and the four skeletal carbon atoms of the stannole ring inequivalently resonated. The ^{1}H NMR signal of the Cp* groups in **3** was observed at 2.08 ppm, which is in a field lower than those of $[Cp^*RuCl]_4$ (1.56 ppm)[8] and **2** (1.70 ppm). In the ^{119}Sn NMR spectrum of **2** and **3**, signals were observed at 859.0 and 735.4 ppm, respectively, which indicates considerable stannylene character of the tin atoms in both **2** and **3**.[19] The ^{7}Li nucleus of **3** resonated at 4.2 ppm, which is in a field much lower than that of **1** (−5.2 ppm)[4b] and is even lower than those of compounds bearing Ru–Li bonds (−14.85[10a] and −1.4[10b] ppm).

To understand the very short Ru–Ru bond in the butterfly complex **2**, theoretical calculations were performed using the *GAUSSIAN 03* program.[9,20] The optimized geometry of **2** is in good agreement with the X-ray measured structure [Ru–Ru = 2.363 Å (calcd) vs 2.343 Å (X-ray)]. According to the localized molecular orbital analysis, one σ bond is formed between the ruthenium atoms, which may be regarded as a banana bond (Figure 3). In addition, two three-centered bonds are delocalized over each of the Ru_2Sn three-membered rings (Figure 4), which also contribute to Ru–Ru bonding.

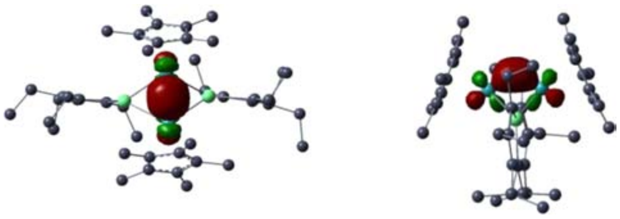

Figure 3. Ru–Ru σ bond (left, top view; right, side view).

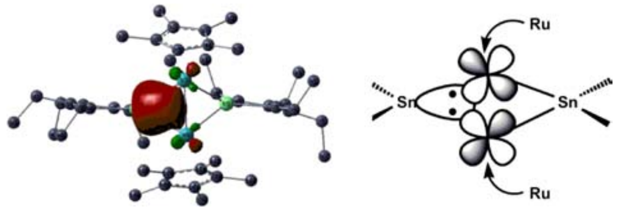

Figure 4. One of the two three-centered bonds delocalized over the Ru_2Sn three-membered rings.

In summary, novel bis(stannylene)-bridged dinuclear ruthenium complex **2** and its dianion equivalent **3** were synthesized by reactions of dilithiostannole **1** with $[Cp^*RuCl]_4$. This result is of considerable interest in terms of its sharp contrast to reactions of lithiometalloles with transition-metal reagents to afford η^5-metallole complexes. The dilithium complex **3** was oxidized by $[Cp^*RuCl]_4$ and O_2 to give complex **2**, while reduction of **2** with lithium provided **3**, and the redox system between the two complexes is therefore reversible. The very short Ru–Ru bond of **2** is derived from one σ bond between the ruthenium atoms and two three-centered bonds delocalized over the Ru_2Sn three-membered rings.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and NMR data, full author list of ref 20, Cartesian coordinates of the optimized structure, and CIF files of compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Professor Guy Bertrand on the occasion of his 60th birthday.

■ REFERENCES

(1) For examples of recent reviews, see: (a) Saito, M.; Yoshioka, M. *Coord. Chem. Rev.* **2005**, *249*, 765. (b) Lee, V. Y.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 6596. (c) Lee, V. Y.; Sekiguchi, A. *Organometallic Compounds of Low-coordinate Si, Ge, Sn and Pb*; Wiley: Chichester, U.K., 2011, p 335. (d) Saito, M. *Coord. Chem. Rev.* **2012**, *256*, 627.

(2) (a) West, R.; Sohn, H.; Bankwitz, U.; Calabrese, J.; Apeloig, Y.; Müller, T. *J. Am. Chem. Soc.* **1995**, *117*, 11608. (b) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457.

(3) (a) West, R.; Sohn, H.; Powell, D. R.; Müller, T.; Apeloig, Y. *Angew. Chem., Int. Ed.* **1996**, *35*, 1002. (b) Choi, S.-B.; Boudjouk, P.; Hong, J.-H. *Organometallics* **1999**, *18*, 2919.

(4) (a) Saito, M.; Haga, R.; Yoshioka, M.; Ishimura, K.; Nagase, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 6553. (b) Saito, M.; Kuwabara, T.; Kambayashi, C.; Yoshioka, M.; Ishimura, K.; Nagase, S. *Chem. Lett.* **2010**, *39*, 700.

(5) (a) Goldfuss, B.; Schleyer, P. v. R.; Hampel, F. *Organometallics* **1996**, *15*, 1755. (b) Goldfuss, B.; Schleyer, P. v. R. *Organometallics* **1997**, *16*, 1543.

(6) Saito, M.; Sakaguchi, M.; Tajima, T.; Ishimura, K.; Nagase, S.; Hada, M. *Science* **2010**, *328*, 339.

(7) (a) Freeman, W. P.; Tilley, T. D.; Rheigold, A. L.; Ostrander, R. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1744. (b) Freeman, W. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 8428. (c) Dysard, J. M.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 8245. (d) Dysard, J. M.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 3097. (e) Freeman, W. P.; Dysard, J. M.; Tilley, T. D. *Organometallics* **2002**, *21*, 1734. (f) Lee, V. Y.; Kato, R.; Sekiguchi, A.; Krapp, A.; Frenking, G. *J. Am. Chem. Soc.* **2007**, *129*, 10340. (g) Yasuda, H.; Lee, V. Y.; Sekiguchi, A. *J. Am. Chem. Soc.* **2009**, *131*, 9902.

(8) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

(9) For experimental and theoretical details and a plausible mechanism for the formation of **3**, see the Supporting Information.

(10) (a) Alexander, C. S.; Rettig, S. J.; James, B. R. *Organometallics* **1994**, *13*, 2542. (b) Ohashi, M.; Matsubara, K.; Iizuka, T.; Suzuki, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 937.

(11) Crystallographic data for compounds **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre as CCDC 866870 and 880892, respectively. Copies of these data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (+41)1223-336-033; e-mail deposit@ccdc.cam.ac.uk].

(12) Takao, T.; Amako, M.; Suzuki, H. *Organometallics* **2003**, *22*, 3855.

(13) For recent examples, see: (a) Herdtweck, E.; Köhler, F. H.; Mölle, R. *Eur. J. Inorg. Chem.* **2005**, 952. (b) Saito, M.; Nakamura, M.; Tajima, T.; Yoshioka, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1504. (c) Fernández-Cortabitarte, C.; Garcia, F.; Morey, J. V.; McPartlin, M.; Singh, S.; Wheatley, A. E.; Wright, D. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 5425. (d) Sänger, I.; Kückmann, T. I.; Dornhaus, F.; Bolte, M.; Wagner, M.; Lerner, H.-W. *Dalton Trans.* **2012**, *41*, 6671.

(14) Hope, H.; Oram, D.; Power, P. P. *J. Am. Chem. Soc.* **1984**, *106*, 1149.

(15) Takao, T.; Obayashi, N.; Zhao, B.; Akiyoshi, K.; Omori, H.; Suzuki, H. *Organometallics* **2011**, *30*, 5057.

(16) For recent examples of stannylene-bridged ruthenium complexes in these 5 years, see: (a) Adams, R. D.; Boswell, E. M.; Captain, B.; Hungria, A. B.; Midgley, P. A.; Raja, R.; Thomas, J. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8182. (b) Adams, R. D.; Captain, B.; Trufan, E. *J. Organomet. Chem.* **2008**, *693*, 3593. (c) Adams, R. D.; Trufan, E. *Organometallics* **2008**, *27*, 4108. (d) Cabeza, J. A.; Garcia-Alvarez, P.; Polo, D. *Inorg. Chem.* **2012**, *51*, 2569.

(17) Fukawa, T.; Nakamoto, M.; Lee, V. Y.; Sekiguchi, A. *Organometallics* **2004**, *23*, 2376.

(18) Mantina, M.; Chamberlin, A. C.; Valero, R.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. A* **2009**, *113*, 5806.

(19) For recent examples of ^{119}Sn NMR spectra for stannylene complexes, see: (a) Zabula, A. V.; Pape, T.; Hepp, A.; Hahn, F. E. *Organometallics* **2008**, *27*, 2756. (b) Mansell, S. M.; Herber, R. H.; Nowik, I.; Ross, D. H.; Russell, C. A.; Wass, D. F. *Inorg. Chem.* **2011**, *50*, 2252. For the stannylene-bridged ruthenium complex, see: (c) Adams, R. D.; Captain, B.; Hall, M. B.; Trufan, E.; Yang, X. *J. Am. Chem. Soc.* **2007**, *129*, 12328. For reviews, see: (d) Lappert, M. F.; Rowe, R. S. *Coord. Chem. Rev.* **1990**, *100*, 267. (e) Agustin, D.; Ehses, M. *C. R. Chim.* **2009**, *12*, 1189.

(20) Frisch, M. J. et al. *GAUSSIAN 03*, revision E.01; Gaussian, Inc.: Wallingford, CT, 2004. For all calculations, the hybrid density functional theory at the B3PW91 level was used with the LANL2DZ basis set augmented by d polarization functions (d exponent 0.186) for tin and f polarization functions (f exponent 1.235) for ruthenium and the 6-31G(d) basis set for carbon and hydrogen.