Supporting Information

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Octahedral Coordination Compounds of the Ni, Pd, Pt Triad

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Experimental: Solvents were dried and purified by standard methods and were stored under argon. NMR spectra were recorded on a Bruker DRX-250 NMR spectrometer equipped with a 5 mm ATM probe head and operating at 250.13 (^1H), 80.25 (^{11}B), 62.90 (^{13}C), 93.25 MHz (^{119}Sn) and 53.77 MHz (^{195}Pt). Chemical shifts are reported in δ values in ppm relative to external TMS (^1H , ^{13}C), $\text{BF}_3\text{Et}_2\text{O}$ (^{11}B), SnMe_4 (^{119}Sn) or K_2PtCl_6 (^{195}Pt) using the chemical shift of the solvent ^2H resonance frequency. Elemental analyses were performed by the Institut für Anorganische Chemie Universität Tübingen using a Vario EL analyzer. The compounds K_2PdCl_6 and K_2PtCl_6 were purchased from commercial suppliers. The starting materials dpp-BIAN (dpp-BIAN = 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene)^[1] and [(dpp-BIAN)NiBr₂]^[2] were prepared according to literature procedures. $[\text{Bu}_3\text{NH}]_2[\text{SnB}_{11}\text{H}_{11}]$ and $[\text{Na}]_2[\text{SnB}_{11}\text{H}_{11}]$ was synthesized using a modified protocol of the original work of the group of Todd.^[3]

Figure S1. Simulated (a) and experimental (b) electrospray mass spectrum (negative ion mode) of **1** recorded from a CD_2Cl_2 solution, showing the anion $[\text{Bu}_3\text{NH}]_7[\text{Ni}(\text{SnB}_{11}\text{H}_{11})_6]$.

Crystallography: X-ray data for compounds **1–4** were collected on a Stoe IPDS 2T diffractometer and were corrected for Lorentz and polarization effects and absorption by air. The programs used in this work are Stoe's X-Area^[4] and the WinGX suite of programs^[5] including SHELXS^[6] and SHELXL^[7] for structure solution and refinement. Numerical absorption correction based on crystal-shape optimization was applied for compounds **1**, **3** and **4** with Stoe's X-Red and X-Shape.^[8,9]

Figure S2 Molecular structure of the anion of $[\text{Bu}_3\text{NH}]_2[\text{K}]_2[\text{Na}]_4[\text{Pd}(\text{SnB}_{11}\text{H}_{11})_6]$ (**3**), H atoms and cations have been omitted for clarity, ellipsoids at 30% probability. Interatomic distances [Å] and angles [°]: Pd–Sn1: 2.6144(5), Pd–Sn2: 2.6122(5), Pd–Sn3: 2.6136(5), Sn1–Pd–Sn2: 90.077(16), Sn2–Pd–Sn3: 89.389(16), Sn1–Pd–Sn3: 88.826(17).

Figure S3 Molecular structure of the anion of $[\text{Bu}_3\text{NH}]_2[\text{K}]_2[\text{Na}]_4[\text{Pt}(\text{SnB}_{11}\text{H}_{11})_6]$ (**4**), H atoms and cations have been omitted for clarity, ellipsoids at 30% probability. Interatomic distances [Å] and angles [°]: Pt–Sn1: 2.6186(5), Pt–Sn2: 2.6162(5), Pt–Sn3: 2.6171(5), Sn1–Pt–Sn2: 90.010(16), Sn2–Pt–Sn3: 90.470(16), Sn1–Pt–Sn3: 89.091(16).

CCDC 650852 (**1**), CCDC-650853 (**2**), CCDC-650854 (**3**) and CCDC-650855 (**4**) contain 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.

Table 1: Crystal and structure refinement parameters for compounds **1**, **2**, **3** and **4**.

	1	2	3	4
empirical formula	C ₁₄₅ H ₃₃₈ B ₆₆ N ₈ NiSn ₆	C ₈₄ H ₂₂₄ B ₄₄ N ₆ NiSn ₄	C ₇₂ H ₂₁₈ B ₆₆ K ₂ N ₂ Na ₄ O ₁₂ PdS ₆	C ₇₂ H ₂₁₈ B ₆₆ K ₂ N ₂ Na ₄ O ₁₂ PtSn ₆
M _r [g mol ⁻¹]	3678.6	2327.6	3006.6	3095.45
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
temperature [K]	173	173	173	173
crystal system	monoclinic	triclinic	monoclinic	monoclinic
θ range [°]	5.68–25.68	5.68–25.68	5.67–25.68	3.02–27.00
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
a [Å]	16.9482(11)	14.1863(15)	14.9148(8)	14.9048(8)
b [Å]	34.791(2)	16.0046(18)	29.0382(16)	29.0561(10)
c [Å]	16.9165(10)	16.5138(16)	16.6765(9)	16.6484(15)
α [°]	90.00	78.190(8)	90.00	90.00
β [°]	95.428(5)	85.384(8)	96.581(4)	96.765(4)
γ [°]	90.00	64.018(6)	90.00	90.00
volume [Å ³]	9930.0(10)	3298.9(6)	7176.7(7)	7159.8(8)
Z	2	1	2	2
ρ _{calc} [g/cm ⁻³]	1.23	1.172	1.391	1.435
μ [mm ⁻¹]	0.880	0.925	1.266	2.119
R _{int}	0.0811	0.0587	0.0640	0.0937
reflections collected	58330	37368	53047	91152
unique reflections	18563	12323	13484	15243
observed reflections	13499	9264	10364	12365
parameters/restraints	1012/24	520/125	547/152	571/152
absorption correction	numerical	numerical	numerical	numerical
max./min. transmission	0.7928/0.9348	0.7519/0.8764	0.7928/0.9348	0.7519/0.8764
R ₁ (all/obs. data)	0.0881/0.0551	0.0915/0.0637	0.0946/0.0674	0.0729/0.0578
wR ₂ (all/obs. data)	0.1241/0.1116	0.1489/0.136	0.1657/0.1528	0.1419/0.1337
GOF (all/obs. data)	1.041/1.040	1.106/1.106	1.125/1.124	1.093/1.093

¹¹⁹Sn Mössbauer spectroscopy: A Ca^{119m}SnO₃ source was available for the ¹¹⁹Sn Mössbauer spectroscopic investigation. The sample was placed within a thin-walled glass container at a thickness of about 10 mg Sn/cm². A palladium foil of 0.05 mm thickness was used to reduce the tin K X-rays concurrently emitted by this source. The measurement was conducted in the usual transmission geometry at 77 K.

¹¹⁹Sn VACP-MAS: NMR spectra of solid samples were obtained on a Bruker DSX-200 NMR spectrometer operating at 200.13 (¹H) and 74.60 MHz (¹¹⁹Sn). The powdered samples were spinning about the magic angle at 10 kHz in 4 mm o.d. zirconia rotors. ¹¹⁹Sn NMR spectra were obtained after single-pulse excitation, or VACP, and under high-power ¹H decoupling. Chemical shifts are referenced with respect to external SnMe₄ (¹¹⁹Sn) using the chemical shift of SnCy₄, -97.35 ppm, as secondary chemical shift reference. MAS spectra were analyzed using the program HBA32^[10]. Errors in chemical shifts are estimated to be 2 ppm, because of the greater line widths in the ¹¹⁹Sn MAS spectra (2.5 kHz) attributed to ¹¹⁹Sn–¹¹B spin-spin interactions. Principal components of the chemical shift tensors are accurate to about 2% of Ω. The simulation of the MAS ¹¹⁹Sn spectrum has been performed using the program WSolids1.^[11]

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