



Supporting Information

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## Bimetallic Ru-Sn Nanoparticle Catalysts for the Solvent-free, Selective Hydrogenation of 1,5,9-Cyclododecatriene to Cyclododecene

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*General Data.* All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Reagent grade solvents were dried by standard procedures and were freshly distilled prior to their use. Nonane, 99%, was purchased from Alfa Aesar and used without further purification. Infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrophotometer. <sup>1</sup>H-NMR spectra were recorded on a Varian Mercury 400 spectrometer operating at 400 MHz. Mass spectrometric measurements performed by direct exposure probe using electron impact ionization (EI) were made on a VG 70S instrument. Triphenylstannane, Ph<sub>3</sub>SnH, was purchased from Aldrich and was used without further purification. Ru<sub>4</sub>(CO)<sub>12</sub>(μ-H)<sub>4</sub><sup>[1]</sup> was prepared via

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literature methods. Product separations were performed by TLC in air by using Analtech 0.25, 0.5, and 1.0 mm silica gel 60 Å F<sub>254</sub> glass plates.

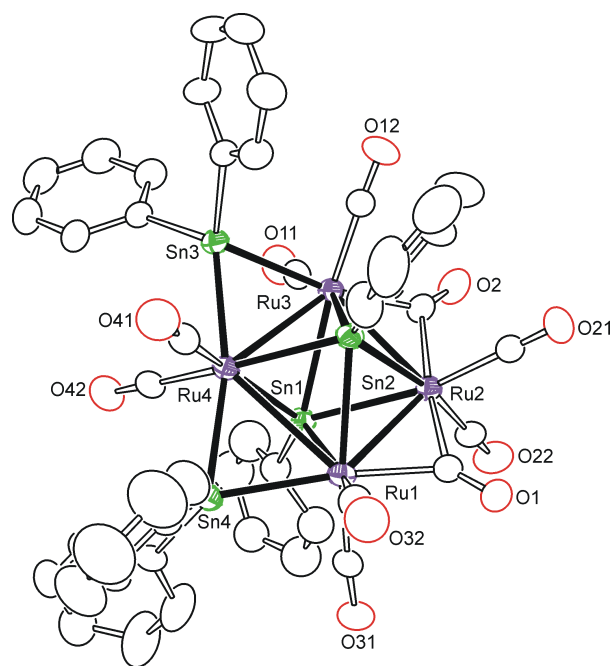
*Crystallographic Analyses:* Dark single crystals of **1** suitable for x-ray diffraction analyses were obtained by slow evaporation of solvent from a solution of octane/methylene chloride at – 25 °C. Dark purple single crystals of **2** were obtained by slow evaporation of solvent at – 25 °C from a solution of octane/methylene chloride. Dark purple crystals of **3** were grown from slow evaporation of solvent from a solution in an octane/diethylether solvent mixture at 7 °C. Dark blue single crystals of **4** were obtained by slow evaporation of solvent from a solution in an octane/diethylether solvent mixture at 7 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.<sup>[2]</sup> Correction for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F<sup>2</sup>, using the SHELXTL software package.<sup>[3]</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Tables 1 and 2. Selected bond distances and angles are listed in Tables 3 – 6.

Compound **1 - 4** all crystallized in the triclinic crystal system. The space group  $P\bar{1}$  was assumed and confirmed by the successful solution and refinement of the structure. For

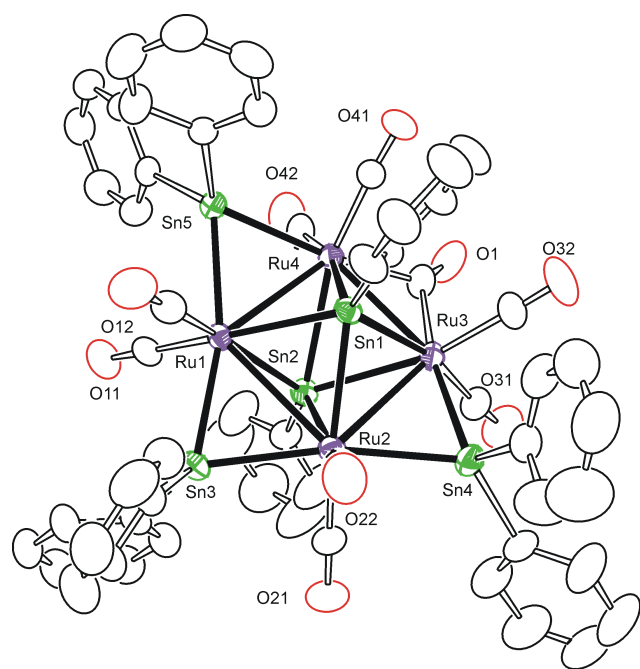
compounds **1** and **4**, the molecule lies on a center of symmetry. Only half a formula equivalent of the molecule occupies the asymmetric crystal unit.

**References.**

- [1] H. D. Kaesz, S. A. R. Knox, J. W. Koepke, M. A. Andrews, *J. Am. Chem. Soc.* **1975**, 97, 3942.
- [2] SAINT+ Version 6.2a. Bruker Analytical X-ray System, Inc., Madison, Wisconsin, USA, 2001.
- [3] G. M. Sheldrick, SHELXTL Version 6.1; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1997.



**Figure 1.** An ORTEP diagram of **2** showing 30% thermal ellipsoid probability.



**Figure 2.** An ORTEP diagram of **3** showing 30% thermal ellipsoid probability.

**Table 1. Crystallographic Data for Compounds 1 and 2.**

	<b>1</b>	<b>2</b>
Empirical formula	Ru <sub>4</sub> Sn <sub>2</sub> O <sub>12</sub> C <sub>24</sub> H <sub>10</sub>	Ru <sub>4</sub> Sn <sub>4</sub> O <sub>10</sub> C <sub>46</sub> H <sub>30</sub>
Formula weight	1131.98	1621.74
Crystal system	Triclinic	Triclinic
Lattice parameters		
<i>a</i> (Å)	9.1416(4)	11.8757(6)
<i>b</i> (Å)	9.6670(4)	12.9166(7)
<i>c</i> (Å)	9.7105(4)	18.0535(9)
α (deg)	74.889(1)	80.993(1)
β (deg)	66.258(1)	81.988(1)
γ (deg)	86.839(1)	66.009(1)
<i>V</i> (Å <sup>3</sup> )	757.16(6)	2490.0(2)
Space group	P-1	P-1
Z value	1	2
ρ <sub>calc</sub> (g / cm <sup>3</sup> )	2.483	2.163
μ (Mo Kα) (mm <sup>-1</sup> )	3.626	3.203
Temperature (K)	294	294
2θ <sub>max</sub> (°)	56.62	56.70
No. Obs. (I > 2σ(I))	3202	10078
No. Parameters	190	559
Goodness of fit	1.073	1.024
Max. shift in cycle	0.001	0.002
Residuals*: R1; wR2	0.0358; 0.0820	0.0354; 0.0817
Absorption Correction,	Multi-scan,	Multi-scan
Max/min	1.000/0.813	1.000/0.894
Largest peak in Final		
Diff. Map (e <sup>-</sup> / Å <sup>3</sup> )	2.090	1.312

\*R =  $\frac{\sum_{\text{hkl}} (|F_{\text{obs}}| - |F_{\text{calc}}|)}{\sum_{\text{hkl}} |F_{\text{obs}}|}$ ; R<sub>w</sub> =  $[\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{\text{hkl}} w F_{\text{obs}}^2]^{1/2}$ ,  
w = 1/σ<sup>2</sup>(F<sub>obs</sub>); GOF =  $[\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}$ .

**Table 2. Crystallographic Data for Compounds 3 and 4.**

	<b>3</b>	<b>4</b>
Empirical formula	Ru <sub>4</sub> Sn <sub>5</sub> O <sub>9</sub> C <sub>57</sub> H <sub>40</sub>	Ru <sub>4</sub> Sn <sub>6</sub> O <sub>8</sub> C <sub>68</sub> H <sub>50</sub>
Formula weight	1866.62	2111.50
Crystal system	Triclinic	Triclinic
Lattice parameters		
<i>a</i> (Å)	13.3973(3)	11.9551(5)
<i>b</i> (Å)	13.8172(3)	12.3520(5)
<i>c</i> (Å)	17.8555(4)	12.6818(5)
α (deg)	89.312(1)	78.933(1)
β (deg)	89.351(1)	70.662(1)
γ (deg)	64.805(1)	75.589(1)
V (Å <sup>3</sup> )	2990.55(11)	1699.12(12)
Space group	P-1	P-1
Z value	2	1
ρ <sub>calc</sub> (g / cm <sup>3</sup> )	2.073	2.064
μ (Mo Kα) (mm <sup>-1</sup> )	3.082	3.078
Temperature (K)	293	293
2θ <sub>max</sub> (°)	56.60	56.58
No. Obs. (I > 2σ(I))	10690	6452
No. Parameters	676	388
Goodness of fit	1.021	0.988
Max. shift in cycle	0.001	0.001
Residuals*: R1; wR2	0.0405; 0.0884	0.0322; 0.0588
Absorption Correction,	Multi-scan	Multi-scan
Max/min	1.000/0.864	1.000/0.870
Largest peak in Final Diff. Map (e <sup>-</sup> / Å <sup>3</sup> )	1.546	0.674

\*R =  $\frac{\sum_{\text{hkl}} (|F_{\text{obs}}| - |F_{\text{calc}}|)}{\sum_{\text{hkl}} |F_{\text{obs}}|}$ ; R<sub>w</sub> =  $\left[ \frac{\sum_{\text{hkl}} w (|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sum_{\text{hkl}} w F_{\text{obs}}^2} \right]^{1/2}$ ,  
w = 1/σ<sup>2</sup>(F<sub>obs</sub>); GOF =  $\left[ \frac{\sum_{\text{hkl}} w (|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{(n_{\text{data}} - n_{\text{vari}})} \right]^{1/2}$ .



**Table 3. Selected Intramolecular Bond Distances for Compounds 1 and 2<sup>a</sup>**

<b>1</b>			<b>2</b>		
atom	atom	distance (Å)	atom	atom	distance (Å)
Ru(1)	Ru(2)	2.9597(6)	Ru(1)	Ru(2)	2.8440(5)
Ru(1)*	Ru(2)	2.9578(6)	Ru(2)	Ru(3)	2.8689(5)
Ru(1)	Sn(1)	2.7135(5)	Ru(3)	Ru(4)	3.1166(5)
Ru(2)	Sn(1)	2.7153(6)	Ru(1)	Ru(4)	3.0937(5)
Ru(1)*	Sn(1)	2.7147(5)	Ru(1)	C(1)	2.053(5)
Ru(1)	Sn(1)*	2.7146(5)	Ru(1)	Sn(4)	2.6925(5)
Ru(2)	Sn(1)*	2.7134(5)	Ru(2)	C(1)	2.122(5)
C	O	1.128(6)(av.)	Ru(2)	C(2)	2.108(5)
			Ru(3)	C(2)	2.088(5)
			Ru(3)	Sn(3)	2.6719(5)
			Ru(4)	Sn(3)	2.6552(5)
			Ru(4)	Sn(4)	2.6227(5)
			Ru(1)	Sn(1)	2.7328(4)
			Ru(2)	Sn(1)	2.7814(5)
			Ru(3)	Sn(1)	2.7122(5)
			Ru(4)	Sn(1)	2.6910(5)
			Ru(1)	Sn(2)	2.7320(5)
			Ru(2)	Sn(2)	2.7571(5)
			Ru(3)	Sn(2)	2.7343(5)
			Ru(4)	Sn(2)	2.6581(4)
			C	O	1.137(6)(av.)

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

\* Denotes atoms generated by symmetry

**Table 4. Selected Intramolecular Bond Angles for Compounds 1 and 2<sup>a</sup>.**

1				2			
atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Ru(1)	Ru(2)	Ru(1)*	88.99(7)	Ru(1)	Ru(2)	Ru(3)	94.83(4)
Ru(2)*	Ru(1)	Ru(2)	90.01(7)	Ru(2)	Ru(3)	Ru(4)	89.48(4)
Ru(1)	Sn(1)	Ru(2)	66.07(5)	Ru(3)	Ru(4)	Ru(1)	85.27(3)
Ru(2)	Sn(1)	Ru(1)*	66.01(5)	Ru(4)	Ru(1)	Ru(2)	90.39(4)
Ru(1)*	Sn(1)	Ru(2)*	66.09(5)	Ru(1)	C(1)	Ru(2)	85.89(8)
Ru(2)*	Sn(1)	Ru(1)	66.05(5)	Ru(2)	C(2)	Ru(3)	86.3(8)
Ru(1)	Sn(1)	Ru(1)*	100.85(5)	Ru(3)	Sn(3)	Ru(4)	71.61(3)
Ru(2)	Sn(1)	Ru(2)*	100.86(6)	Ru(4)	Sn(4)	Ru(1)	71.18(3)
				Ru(1)	Sn(1)	Ru(2)	62.09(2)
				Ru(2)	Sn(1)	Ru(3)	62.95(3)
				Ru(3)	Sn(1)	Ru(4)	70.45(3)
				Ru(4)	Sn(1)	Ru(1)	69.55(3)
				Ru(1)	Sn(2)	Ru(2)	64.41(2)
				Ru(2)	Sn(2)	Ru(3)	62.99(2)
				Ru(3)	Sn(2)	Ru(4)	70.59(2)
				Ru(4)	Sn(2)	Ru(1)	70.04(2)
				Ru(1)	Sn(1)	Ru(3)	101.16(4)
				Ru(2)	Sn(1)	Ru(4)	100.79(4)
				Ru(1)	Sn(2)	Ru(3)	100.62(4)
				Ru(2)	Sn(2)	Ru(4)	102.26(4)

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

\* Denotes atoms generated by symmetry

**Table 5. Selected Intramolecular Bond Distances for Compounds 3 and 4<sup>a</sup>**

<b>3</b>			<b>4</b>		
atom	atom	Distance(Å)	atom	atom	distance(Å)
Ru(1)	Ru(2)	3.1032(6)	Ru(1)	Ru(2)	3.0580(5)
Ru(2)	Ru(3)	3.0890(6)	Ru(1)	Ru(2)*	3.0656(5)
Ru(3)	Ru(4)	2.8371(6)	Ru(1)	Sn(2)	2.6477(4)
Ru(4)	Ru(1)	3.0555(6)	Ru(1)	Sn(3)	2.6187(4)
Ru(1)	Sn(3)	2.6399(5)	Ru(2)	Sn(3)	2.6519(4)
Ru(1)	Sn(5)	2.6446(5)	Ru(2)	Sn(2)*	2.6269(4)
Ru(2)	Sn(3)	2.6402(6)	Ru(1)	Sn(1)	2.7327(4)
Ru(2)	Sn(4)	2.6449(6)	Ru(2)	Sn(1)	2.7413(4)
Ru(3)	Sn(4)	2.6612(6)	Ru(1)*	Sn(1)	2.7310(4)
Ru(3)	C(1)	2.064(6)	Ru(2)*	Sn(1)	2.7383(4)
Ru(4)	C(1)	2.109(6)	Ru(1)	Sn(1)*	2.7311(4)
Ru(4)	Sn(5)	2.6669(6)	Ru(2)	Sn(1)*	2.7383(4)
Ru(1)	Sn(1)	2.7716(5)			
Ru(2)	Sn(1)	2.7007(5)			
Ru(3)	Sn(1)	2.7567(6)			
Ru(4)	Sn(1)	2.7310(5)			
Ru(1)	Sn(2)	2.7069(5)			
Ru(2)	Sn(2)	2.7041(6)			
Ru(3)	Sn(2)	2.7619(6)			
Ru(4)	Sn(2)	2.7783(6)			
C	O	1.134(6)(av.)			

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

\* Indicates atoms generated by symmetry

**Table 6. Selected Intramolecular Bond Angles for Compounds 3 and 4<sup>a</sup>.**

<b>3</b>				<b>4</b>			
atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Ru(1)	Ru(2)	Ru(3)	87.37(5)	Ru(1)	Ru(2)	Ru(1)*	89.73(2)
Ru(2)	Ru(3)	Ru(4)	91.96(6)	Ru(2)	Ru(1)	Ru(2)*	90.27(2)
Ru(3)	Ru(4)	Ru(1)	92.99(6)	Ru(1)	Sn(3)	Ru(2)	70.93(2)
Ru(4)	Ru(1)	Ru(2)	87.66(5)	Ru(1)	Sn(2)	Ru(2)*	71.07(2)
Ru(1)	Sn(3)	Ru(2)	71.99(6)	Ru(1)	Sn(1)	Ru(2)	67.92(2)
Ru(2)	Sn(4)	Ru(3)	71.24(6)	Ru(2)	Sn(1)	Ru(1)*	68.14(1)
Ru(3)	C(1)	Ru(4)	85.6(2)	Ru(1)*	Sn(1)	Ru(2)*	67.99(2)
Ru(4)	Sn(5)	Ru(1)	70.24(5)	Ru(2)*	Sn(1)	Ru(1)	68.16(2)
Ru(1)	Sn(1)	Ru(2)	69.79(5)	Ru(1)	Sn(1)	Ru(1)*	104.50(2)
Ru(2)	Sn(1)	Ru(3)	68.94(6)	Ru(2)	Sn(1)	Ru(2)*	104.75(2)
Ru(3)	Sn(1)	Ru(4)	62.26(5)				
Ru(4)	Sn(1)	Ru(1)	68.30(5)				
Ru(1)	Sn(2)	Ru(2)	69.99(5)				
Ru(2)	Sn(2)	Ru(3)	68.81(5)				
Ru(3)	Sn(2)	Ru(4)	61.61(5)				
Ru(4)	Sn(2)	Ru(1)	67.69(5)				
Ru(1)	Sn(1)	Ru(2)	102.91(7)				
Ru(2)	Sn(1)	Ru(4)	103.48(7)				
Ru(1)	Sn(2)	Ru(2)	102.90(7)				
Ru(2)	Sn(2)	Ru(4)	102.14(7)				

<sup>a</sup>Estimated standard deviations in the least significant figure are given in parentheses.

\* Indicates atoms generated by symmetry