Supplementary Information of the Article Entitled "Heterobimetallic triple-decker complexes derived from an dianionic aromatic stannole ligand"

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Contents

General procedure for the preparation of complexes: All experiments were performed under argon atmosphere in a glovebox or using a standard Schlenk technique. Diethyl ether, toluene, and benzene-d_6 for NMR measurement were purified potassium mirror before used. ^{1}H NMR (400 or 500 MHz), ^{13}C NMR (101 MHz), ^{7}Li NMR (194 MHz), ^{29}Si NMR (99 MHz) and ^{119}Sn NMR (186 MHz) were recorded on a Bruker AVANCE-400 Cryo, AVANCE-500 or AVANCE-500T spectrometers at 27 ºC. The intensity data for X-ray crystallographic analyses were collected at −173 or −223 °C on a Bruker SMART APEXII ULTRA diffractometer equipped with a CCD area detector with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods, and refined by full-matrix least-squares method by SHELXL-97 program. Cyclic voltammetry was measured on a Gamry Interface 1000. The melting points were determined by a Yanaco macro melting point MP-S3 apparatus and were uncorrected. Elemental analysis was carried out at the Microanalytical Laboratory of Molecular Analysis and Life Science Center, Saitama University.

Preparation and characterization of nanoparticles (NPs).

(a) General procedure.

All experiments were performed under an inert nitrogen or argon atmosphere by using standard Schlenk and glove-box techniques.

The ionic liquid (denoted as IL) [BMIm][BF_4] (BMIm = 1-butyl-3-methylimidazolium) was prepared by treating 1-methylimidazole with 1-chlorobutane to yield first [BMIm][Cl], which further reacted with HBF_4 to give [BMIm][BF_4]. The IL [BMIm][NTf_2] was synthesized by treating 1-methylimidazole with 1-chlorobutane to yield first [BMIm][Cl], which further reacted with lithium bis(trifluoromethansulfonyl)imide (Li(NTf_2)) to give [BMIm][NTf_2]. Both ILs were dried under high vacuum (10^{-7} mbar) at 80 °C for several days. Quantitative anion exchange and, thus, IL purity of >99% was assessed by ion chromatography (Dionex ICS-1100, with IonPac® AS14, 4 x 250 mm column). Water content was measured by coulometric Karl Fischer titration (ECH/Analytik Jena AQUA 40.00) to below 10 ppm for [BMIm][BF_4] and below 30 ppm for [BMIm][NTf_2].

Transmission electron microscopy (TEM) and scanning transmission electron microscope (STEM) images were taken on a FEI Tecnai G2 F20 (FZ Jülich)[S1] and on a JEOL JEM-2200FS (ICAN University Duisburg-Essen) operating at an accelerating voltage of 200 kV. Samples were prepared using 200 mm carbon-coated gold grids. A

drop of the nanoparticle suspension obtained through microwave heating or hydrogenation-assisted thermal decomposition (*vide infra*) was placed on the carbon-coated gold grid. After immobilization, the grid was washed three times with 2 mL of acetonitrile each to remove excess residues of the IL. Thereafter the grid was dried under vacuum and stored under inert conditions until TEM measurement. The size distribution was determined from a minimum of 50 nanoparticles. Energy dispersive X-ray (EDX) spectra were obtained on an FEI Tecnai G2 F20 with an EDAX detector (FZ Jülich) and on a SDD X-MaxN 80 with TLE detector (Interdisciplinary Center for Analytics on the Nanoscale (ICAN, University Duisburg-Essen). Large area EDX spectra were acquired with an exposure time of 3 min and the elemental maps were recorded over 9 min.

List of used *k*-factors:

	k (K-lines)	*k* (L-lines)
Ru	5.245	2.597
Rh	5.739	2.573
Sn	10.461	2.653

(b) Preparation of nanoparticles.

(i) Microwave-heating induced decomposition in IL. Ru−Rh triple-decker complex (denoted as Ru−Rh) **3** was suspended for 24 h under argon atmosphere in a glove box at room temperature in the ILs ([BMIm][BF_4] and [BMIm][NTf_2]). To obtain an 1 wt% in total metal dispersion (Ru+Rh+Sn), a portion of 5 mg (0.005 mmol) was combined with 0.16 g of [BMIm][BF_4] or [BMIm][NTf_2]. The two mixtures were placed in vials in a microwave (CEM, Discover) and were thermally decomposed by microwave heating for 15 min at a power of 50 W, reaching a temperature of 220 °C.

(ii) Hydrogen-assisted thermal decomposition (hydrogenolysis) in ILs. Two mixtures of Ru−Rh **3** and [BMIm][BF_4] or [BMIm][NTf_2] were placed in a glass autoclave (Büchi miniclave) and the N_2 atmosphere was replaced by H_2. The autoclave was heated to 120 °C, charged with 5 bar H_2 and stirred (900 rpm) for 3 hours.

In an attempt to increase the very small nanoparticle size for a clearer EDX elemental composition analysis on larger nanoparticles the nanoparticles were tried to grow by annealing at 150 °C for 48 h following their synthesis.

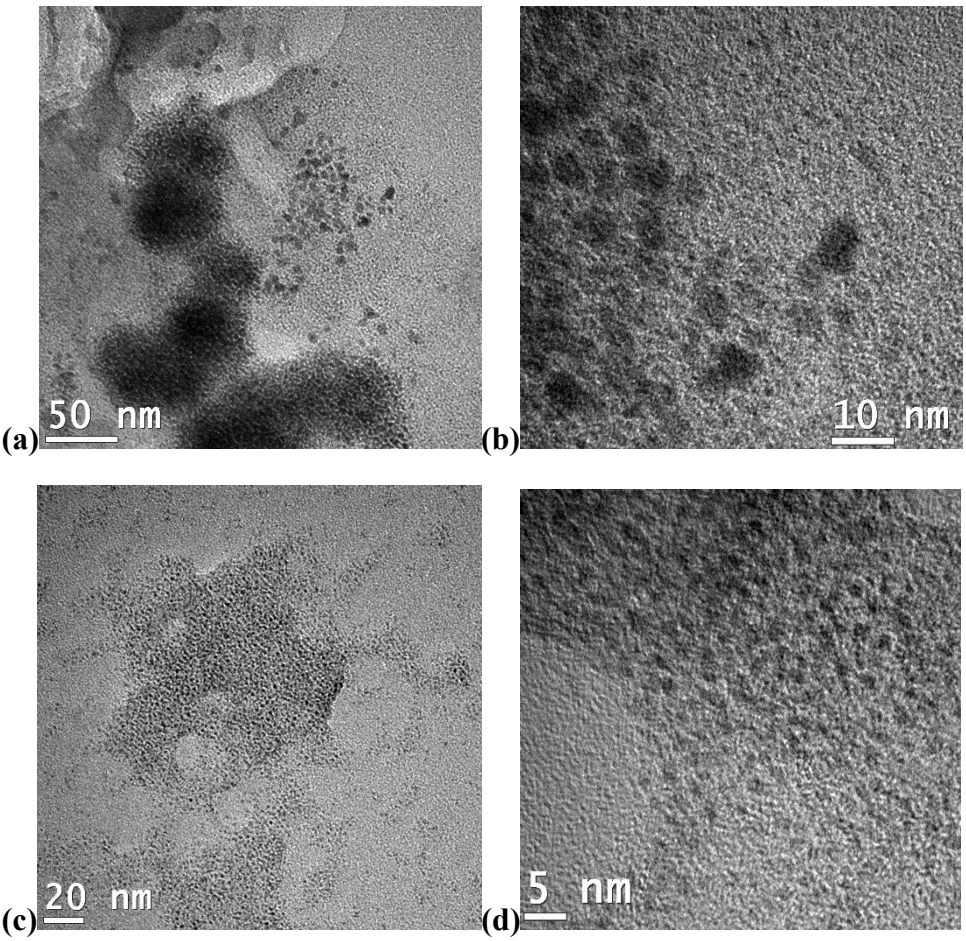
From the amount available for each decomposition experiment of Ru−Rh **3** (5 mg), only

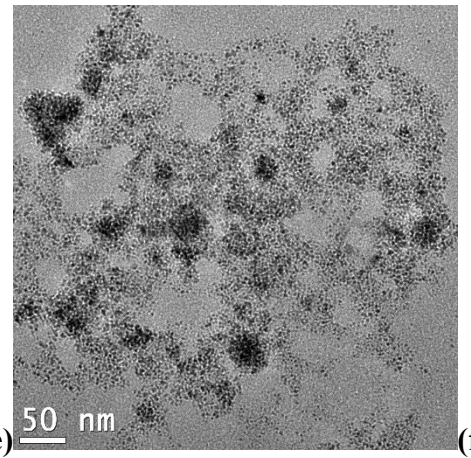
a small metal mass (32 wt% combined for Ru/Rh/Sn, 1.76 mg) was transformed into prospective Ru/Rh/Sn metal nanoparticles.

(c) Characterization of metal nanoparticles synthesized from 3.

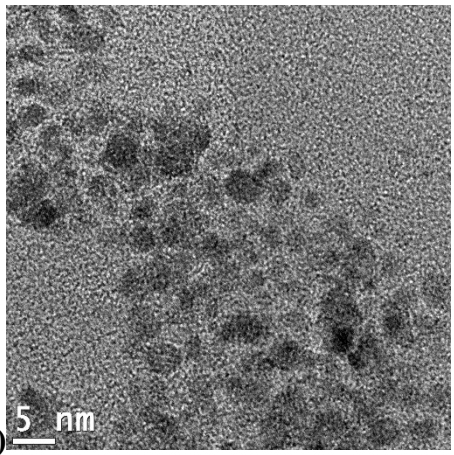
(i) TEM images and nanoparticle distribution

The nanoparticle size and size dispersions were obtained from TEM images which are given in Fig. S1 together with their histogram size analysis.

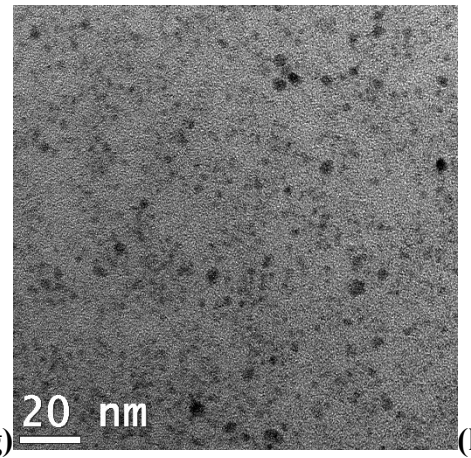



50 nm

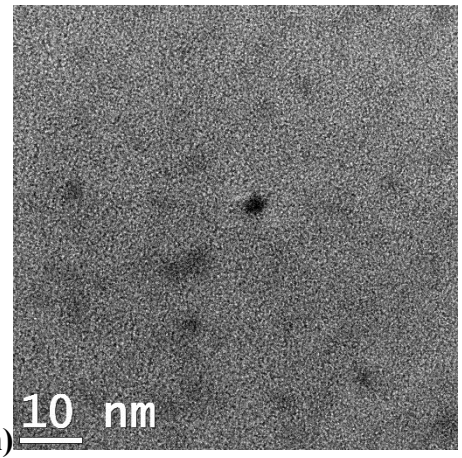
(e)


5 nm

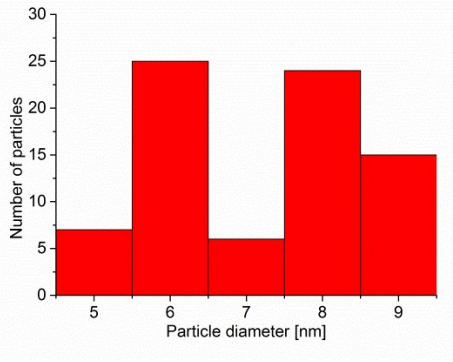
(f)


20 nm

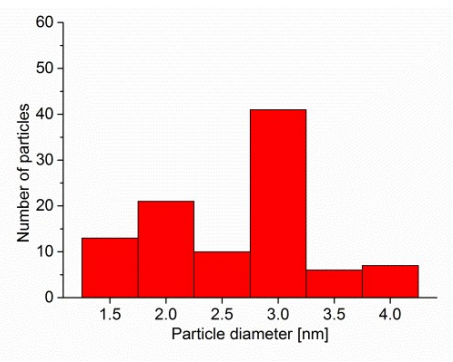
(g)


10 nm

(h)


Number of particles
Particle diameter [nm]
0
5
10
15
20
25
30
5
6
7
8
9

(i)


Number of particles
Particle diameter [nm]
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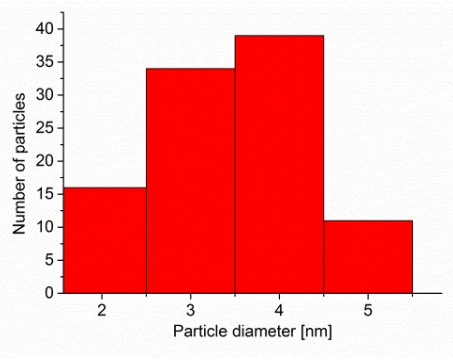
20
30
40
50
60
1.5
2.0
2.5
3.0
3.5
4.0

(j)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Particle diameter [nm]
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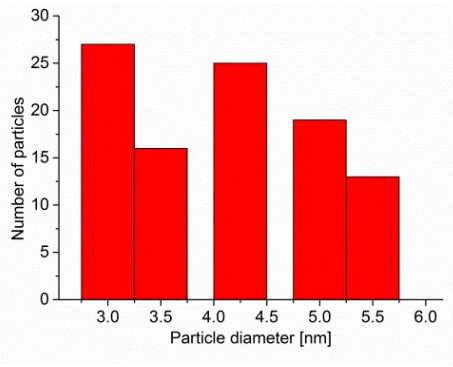
10
15
20
25
30
35
40
2
3
4
5

(k)


Number of particles
Particle diameter [nm]
0
5
10
15
20
25
30
3.0
3.5
4.0
4.5
5.0
5.5
6.0

(l)

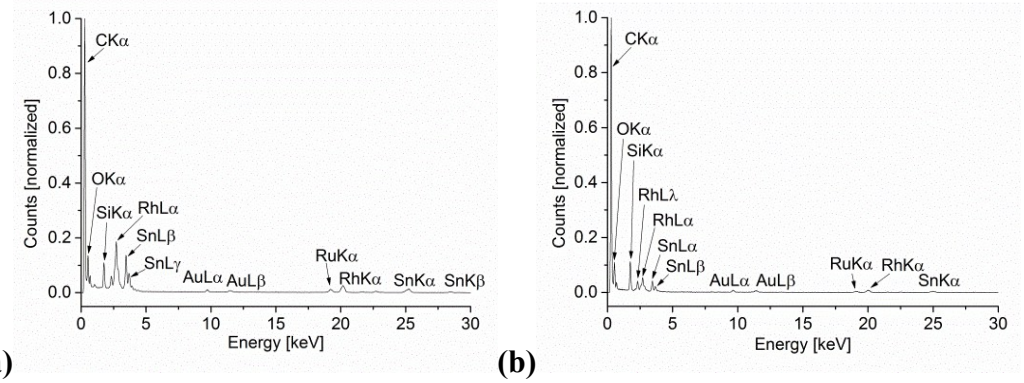
Fig. S1 TEM images of Rh/Ru/Sn-NPs in [BMIm][BF_4] ((a) and (b) with histogram (i)) and [BMIm][NTf_2] ((c) and (d) with histogram (j)) synthesized through microwave heating (50 W, 15 min, 220 °C). TEM images of Ru/Rh/Sn-NPs in [BMIm][BF_4] ((e) and (f) with histogram (k)) and [BMIm][NTf_2] ((g) and (h) with histogram (l)) synthesized through hydrogen-assisted thermal decomposition (5 bar H_2, 120 °C, 3 h). (i)-(l) correspondent histograms of particle diameter measured on a minimum of 50 particles, each bar covers the range of ± 0.5 nm or 0.25 nm around its mid-point, respectively.

The TEM images in Fig. S1a-d show nanoparticles stabilized in [BMIm][BF_4] or [BMIm][NTf_2] and synthesized through microwave heating (50 W, 15 min., 220 °C) with a diameter from 5 to 9 nm (average 7 ± 2 nm in [BMIm][BF_4]) and from 1.5 to 4 nm (2.8 ± 0.9 nm in [BMIm][NTf_2]) (see also histogram of particle diameter (Fig. S1i and j)). The TEM images in Fig. S1e–h show nanoparticles synthesized through hydrogenation-assisted thermal decomposition (5 bar H_2, 120 °C, 3 h) with a diameter from 2 to 5 nm (3.5 ± 2 nm in [BMIm][BF_4]) and from 3 to 5.5 nm (4 ± 1 nm in [BMIm][NTf_2]) (see also histogram of particle diameter (Fig. S1k and l). Nanoparticle size distribution shows a similar size ratio for both synthetic routes. Upon attempted annealing the size of the metal nanoparticles did not increase but was found to even slightly decrease (not shown).

(ii) Overview EDX and SAED analysis

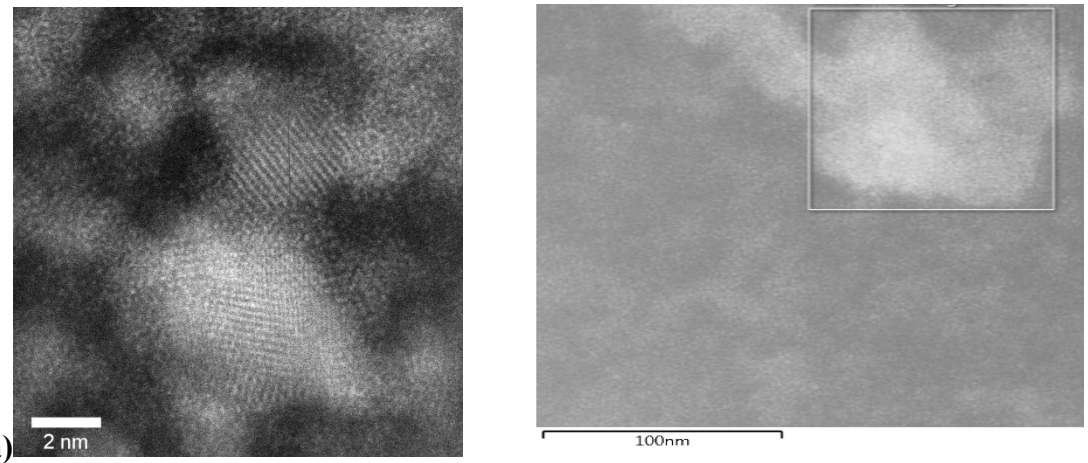
The energy-dispersive X-ray spectrum (EDX) of the nanoparticles synthesized in [BMIm][BF_4] (Fig. S2a) shows all three metals in the nanoparticle suspension with a molar atom fraction of Ru, Rh and Sn as 15%:42%:43%. The EDX analysis is integrated over a large sample region and also a signal for silicon (Si) was found, which is due to the precursor.

In both ILs (see Fig. S2b for [BMIm][NTf_2]) the metal ratio found by EDX matches the average composition of "$Ru_{0.33}RhSn$". The EDX of the annealed nanoparticles synthesized in [BMIm][NTf_2] by thermal hydrogenolysis (Fig. S3) also matched the average composition of "$Ru_{0.33}RhSn$". The 1:1 ratio of Rh and Sn is as given in the precursor. We note that the phases Rh_3Sn_2 and RhSn are the most stable Rh/Sn phases,[S2] while the most stable Ru/Sn phase is Ru_3Sn_7.[S3]

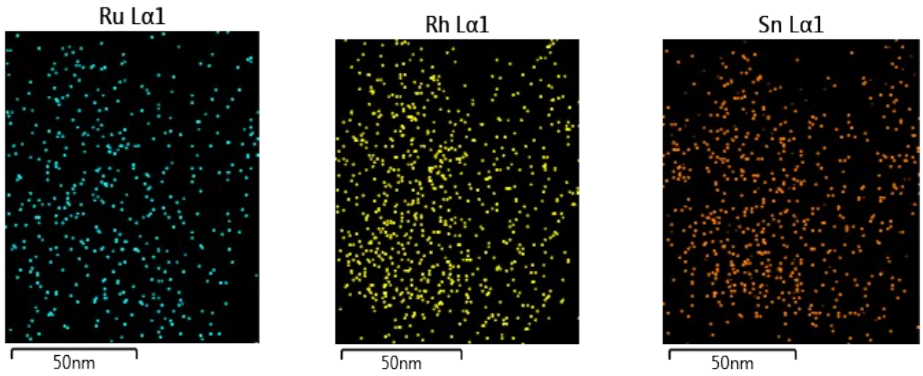


(a) **(b)**

Fig. S2 EDX-spectra of nanoparticles in [BMIm][BF_4] (a) and [BMIm][NTf_2] (b) synthesized through microwave heating (50 W, 15 min., 220 °C). C and Au signals are due to the sample holder.



(a)



(b)

Fig. S3 TEM and EDX mapping of the annealed nanoparticles synthesized in [BMIm][NTf_2] by thermal hydrogenolysis. (a) HR-TEM image of the Rh/Ru/Sn nanoparticles (left) and HAADF-STEM image corresponding to EDX mapping (right). (b) EDX mapping (qualitative) for the HAADF-STEM image area (a, right). HR-TEM image, Qualitative analysis of the comparative L- shells of the three different metals (Ru-L, Rh-L Sn-L) shows a superposition of three metals within the nanoparticles with an average composition of "$Ru_{0.33}RhSn$".

Figure S4 shows the SAED pattern of the nanoparticles synthesized in [BMIm][BF_4] and [BMIm][NTf_2] through hydrogen-assisted thermal decomposition (thermal hydrogenolysis at 5 bar H_2, 120 °C, 3h) together with the calculated diffraction rings of a cubic fcc crystal with lattice constant 4.02 Å which coincide with the observed nanoparticle reflections. The SAED patterns of the synthesized nanoparticles show reflections, which is a clear indication of crystallinity (Fig. S4). The crystallinity of the nanoparticles is also supported by the TEM close-view image in Fig. S3a, which shows the interference patterns within the particles. The reflections in the SAED coincide with the lattice spacings of a face-centered cubic crystal packing, fcc. There are no additional diffraction rings, which could include a different phase than the fcc phase.

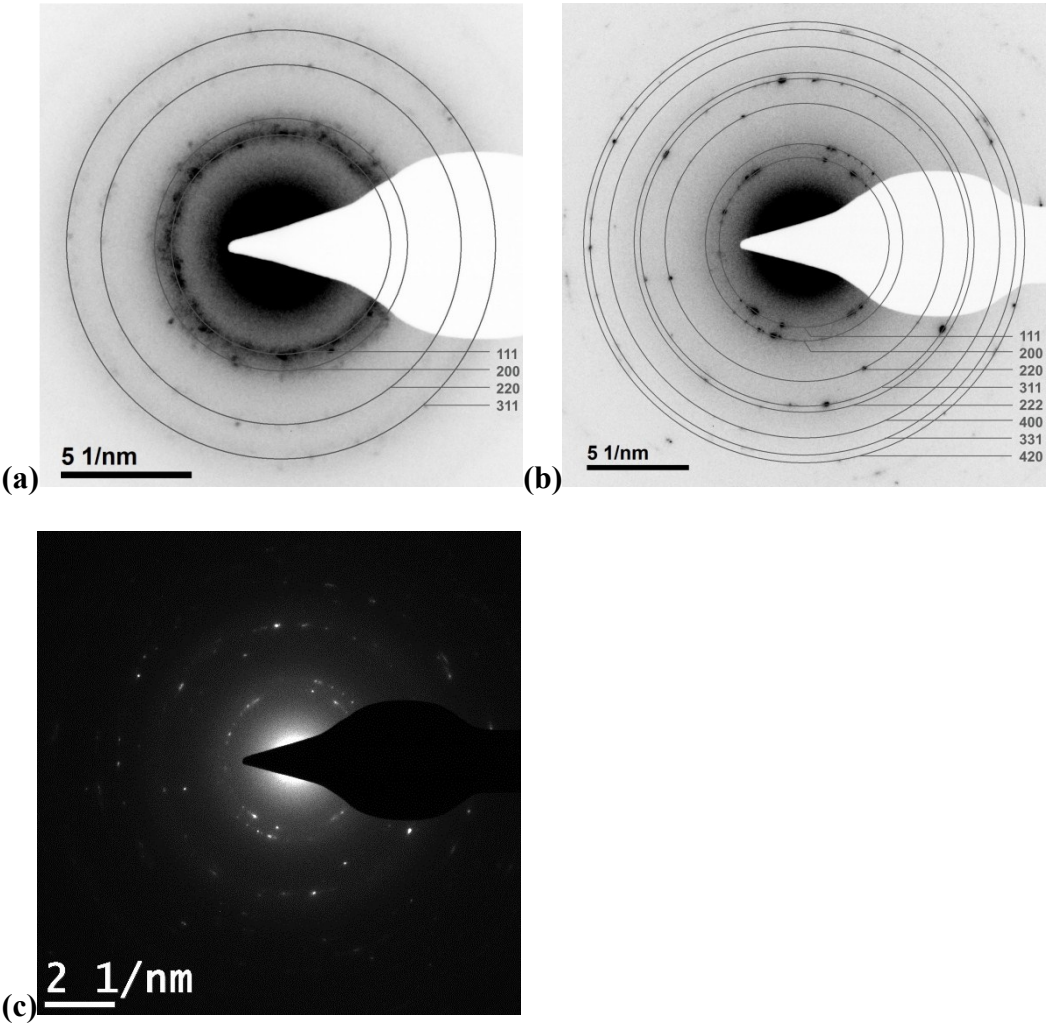


Fig. S4 Selected area diffraction pattern (SAED) pattern of the nanoparticles in (a) [BMIm][BF_4] and (b,c) [BMIm][NTf_2] synthesized through hydrogenation-assisted thermal decomposition (5 bar H_2, 120 °C, 3 h), superimposed with calculated diffraction rings of a simulated cubic fcc crystal with 4.02 Å lattice constant (and uni-atomic structure factor).

(iii) Small-range STEM-EDX analysis of the nanoparticles synthesized from ***3*** *in [BMIm][BF_4] and [BMIm][NTf_2] through hydrogen-assisted thermal decomposition*

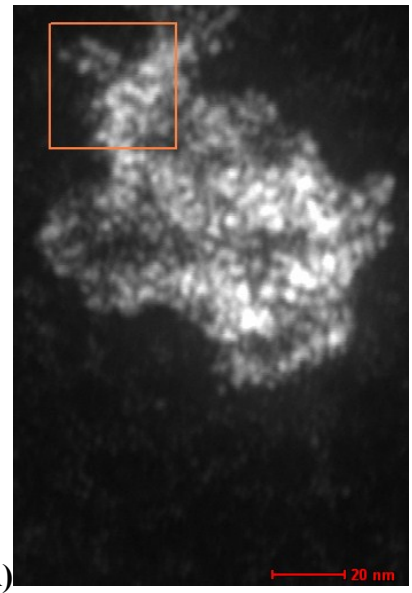
(iii-1) in [BMIm][BF_4]

For analysis of the near-individual nanoparticle composition in [BMIm][BF_4] an EDX mapping over a small nanoparticle area was done (Fig. S5). The nanoparticle composition determined in this small area indicates mixed-metal nanoparticles. Qualitative analysis of the comparative L- and K-shells of three different metals (Ru-L, Rh-L, Sn-L and Ru-K, Rh-K and Sn-K) shows a superposition of three metals within

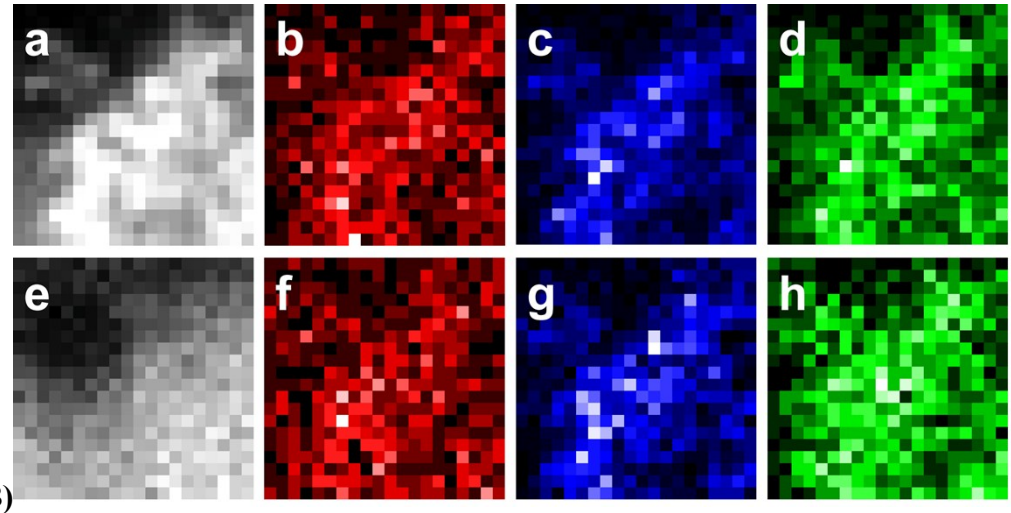
the nanoparticles.

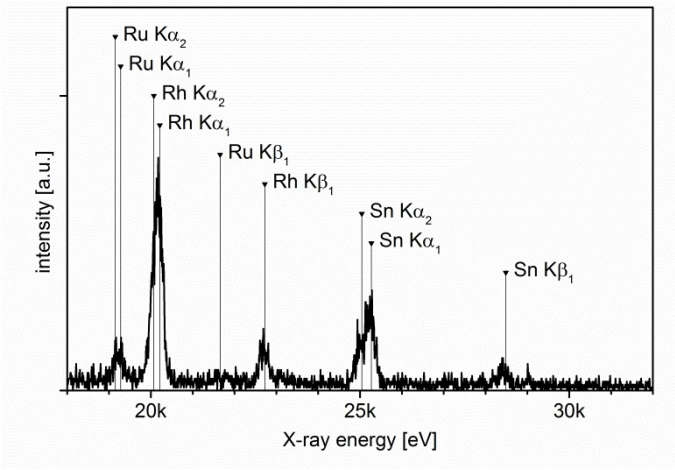
A rather approximate average composition of "$Ru_{0.1}Rh_{0.5}Sn_{0.4}$" (with an error for each element fraction of about ±0.1) is suggested from an area with sufficient particle concentration using the Cliff-Lorimer method for the respective K-Line intensities.[S4]

(A)



(B)





(C)

Fig. S5 (A) HAADF-STEM image with area for EDX mapping of Ru/Rh/Sn-NPs in [BMIm][BF_4] synthesized through hydrogen-assisted thermal decomposition (5 bar H_2, 120 °C, 3 h) with individual nanoparticle composition analyzed from EDX mapping. (B) EDX element maps of a small sample area containing nano-particles. (a) HAADF STEM image with white contrast indicates the presence of particles. (b), (c) and (d) are simultaneously recorded L_α-line maps, while (f), (g) and (h) are K_α-line maps of Ru (red), Rh (blue) and Sn (green), respectively. (e) Si-K_α map indicating an increasing Si contamination during the scanning acquisition from top to bottom. The width of the maps is 35 nm. Note that the intensity in the maps is not proportional to the element fraction. (C) Related EDX spectrum for K_α-line maps of Ru, Rh and Sn.

(iii-2) in [BMIm][NTf_2]

For analysis of the nanoparticle composition in [BMIm][NTf_2] an EDX line scan over a rare larger nanoparticle or agglomerate was done (see Fig. S6). The element concentration measured on this nanoparticle indicates mixed-metal nanoparticles. Qualitative analysis of the comparative L- and K-shells of three different metals (Rh-L, Ru-L, Sn-L and Rh-K, Ru-K and Sn-K) shows a superposition of the three metals in this nanoparticle. For comparison, a HAADF figure has been added which only shows the contrast of the scanned particle (Fig. S6a).

A rather approximate average composition of "$Ru_{0.1}Rh_{0.75}Sn_{0.25}$" (with an error for each element fraction of about ±0.2) is suggested from an area with sufficient particle concentration using the Cliff-Lorimer method for the respective K-Line intensities.[S4]

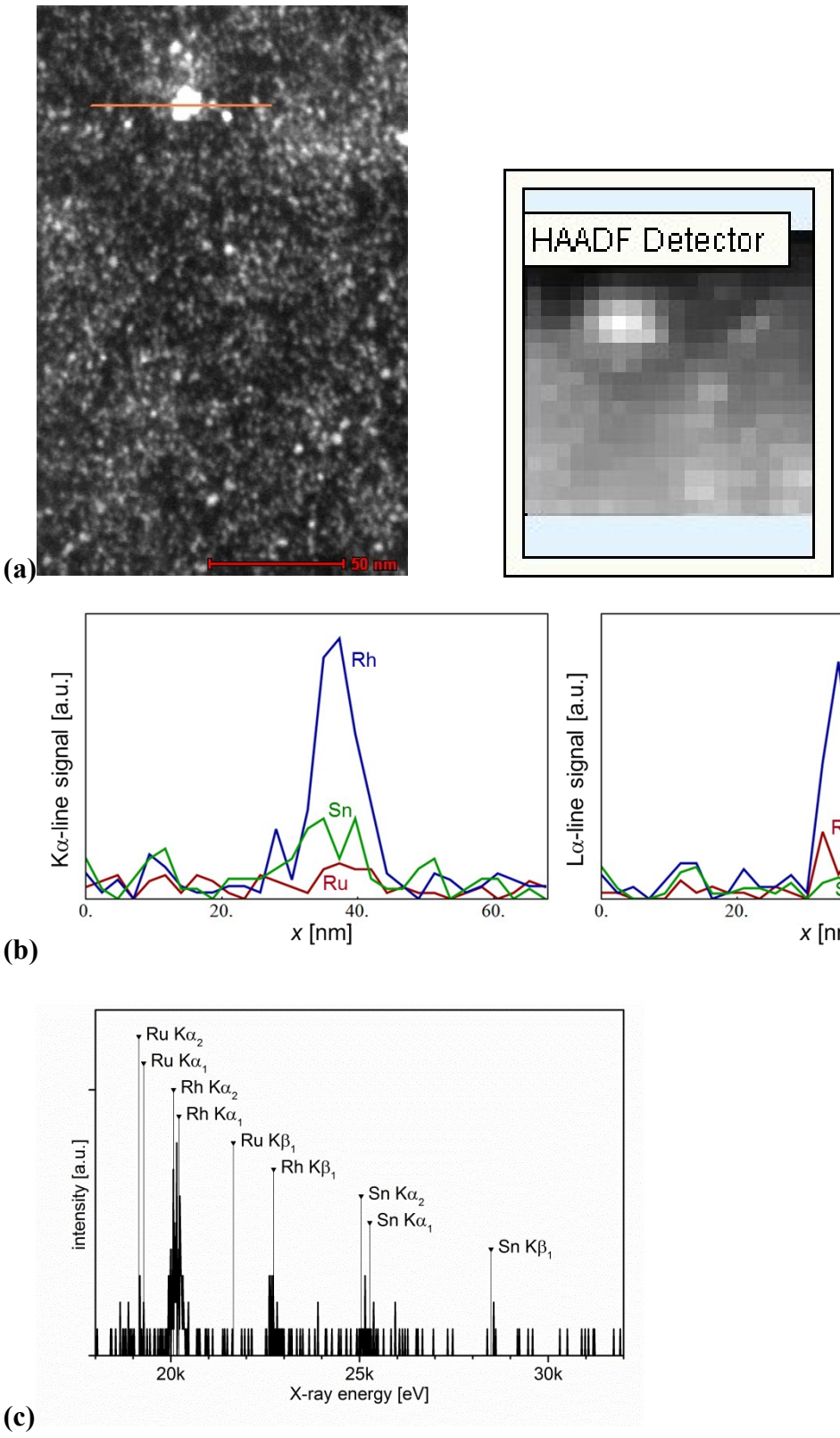


Fig. S6 (a) STEM image with line-scan for EDX mapping indicated for Ru/Rh/Sn-NPs in [BMIm][NTf_2] synthesized through hydrogenation-assisted thermal decomposition (5

bar H_2, 120 °C, 3 h) with corresponding HAADF figure. (b) Profiles of the X-ray K_α-line (left) and L_α-line (right) emission signals of Ru (red), Rh (blue) and Sn (green) recorded while scanning the electron probe over a particle of ca. 15 nm diameter. The profile intensities have been scaled to reflect approximately the relative concentration of the three metal components in the electron beam path. (c) Related EDX spectrum for the evaluation of K_α-line maps of Ru, Rh and Sn.

Furthermore, a localized point-EDX-spectrum was measured for a more accurate analysis of an individual nanoparticle composition of the annealed nanoparticles synthesized in [BMIm][NTf_2] by thermal hydrogenolysis (Fig. S7).

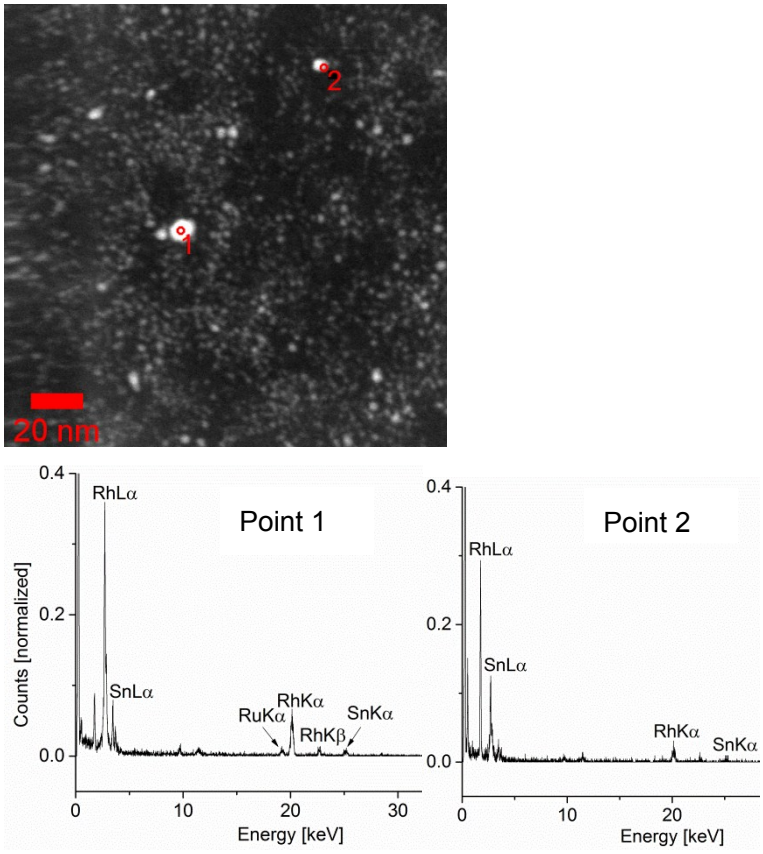


Fig. S7 HAADF-STEM image and point-EDX-spectra of an accumulation of several Ru/Rh/Sn nanoparticles.

Measurement of a point-EDX-spectrum was only possible over a rare larger nanoparticle (Fig. S7). The metal ratio found at point 1 corresponds to the average composition of "$Ru_{0.08}Rh_{0.77}Sn_{0.15}$" and at point 2 to the average composition of "$Rh_{0.8}Sn_{0.2}$".

Theoretical calculations. Quantum-chemical calculations were performed by the Gaussian 03 program[S5] with hybrid density functional theory at the B3LYP level using LANL2DZ for Sn, Ru, and Rh, and 6-31G(d) for C, H and Si.

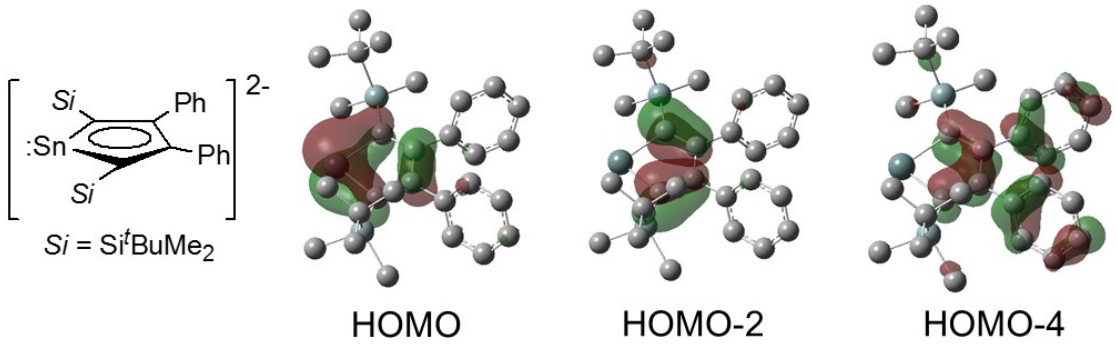


Fig. S8 p-Type molecular orbitals on the stannole ring of the stannole dianion (isovalue = 0.04). HOMO contributes to a bonding interaction between the two C_β carbon atoms, while HOMO-2 causes an anti-bonding interaction between the two C_β carbon atoms.

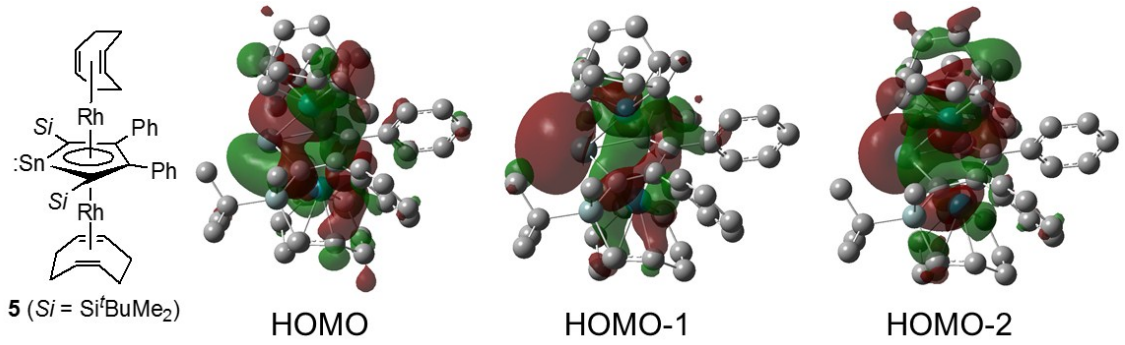


Fig. S9 Frontier molecular orbitals of compound **5** (isovalue = 0.02).

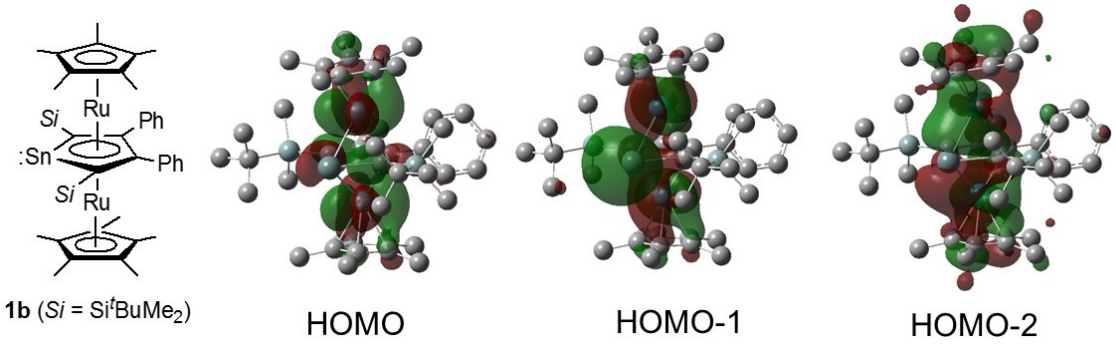


Fig. S10 Frontier molecular orbitals of compound **1b** (isovalue = 0.02).

Cartesian coordinates for the opitimized structure of compound 1b.

H	2.84941372	-1.33967759	-3.61029833
H	4.19894226	-2.44087678	-3.29262594
H	-3.39438891	1.37774886	-3.08576984
H	3.67159858	0.79302319	-3.12912543
H	-5.09849062	1.16008973	-2.66055297
C	3.23031566	-2.08682974	-2.90782996
H	2.53904450	-2.93282866	-2.92561522
C	0.95886693	3.90732355	-2.34269461
H	-4.03176727	-0.24224931	-2.80766451
H	5.32828180	0.58164075	-2.54882255
C	-4.07898077	0.79319162	-2.46425596
C	4.29826099	0.80986932	-2.23472248
C	-1.55652184	-3.61213325	-2.40588176
H	-3.02531536	3.42453341	-2.02079734
H	-4.44785445	3.85107935	-1.06759202
Sn	-0.13883794	0.07412013	-2.04360723
H	4.29517314	1.82968764	-1.84626781
H	0.86426597	-4.84029890	-0.81142100
H	-0.56845784	-5.53169241	-0.03721327
C	-3.41245973	3.48203193	-1.00261399
C	3.38362221	-1.52232798	-1.52568703
C	0.08255918	-4.65043420	-0.07579492
C	3.84570437	-0.18841041	-1.21317268
H	-2.83457520	4.23566836	-0.46643959
C	-3.75331132	0.91158497	-1.00299005
H	-0.31151435	5.38380499	-0.03694365
H	-1.20815687	4.01663307	0.64537615
H	2.82654945	-4.22932723	-1.05112245
Si	0.92662029	3.21470067	-0.47451922
H	-4.40457695	-1.96495018	-0.99937010
C	-3.40997085	2.14177071	-0.32884406
Si	-1.06247514	-3.15757144	-0.52508098
H	2.78402856	4.64042314	0.40286067
C	-0.21415258	4.43382961	0.49893693
H	3.47446131	3.22862914	-0.41719345

H	0.53858765	-4.54140168	0.90738666
C	0.38506677	1.35328677	-0.24035842
H	-5.86135533	-1.05329353	-0.60317159
C	3.38360051	-2.28383246	-0.29643088
C	2.67546440	3.56067978	0.24900606
C	-0.38015349	-1.34119790	-0.27259509
H	4.36558793	-4.17469044	-0.19103586
Ru	1.82938705	-0.54574104	-0.20658263
C	3.33790255	-3.77935692	-0.19909767
C	-4.85728887	-1.32369636	-0.24377919
C	-4.07339109	-0.06839177	0.00874341
Ru	-1.80990196	0.53926048	0.11738536
H	4.96468786	1.85465915	0.31635964
C	4.10736449	-0.12497214	0.20656616
H	-3.37797537	-3.95586341	0.21126923
H	0.22168717	4.63834499	1.48111638
C	-2.53724223	-3.44296717	0.68990152
H	2.84974592	-4.13521181	0.71133821
H	2.79603964	3.06326427	1.21434027
C	-3.46480406	1.90438736	1.09205443
C	3.81525695	-1.41763164	0.76548435
H	-4.98344190	-1.91717214	0.66315772
C	4.85200654	0.96097687	0.93081833
C	0.32889835	0.69121126	1.05834978
H	-2.18358719	-4.06613050	1.51838858
C	-0.10662997	-0.76558778	1.04278943
H	-2.86649300	3.82995668	1.89734808
C	-3.86852063	0.53364627	1.29588263
H	5.86254773	0.61256538	1.18978553
H	-2.88830088	-2.49833849	1.10343910
H	4.36225694	1.26435112	1.86083926
C	-3.47773424	2.96258160	2.15937609
H	1.36656996	-2.88151857	1.88042114
H	-4.50468414	3.32784164	2.31126071
H	-0.98531450	2.63393216	2.44757784
H	5.05539229	-2.52162812	2.12427099

C	4.17335711	-1.86502649	2.15528075
C	0.70270885	1.31894006	2.37488358
C	-0.20517202	-1.50544068	2.34708500
C	0.63185026	-2.59978469	2.62169667
H	-3.12594835	2.58353200	3.12367671
C	-0.08856988	2.32114215	2.95857809
C	-4.29594465	-0.06565920	2.60575032
H	-5.38796342	0.00675507	2.71819992
H	3.37085735	-2.42330205	2.64547004
H	4.42603241	-1.01718375	2.79818832
H	-4.02680910	-1.12255630	2.68890431
H	2.45195767	0.10976795	2.64818936
C	1.84860791	0.89890965	3.07423897
H	-3.85105858	0.45635214	3.45786350
H	1.19385454	-4.14795970	4.01160805
H	-1.75067451	-0.25690077	3.15208307
C	0.53859189	-3.30128011	3.82850159
C	-1.12030070	-1.11450544	3.33931278
C	0.26060941	2.90204730	4.18286468
H	-0.36887719	3.67888146	4.60715276
C	2.19962270	1.47111405	4.30117874
C	1.40911802	2.48096347	4.86091378
C	-1.21345601	-1.80609333	4.55094194
C	-0.38883141	-2.90883210	4.79986497
H	3.08731379	1.12370297	4.82158023
H	1.68024648	2.92693111	5.81272474
H	-1.92886732	-1.48152863	5.30067775
H	-0.46185553	-3.44854448	5.73883381
C	1.88295876	3.10099257	-3.28031321
H	1.57804689	2.05273788	-3.36759210
H	1.85630200	3.53650555	-4.29103930
H	2.92132389	3.12906137	-2.93878270
C	1.51460955	5.35691924	-2.28749604
H	1.52534401	5.78035735	-3.30287100
H	0.90216432	6.01868841	-1.66544535
H	2.54179348	5.38645849	-1.90758095

C	-0.45612487	3.96085142	-2.96001382
H	-0.90475022	2.96409964	-3.04220871
H	-1.12713696	4.59406977	-2.37126165
H	-0.40499344	4.38477326	-3.97467733
C	-0.29933043	-3.59019604	-3.31054261
H	0.12467721	-2.58409267	-3.39834101
H	0.48335667	-4.26131794	-2.93963180
H	-0.56555082	-3.92369091	-4.32507629
C	-2.12779853	-5.05580575	-2.41257440
H	-2.44619948	-5.31707801	-3.43279113
H	-1.38501831	-5.79734843	-2.10227016
H	-3.00338165	-5.15558280	-1.75993387
C	-2.62136883	-2.68896559	-3.03415638
H	-3.58426988	-2.78167132	-2.52190119
H	-2.31984592	-1.63755002	-3.01914192
H	-2.78535338	-2.97111988	-4.08559005

Cartesian coordinates for the opitimized structure of compound 3.

C	0.40294597	-2.88611313	4.79835511
C	-0.83219575	-2.49505684	4.27840052
C	-3.33834727	-3.44338674	1.07924351
C	-4.52892774	-0.63808615	1.94106889
C	1.56461139	-2.57769204	4.09061904
C	-0.89916620	-1.81147941	3.06443764
C	-3.34702560	-2.20603041	0.22762556
C	-1.49912293	2.40847197	4.84721709
C	-3.88700386	-0.93209020	0.61293158
C	-2.44452444	2.15315543	3.85328640
C	-0.16243471	2.09093518	4.60608271
C	1.48976431	-1.88953127	2.87746340
C	0.24285797	-4.44206249	0.24062031
C	0.25699384	-1.50110017	2.33327878
C	-2.83912716	-3.36005642	-2.05286518
C	-3.09391133	-2.16675678	-1.18293471
C	-2.05078577	1.59670039	2.63565924
C	-3.94948291	-0.10185483	-0.55441664

C	0.22237402	1.53255242	3.38597219
C	-0.71068819	1.28415212	2.36744811
C	-4.66796887	1.21016275	-0.66326388
C	-3.44927206	-0.85951894	-1.66809955
C	0.16247855	-0.76271972	1.01899064
C	-0.32550859	0.67719797	1.03645971
C	3.00474304	-3.17822700	0.28482485
C	0.49743902	-1.31986859	-0.26118187
C	-3.53338220	-0.45822326	-3.11358024
C	2.10969104	-5.02641008	-2.40561296
C	-2.56023926	3.87480568	0.22620301
C	0.40862111	-3.48214394	-3.33140567
C	-0.50237620	1.34822963	-0.22957271
C	3.43004722	0.81488307	1.84807861
C	1.63557688	-3.55027996	-2.40342198
C	4.73240710	0.10417240	1.53039079
C	3.11242730	2.12129192	1.44187824
C	0.39097903	4.22295648	0.57511845
C	2.76251850	-2.69509229	-3.02218880
C	5.08657222	0.15602255	0.02932742
C	3.85438672	0.29901289	-0.86507871
C	-1.79919176	3.13113060	-3.19356164
C	4.08084609	3.00871907	0.66632215
C	-0.82064059	3.88182942	-2.26627772
C	3.35137684	1.54982766	-1.29714376
C	-1.24679726	5.37211033	-2.26071712
C	3.89018697	2.89748698	-0.86091014
C	0.59442117	3.82466336	-2.87793832
H	0.45872152	-3.41952086	5.74347999
H	-1.74797707	-2.71978338	4.81971381
H	-3.24469238	-3.21182008	2.14293581
H	-4.27998631	-3.99760998	0.94837902
H	-5.44652731	-1.23365938	2.04871957
H	-3.88580820	-0.87838826	2.79307057
H	-2.52135050	-4.11836523	0.81635425
H	-4.81549703	0.41251215	2.03255360

H	-1.80077822	2.84035026	5.79763176
H	2.53651243	-2.86816253	4.48191466
H	-1.85673041	-1.50452120	2.66594216
H	-3.49354559	2.38216803	4.02501976
H	-0.12454520	-4.14146460	1.22655859
H	-3.79531416	-3.84959613	-2.29160500
H	0.58879723	2.26981953	5.37104393
H	0.85954739	-5.33904051	0.37395057
H	-0.61924789	-4.72535438	-0.37107781
H	-2.20808007	-4.10369389	-1.56281610
H	-2.78742451	1.38180388	1.87369339
H	-5.73163393	1.03756059	-0.88472796
H	-4.61680128	1.79442786	0.25793368
H	2.39884359	-1.64861228	2.34502924
H	1.26052880	1.27649243	3.23454220
H	-2.36840121	-3.08565134	-2.99821832
H	2.92016883	-3.56072656	1.30632160
H	1.33620135	-5.70815481	-2.03435495
H	-4.50331599	-0.75603538	-3.53915044
H	-2.79374795	3.51956567	1.23100806
H	-4.26343078	1.82502028	-1.47018148
H	2.91819753	0.42313480	2.72435037
H	-0.37314370	-4.17709639	-3.01206945
H	3.64655261	-3.87242887	-0.26880006
H	3.01239934	-5.18705460	-1.80595058
H	-3.40412530	3.64148175	-0.42768235
H	-2.75034511	-0.93159843	-3.71266154
H	4.63175046	-0.94171962	1.84063284
H	3.51589543	-2.21378737	0.32284858
H	-3.43610259	0.62249682	-3.24141664
H	2.34827654	-5.33452790	-3.43409166
H	-0.02687403	-2.47834888	-3.38217639
H	-2.48628137	4.96740738	0.28361972
H	2.35445539	2.65194995	2.00996568
H	0.32785040	3.96667168	1.63824480
H	5.55508405	0.51827459	2.13612181

H	0.69482871	-3.76430212	-4.35592670
H	-2.83035298	3.17817631	-2.82142609
H	3.68345641	-2.73014865	-2.42836295
H	0.18466077	5.29637633	0.48342707
H	1.41689710	4.04441615	0.24657920
H	5.62587786	-0.75671998	-0.24919724
H	-1.53214279	2.07586192	-3.31490487
H	2.46918665	-1.64499151	-3.13424015
H	3.01023457	-3.06696473	-4.02765937
H	3.66934011	-0.54368336	-1.52506554
H	-2.28805040	5.50795865	-1.95076577
H	5.11123255	2.75497152	0.94238443
H	3.93715337	4.05078187	0.97444083
H	5.77749582	0.98339422	-0.17247221
H	-0.61725605	5.98541332	-1.60516424
H	-1.79686129	3.58205980	-4.19744794
H	2.86385921	1.56963583	-2.27012571
H	0.98010321	2.80306905	-2.95237528
H	3.18035050	3.66146971	-1.19292096
H	-1.15406133	5.78491684	-3.27603963
H	1.31013693	4.41351078	-2.29244216
H	4.83442041	3.11558673	-1.38729237
H	0.58538198	4.24145808	-3.89633127
Si	1.28430014	-3.05188081	-0.53961363
Si	-0.88495320	3.22446307	-0.42201644
Ru	-1.74538229	-0.61872164	-0.23361860
Rh	1.99549520	0.69261928	0.16338803
Sn	0.24455680	0.13825867	-1.99168972

Cartesian coordinates for the opitimized structure of compound 5.

Sn	0.01656046	-0.07488812	-1.97547341
C	0.90922844	-1.09853149	-0.14370242
C	0.58579860	-0.39912267	1.09091509
C	-0.53064368	0.58205654	1.03172394
C	-1.08962866	0.89290361	-0.25899067
Si	2.39164998	-2.31178521	-0.30775314

C	2.13134849	-4.01816901	0.51366221
H	3.09081850	-4.54812904	0.53678958
H	1.42392581	-4.65508608	-0.02910817
H	1.79204784	-3.93022615	1.54870264
C	3.92146285	-1.56157040	0.53808233
H	3.73305148	-1.38480309	1.60153467
H	4.20829753	-0.60783648	0.08510422
H	4.77638167	-2.24423557	0.46277314
C	2.93168661	-2.73942184	-2.14379548
C	1.79941311	-3.36269452	-2.98642420
H	0.97207448	-2.66433186	-3.15556384
H	1.39303209	-4.26898961	-2.52048221
H	2.17973382	-3.65413553	-3.97708278
C	4.07250922	-3.78650330	-2.06993763
H	4.44184518	-4.00009145	-3.08375160
H	3.74018272	-4.73808127	-1.64149181
H	4.92908766	-3.43367139	-1.48401297
C	3.49251244	-1.51600554	-2.89805608
H	4.35082927	-1.07745521	-2.37621710
H	2.74477250	-0.72878635	-3.03769086
H	3.83781321	-1.81488704	-3.89917581
C	1.07823338	-0.83764783	2.45565824
C	1.88017110	-0.03857169	3.28349700
H	2.18876926	0.93941468	2.94713439
C	2.28734350	-0.47434577	4.54627807
H	2.91265142	0.17256008	5.15622201
C	1.89185541	-1.72256956	5.02530333
H	2.20742666	-2.06221257	6.00804258
C	1.07388230	-2.52370691	4.22777414
H	0.73979167	-3.49380838	4.58763436
C	0.67263047	-2.08259473	2.96639660
H	0.01054897	-2.69801546	2.37021461
C	-1.04922823	1.16383370	2.32643617
C	-0.87689695	2.51803150	2.64556165
H	-0.33830537	3.15448736	1.95676774
C	-1.38191222	3.05372053	3.83239653

H	-1.23076351	4.10791827	4.05087340
C	-2.07205079	2.24241105	4.73316439
H	-2.46664138	2.65704392	5.65683335
C	-2.24234957	0.88885587	4.43693022
H	-2.76933313	0.23982519	5.13167814
C	-1.73242491	0.35745038	3.25205161
H	-1.85669946	-0.69869562	3.04444435
Si	-2.45118931	2.21647565	-0.57141173
C	-4.00027474	1.93513124	0.50560140
H	-4.59208053	1.06483595	0.20282820
H	-4.65169902	2.81454373	0.43749580
H	-3.73065603	1.80998795	1.55912402
C	-1.84450327	3.98145364	-0.15563667
H	-2.38291607	4.72544552	-0.75365891
H	-0.77621757	4.11118025	-0.34957408
H	-2.02927456	4.21755548	0.89645595
C	-3.05151671	2.34133043	-2.43291121
C	-4.26129951	3.30921442	-2.47507539
H	-4.58862183	3.44580720	-3.51608434
H	-4.02556777	4.30408406	-2.08068462
H	-5.11908842	2.92176968	-1.91371843
C	-3.52865247	1.00861499	-3.04566844
H	-4.39926067	0.60803902	-2.51219581
H	-2.74800623	0.24101984	-3.04878004
H	-3.83837585	1.16349755	-4.09005731
C	-1.94712665	2.93574989	-3.33593842
H	-1.07363274	2.27811379	-3.41473320
H	-1.60272353	3.91270046	-2.97627667
H	-2.32962081	3.08114796	-4.35729811
Rh	-1.36778388	-1.49108385	-0.03205914
C	-3.53480798	-1.60735565	-0.50032905
H	-3.76307744	-0.63718048	-0.92288913
C	-3.36820715	-1.66428521	0.88841294
H	-3.51325499	-0.73667376	1.43739863
C	-3.44987829	-2.92134451	1.73322907
H	-4.50224508	-3.19815673	1.90977452

H	-3.03254635	-2.68947678	2.72034845
C	-2.66995725	-4.10597616	1.12684097
H	-2.34574235	-4.77459962	1.93299115
H	-3.32327221	-4.71013112	0.48726129
C	-1.44524691	-3.65494734	0.33411063
H	-0.49076167	-3.93494943	0.76689294
C	-1.43808366	-3.40368847	-1.05346510
H	-0.48872380	-3.52970259	-1.56421501
C	-2.64022385	-3.47700692	-1.97391477
H	-2.85719870	-4.52593456	-2.23466910
H	-2.36916824	-2.97865369	-2.91146587
C	-3.89189259	-2.79540956	-1.38387224
H	-4.53477310	-2.44959251	-2.20141889
H	-4.49005481	-3.51425143	-0.81348558
Rh	1.44531864	1.45671029	-0.15496638
C	1.72875707	3.18793759	-1.45891539
H	0.81155983	3.27748292	-2.03685678
C	2.16620814	4.46221845	-0.73950596
H	1.52533447	5.29144818	-1.06158605
H	3.17993014	4.72900830	-1.06029819
C	2.10370540	4.33970647	0.79858056
H	2.83800051	5.01675953	1.26544999
H	1.12148721	4.68398219	1.14222306
C	2.29933154	2.91850818	1.29172083
H	1.83151329	2.71812826	2.25313615
C	3.32754152	2.05910149	0.87599214
H	3.57953558	1.22382917	1.52209355
C	4.43288076	2.47776776	-0.08724187
H	5.36521764	1.97621919	0.19796062
H	4.62733003	3.55097568	0.02027041
C	4.10271651	2.13502271	-1.55549323
H	4.65119031	2.80307236	-2.24045195
H	4.45796759	1.12285193	-1.77436879
C	2.61967855	2.17344513	-1.86305870
H	2.34208194	1.60561658	-2.74930509

Cartesian coordinates for the opitimized structure of the stannole dianion.

Sn	-0.14692526	-2.11770439	-0.79653825
Si	-3.23402400	-0.59714710	-0.52125127
C	-1.24630534	2.10277561	-0.03207818
C	-1.41820152	-0.40517529	-0.38341110
C	-0.61483726	0.76229036	-0.22312466
C	0.81502791	0.66131976	-0.34809342
C	1.64954880	1.88990233	-0.23863521
C	-1.99926825	2.41095164	1.12083912
H	-2.09187458	1.64898395	1.88864065
C	3.25438042	4.25226215	-0.08014875
H	3.86567365	5.15204144	-0.01995136
C	-1.13171842	3.12834478	-0.99767837
H	-0.55608879	2.92616825	-1.89641846
C	1.40157838	-0.62177023	-0.59832827
C	-2.46680741	4.65702260	0.33228698
H	-2.93102095	5.63261878	0.47219818
C	-2.59646590	3.65842250	1.30446795
H	-3.15714933	3.85799422	2.21812068
C	-1.72676926	4.37775789	-0.82060960
H	-1.61372825	5.14088008	-1.59108009
C	2.52071973	2.27586105	-1.28274551
H	2.55441502	1.64981323	-2.16949586
C	1.62213997	2.74124226	0.89227948
H	0.96926261	2.47962882	1.71947455
C	3.30361420	3.42704168	-1.21041212
H	3.95164560	3.68930682	-2.04739228
C	-4.30225211	0.95915792	-0.92375625
H	-5.30458689	0.66754009	-1.27075691
H	-3.82260804	1.53325546	-1.72592417
H	-4.42003136	1.64306938	-0.07625314
C	-4.10545426	-1.41802162	1.06286587
C	-3.69866743	-1.78267111	-1.96214140
H	-4.76601940	-2.05553057	-1.96508694
H	-3.10199651	-2.70124722	-1.93257903
H	-3.47765527	-1.28967095	-2.91770665

C	-3.70509118	-2.90167129	1.17344432
H	-2.61485754	-3.02095570	1.19979367
H	-4.07512968	-3.48640585	0.32129426
H	-4.12367864	-3.35541494	2.09092984
C	-3.65869870	-0.70492867	2.35167179
H	-2.56810003	-0.73715050	2.45418599
H	-4.10252176	-1.18200445	3.24494394
H	-3.96456153	0.34968748	2.35940483
C	-5.64179821	-1.33365940	0.96599979
H	-6.02248404	-1.82210912	0.05886360
H	-5.99502122	-0.29459599	0.95284867
H	-6.12212536	-1.83175513	1.82853524
Si	3.12667763	-1.20426965	-0.40292553
C	3.39345788	-2.90017994	-1.26548568
H	3.38754173	-2.76863960	-2.35523212
H	2.60026844	-3.61533283	-1.02305135
H	4.36177262	-3.34556671	-0.98959635
C	3.67098405	-1.50219677	1.48291342
C	4.59734409	-0.19242181	-1.15390449
H	4.39777665	0.02069167	-2.21238282
H	5.52967915	-0.77420567	-1.10648216
H	4.76940084	0.76948548	-0.65910488
C	2.96723830	-2.75441120	2.03919275
H	3.30399195	-3.66860835	1.53189727
H	1.88008379	-2.69121058	1.90810297
H	3.17812371	-2.87954381	3.11730576
C	5.19315516	-1.69948760	1.62378420
H	5.75177659	-0.80426852	1.32293808
H	5.55792568	-2.53681303	1.01237929
H	5.46916911	-1.91910380	2.67184890
C	3.25057278	-0.29136018	2.33596223
H	3.72760378	0.63741683	1.99746662
H	3.52596251	-0.43889979	3.39691112
H	2.16826547	-0.13585772	2.28195146
C	2.40263414	3.89425135	0.96997597
H	2.34964881	4.51747020	1.86306172

References

S1. Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons (2016). FEI Tecnai G2 F20. Journal of large-scale research facilities, 2, A77. http://dx.doi.org/10.17815/jlsrf-2-138.

S2. K. Schubert, *Z. Naturforsch. A*, 1947, **2**, 120.

S3. O. Schwomma, H. Nowotny and A. Wittmann, *Monatsh. Chem.,* 1964, **95**, 1538.

S4. G. Cliff and G. W. Lorimer, *J. Microsc.,* 1975, **103**, 203.

S5. Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.