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$[Cp^*RuPb_{11}]^{3-}$ and $[Cu@Cp^*RuPb_{11}]^{2-}$: Centered and Non-Centered Transition-Metal Substituted Zintl Icosahedra.

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1. Experimental Section

1.1. General Data

All reactions were performed under nitrogen atmosphere inside a dry box (Vacuum Atmospheres Company). Electrospray mass spectra were recorded from CH_3CN solutions on a Finnigan mass spectrometer by way of direct injection. The samples were ionized by using an ESI probe and detected in the negative ion mode. Energy dispersive X-ray spectroscopy (EDX) analysis was performed on Hitachi SU-70 SEM, operated at an acceleration voltage of 25 keV. Data acquisition was performed with an accumulation time of 60 s. ^{1}H- (104.63 MHz), ^{13}C- (104.63 MHz) and ^{207}Pb- spectra (83.71 MHz, 104.63 MHz and 125.55 MHz) were recorded on a Bruker DRX400/500/600 AVANCE spectrometer. The pulse sequence used ^{207}Pb NMR studies were the standard Bruker pulse programs with 90° pulse strength and 1.0 s relaxation delays were used. The signals were confirmed and verified by repeating the final measurements with different transmitter offsets. The ^{207}Pb shifts were referenced to 1 M $Pb(NO_3)_2$ in D_2O (-2961.2 ppm) at room temperature. ^{63}Cu- spectra (104.63 MHz) were recorded on a Bruker DRX500 AVANCE spectrometer, and ^{63}Cu- shifts were referenced to $\{[Cu(CH_3CN)_4](ClO_4)\}$ in CH_3CN (0 ppm).

1.2. Chemicals

K_4Pb_9 were made by high-temperature fusion (~1100 °C) of stoichiometric amounts of the elements. The chemicals were loaded into evacuated, quartz tubes and carefully heated with a natural gas/oxygen flame behind a blast shield (temperature around 1100 °C). Chloro(pentamethylcyclopentadienyl)(cyclooctadiene)ruthenium(II) ([Cp*Ru(COD)Cl]) was purchased from Sigma-Aldrich. $[Cu(PPh_3)_3Cl]$ was prepared according reported literature.[1] 18-crown-6, *d₆*-DMSO, *d₇*-DMF was purchased from Fisher-Scientific. Anhydrous ethylenediamine (en) and dimethylformamide (DMF) were purchased from Fisher-Scientific, vacuum-distilled from K_4Sn_9, and stored under N_2. Toluene was purchased from Fisher-scientific, distilled from sodium/benzophenone and stored under dinitrogen. The percentage yields were calculated relative to the amount of K_4Pb_9 alloy precursor utilized.

1.3. Preparation of $[K(18\text{-crown-}6)]_2[K(18\text{-crown-}6)(en)_2](1)$

In vial 1, K_4Pb_9 (200 mg, 0.1 mmol) was dissolved in en (~2 mL), giving a dark black solution. Three equivalents of solid 18-crown-6 (80 mg, 0.3 mmol) were added to the solution and allowed to stir for about 30 minutes. In vial 2, [Cp*Ru(COD)Cl] (38 mg, 0.1 mmol) was dissolved in toluene (~1 mL) to produce a light-yellow solution. The contents of vial 2 were slowly added to vial 1 with vigorous stirring. The reaction mixture was stirred first at r.t. for 0.5 h, then increased the temperature to 65 °C for about 3 hours, finally keep at r.t. for another 1 hour stirring, yielding a dark-brown solution. The reaction mixture was then filtered through tightly packed glass wool and carefully layered with toluene in a straight tube. Dark crystals were isolated in the tube after two weeks (c.a. 37% yield, based on K_4Pb_9). EDX analysis on the crystals showed the presence of K, Ru, Pb atoms. (Table S4, Fig. S13) ESI-MS, m/z = 2516, $[Cp^*RuPb_{11}]^{1-}$; 2555, $[Cp^*RuPb_{11}K]^{1-}$; 2819, $[Cp^*RuPb_{11}K(18\text{-crown-}6)]^{1-}$; 3123, $[Cp^*RuPb_{11}K_2(18\text{-crown-}6)_2]^{1-}$. ^{207}Pb NMR (*d₇*-DMF, 25 °C): δ = 315 ppm, -88 ppm, -365 ppm (*v.s.* 1.0 M $Pb(NO_3)_2$, δ = -2961 ppm). Errors in coupling constants were estimated from the experimental digital resolution and line width of the corresponding spectral lines. The average coupling constant is reported in the text.

1.4. Preparation of $\{[K(18\text{-crown-}6)]_2(tol)_2\}(2)$

In vial 1, K_4Pb_9 (200 mg, 0.1 mmol) was dissolved in en (~2 mL), giving a dark black solution. Three equivalents of solid 18-crown-6 (80 mg, 0.3 mmol) were added to the solution and allowed to stir for about 30 minutes. Then solid $[Cu(PPh_3)_3Cl]$ (89 mg, 0.1 mmol) was added into vial 1, and kept siring for about two hours at room temperature. In vial 2, [Cp*Ru(COD)Cl] (38 mg, 0.1 mmol) was dissolved in tol (~1 mL) to produce a light-yellow solution. The contents of vial 2 were slowly added to vial 1 with vigorous stirring. The reaction mixture was stirred first at r.t. for 0.5 h, then increased the temperature to 65 °C for about 3 hours, finally cooling down to r.t. for another 1 hour with stirring, yielding a dark-black solution. The reaction mixture was then filtered through tightly packed glass wool and carefully layered with toluene in a straight tube. Dark crystals were isolated in the tube after one weeks (c.a. 15% yield, based on K_4Pb_9). EDX analysis on the crystals showed the presence of K, Cu, Ru, Pb atoms. (Table S5, Fig. S14) ESI-MS, m/z = 2581, $[Cu@Cp^*RuPb_{11}]^{1-}$; 2619, $[Cu@Cp^*RuPb_{11}K]^{1-}$; 2883, $[Cu@Cp^*RuPb_{11}K(18\text{-crown-}6)]^{1-}$. ^{207}Pb NMR (*d₆*-DMSO, 25 °C): δ = -430 ppm, -623 ppm (*v.s.* 1.0 M $Pb(NO_3)_2$, δ = -2961 ppm). ^{63}Cu NMR (*d₆*-DMSO, 25 °C): δ = 885 ppm, $\Delta\nu_{1/2}$ = 9015 Hz. Errors in coupling constants were estimated from the experimental digital resolution and line width of the corresponding spectral lines. The average coupling constant is reported in the text.

2. Crystallographic Studies

2.1. [K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$](1)

A black needle crystal with dimensions 0.19 x 0.10 x 0.019 mm^3 was placed and optically centered on the Bruker Smart Apex II CCD system at 150(2) K. The crystal was kept at 150(2) K during the data collection period. The integral intensity data were corrected for absorption using the multi-scan method of SADABS software.[2] The structure was solved with the ShelXT program and refined with the XL program and Least Squares minimization using ShelX software package.[3-5] H atoms were positioned from geometric considerations and refined as riding on the attached atom with U_{iso} constrained to be 20% larger than U_{eqv} of the attached atom. Two of the three K-crown counter-ions and both ethylenediamine molecules are disordered in two alternative orientations. Therefore, they were refined with geometry restrained to be similar and atomic displacement parameters to correspond to rigid body motions.

2.2. {[K(18-crown-6)]$_2$(tol)$_2$}(2)

A black plate crystal with dimensions 0.51 × 0.175 × 0.008 mm^3 was placed and optically centered on the Bruker Smart Apex II CCD system at 150(2) K. The crystal was kept at 150(2) K during the data collection period. The integral intensity data were corrected for absorption using the multi-scan method of SADABS software.[2] The structure was solved with the ShelXT program and refined with the XL program and Least Squares minimization using ShelX software package.[3-5] One of the two [K-18-crown-6] as well as one toluene solvent molecules are disordered in two different alternative orientations in about 1:1 ratio. Therefore, they were refined with geometry restrained to be similar and atomic displacement parameters to be similar and correspond to rigid body motions. H atoms were positioned from geometric considerations and refined as riding on the attached atom with U_{iso} constrained to be 20% (50% for methyl group) larger than U_{eqv} of the attached atom.

References:

[1] Reichle, W. T. *Inorg. Chim. Acta*. **1971**, 325-332.

[2] Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.

[3] Sheldrick, G. M. *SHELXL-2014.* **2014**, University of Gottingen, Germany.

[4] Sheldrick, G. M. *Acta Cryst*. **2015**, *C17*, 3-8.

[5] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

3. X-ray Crystal Structure Supporting Figures and Tables for [K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$](1) and {[K(18-crown-6)]$_2$(tol)$_2$}(2)

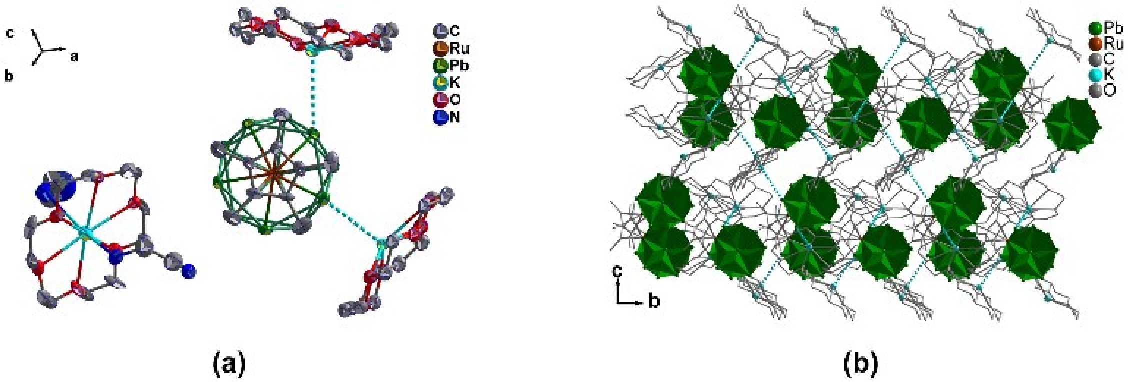


Fig. S1 (a) The molecular structure of {[K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$]}**1**, with blue dashed lines showing the ion pair contacts between K and Pb atoms; (b) The packing diagram of **1** salt in *bc* plane, the thick blue dashed lines representing the short contacts between K and the Pb atoms, which facilitates the supramolecular packing.

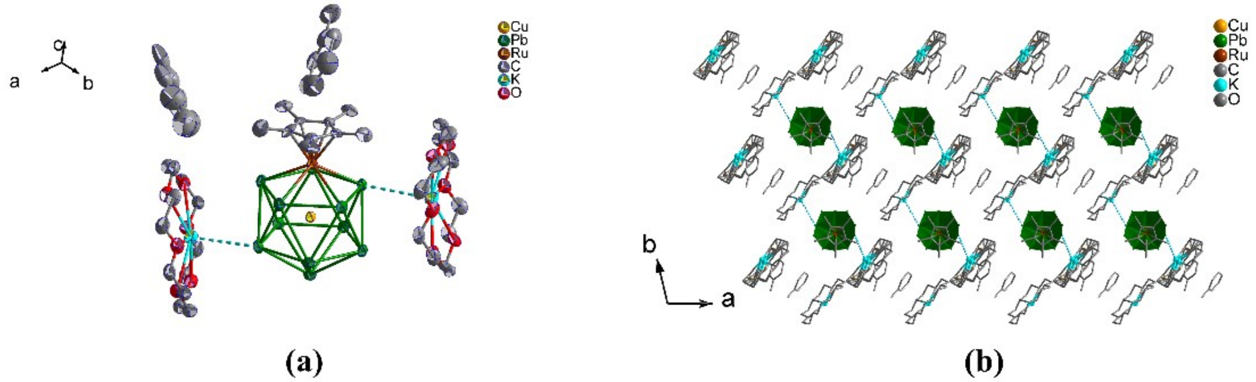


Fig. S2 (a) The molecular structure of {[K(18-crown-6)]$_2$(tol)$_2$}**2**, with blue dashed lines showing the ion pair contacts between K and Pb atoms; (b) The packing diagram of **2** salt in *ab* plane, the thick blue dashed lines representing the short contacts between K and the Pb atoms, which facilitates the supramolecular packing.

Table S1. Crystallographic Data and Parameters for {[K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$]}(**1**) and {[K(18-crown-6)]$_2$(tol)$_2$}(**2**).

Compound	{[K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$]}(**1**)	{[K(18-crown-6)]$_2$(tol)$_2$}(**2**)
Empirical formula	$C_{49}H_{99}K_3N_3O_{18}Pb_{11}Ru$	$C_{45}H_{75}CuK_2O_{12}Pb_{11}Ru$
Formula weight	3515.77	3323.94
Crystal size	0.19 × 0.10 × 0.015	0.51 × 0.175 × 0.008
Crystal system	Monoclinic	Triclinic
Space group	*C2/c (No. 15)*	*P-1 (No. 2)*
a (Å)	45.648(5)	13.1800(9)
b (Å)	14.2377(16)	13.1850(9)
c (Å)	25.141(3)	20.7259(14)
α (°)	90	92.8432(11)
β (°)	93.2134(16)	104.2737(11)
γ (°)	90	102.1908(10)
V (Å^3)	16314(3)	3392.1(4)
Z	8	2
D_{calc} (g/cm^3)	2.863	3.254
μ(Mo-Kα) (mm^{-1})	22.996	27.875
F(000)	12488.0	2902.0
Reflections collected	47125	50338
Independent reflections	14365	19178
Data/Restraints/Parameter	14365/2148/1124	19178/979/854
Goodness-of-fit	0.946	0.956
R_1 [$I > 2\sigma(I)$]^a	0.0433	0.0346

wR_2 (all data)[b]	0.1161	0.0552
CCDC number	1999074	1999075

$^aR_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, $^bwR_2 = \{\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$

Table S2. Selected bond lengths (Å) and bond angles (°) of $\{[K(18\text{-crown-6})]_2[K(18\text{-crown-6})(en)_2]\}$**1**.

C1-Ru1	2.211(13)	Ru1-Pb4	2.9346(12)	Pb3-Pb4	3.0142(8)	Pb5-Pb11	3.2294(9)
C2-Ru1	2.189(14)	Ru1-Pb3	2.9384(12)	Pb3-Pb9	3.2167(8)	Pb5-Pb10	3.2548(8)
C3-Ru1	2.203(14)	Ru1-Pb5	2.9443(13)	Pb3-Pb8	3.2425(8)	Pb6-Pb7	3.2089(8)
C4-Ru1	2.193(14)	Pb2-Pb3	3.0163(8)	Pb4-Pb5	3.0251(8)	Pb6-Pb11	3.2537(8)
C5-Ru1	2.209(14)	Pb2-Pb6	3.0313(8)	Pb4-Pb10	3.2330(9)	Pb7-Pb11	3.1358(9)
Ru1-Pb2	2.9080(12)	Pb2-Pb7	3.2283(9)	Pb4-Pb9	3.2527(8)	Pb7-Pb8	3.1559(8)
Ru1-Pb6	2.9267(12)	Pb2-Pb8	3.2296(8)	Pb5-Pb6	3.0303(8)	Pb7-Pb12	3.1835(8)
Pb8-Pb12	3.1616(8)	Pb9-Pb10	3.1379(9)	Pb10-Pb11	3.1388(9)	Pb11-Pb12	3.1728(9)
Pb8-Pb9	3.1703(8)	Pb9-Pb12	3.1647(9)	Pb10-Pb12	3.1628(8)		

Pb2-Ru1-Pb6	62.60(3)	Pb3-Pb2-Pb6	108.33(2)
Pb2-Ru1-Pb4	113.08(4)	Ru1-Pb2-Pb7	107.46(3)
Ru1-Pb2-Pb6	59.00(3)	Pb7-Pb2-Pb8	58.509(17)

Table S3. Selected bond lengths (Å) and bond angles (°) of $\{[K(18\text{-crown-6})]_2(tol)_2\}$**2**.

Cu1-Ru1	2.8428(13)	Cu1-Pb12	3.0748(11)	Pb8-Pb3	3.2327(5)	Pb3-Pb4	3.0696(4)
Cu1-Pb7	2.9624(9)	Pb12-Pb10	3.1622(4)	Pb8-Pb2	3.2684(5)	Pb3-Pb2	3.0781(4)
Cu1-Pb4	2.9762(9)	Pb12-Pb9	3.1668(5)	Pb9-Pb10	3.1627(4)	Pb4-Ru1	2.9412(7)
Cu1-Pb5	2.9886(8)	Pb12-Pb7	3.2109(5)	Pb9-Pb4	3.2590(5)	Pb4-Pb5	3.0493(4)
Cu1-Pb8	2.9896(8)	Pb12-Pb8	3.2193(5)	Pb9-Pb3	3.2994(6)	Pb5-Ru1	2.9659(7)
Cu1-Pb6	3.0039(9)	Pb12-Pb11	3.2333(4)	Pb10-Pb11	3.1829(4)	Pb5-Pb6	3.0812(5)
Cu1-Pb11	3.0088(10)	Pb7-Pb8	3.1352(4)	Pb10-Pb4	3.2865(6)	Pb6-Ru1	2.9459(7)
Cu1-Pb3	3.0111(10)	Pb7-Pb11	3.1580(4)	Pb10-Pb5	3.2940(5)	Pb6-Pb2	3.0615(4)
Cu1-Pb2	3.0168(11)	Pb7-Pb6	3.2547(5)	Pb11-Pb5	3.2341(5)	Pb2-Ru1	2.9251(6)
Cu1-Pb9	3.0367(9)	Pb7-Pb2	3.2681(6)	Pb11-Pb6	3.2710(6)	Ru1-C4	2.197(7)
Cu1-Pb10	3.0518(10)	Pb8-Pb9	3.1837(5)	Pb3-Ru1	2.9462(6)	Ru1-C5	2.203(7)
Ru1-C2	2.207(9)	Ru1-C1	2.234(9)	Ru1-C3	2.241(8)		

Ru1-Cu1-Pb7	116.69(4)	Cu1-Pb3-Pb9	57.31(2)
Ru1-Cu1-Pb4	60.67(2)	Pb8-Pb3-Pb9	61.428(11)
Ru1-Pb3-Pb9	106.328(17)	Pb11-Pb3-Pb9	108.909(13)
Cu1-Ru1-Pb4	61.91(2)	Ru1-Pb4-Pb5	59.320(14)
Pb2-Ru1-Pb4	115.19(2)	Ru1-Pb4-K1	129.40(3)
Ru1-Pb4-Cu1	57.42(3)	Cu1-Pb4-K1	130.30(3)
Pb7-Cu1-Pb4	177.36(4)	Pb10-Pb12-Pb7	106.459(13)
Cu1-Pb12-Pb10	58.569(19)	Cu1-Pb12-Pb8	56.661(18)
Pb5-Pb4-K1	168.52(3)	Pb3-Pb4-K1	82.67(3)

4. ESI Mass Spectra for [K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$](1) and {[K(18-crown-6)]$_2$(tol)$_2$}(2)

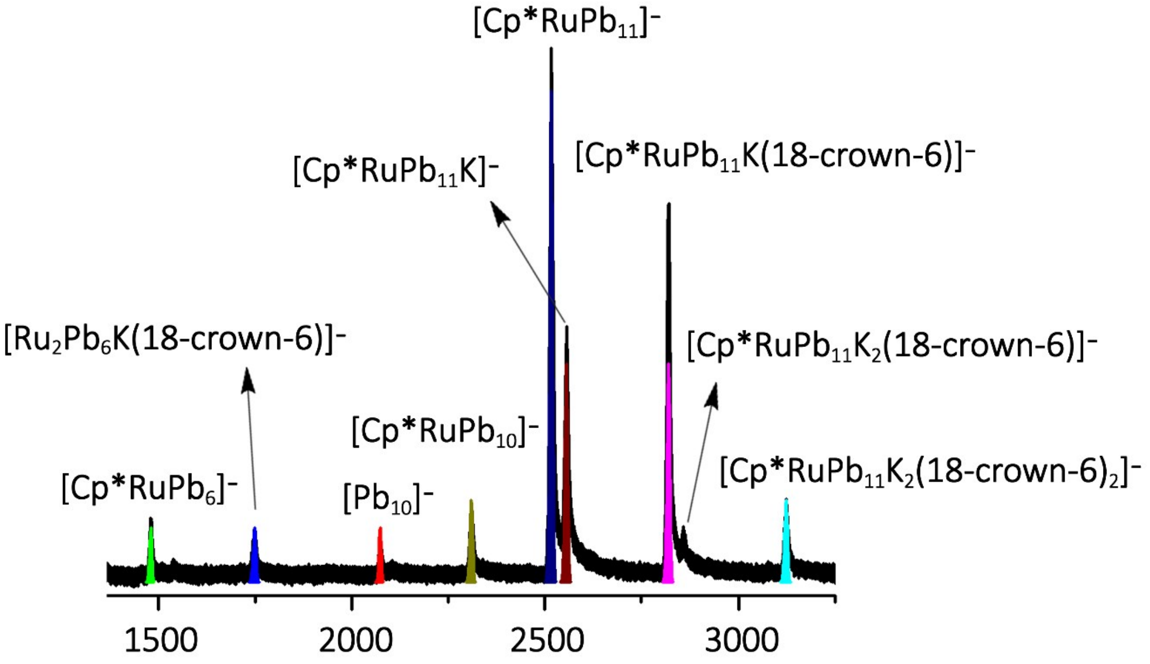
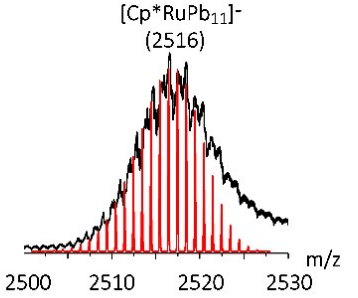
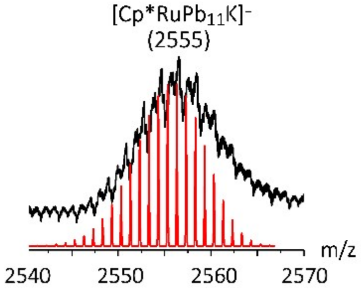


Fig. S3 Electrospray mass spectrum (negative ion mode) of [K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$](**1**) recorded from a CH$_3$CN solution, showing a dominant peak corresponding to [Cp*RuPb$_{11}$]$^{1-}$ (m/z = 2516) along with its corresponding K/crown anions, [Cp*RuPb$_{11}$K]$^{1-}$ (m/z = 2555), [Cp*RuPb$_{11}$K(18-crown-6)]$^{1-}$ (m/z = 2819), [Cp*RuPb$_{11}$K$_2$(18-crown-6)]$^{1-}$ (m/z = 2858), [Cp*RuPb$_{11}$K$_2$(18-crown-6)$_2$]$^{1-}$ (m/z = 3122), as well as some weaker peaks assigned to [Cp*RuPb$_{10}$]$^{1-}$ (m/z = 2308), [Pb$_{10}$]$^{1-}$ (m/z = 2073), [Ru$_2$Pb$_6$K(18-crown-6)]$^{1-}$ (m/z = 1749) and [Cp*RuPb$_6$]$^{1-}$ (m/z = 1408).


[Cp*RuPb$_{11}$]$^-$
(2516)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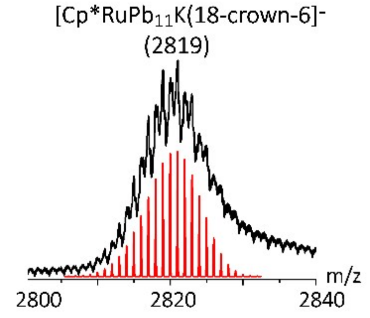
(2555)


[Cp*RuPb$_{11}$K(18-crown-6]$^-$
(2819)

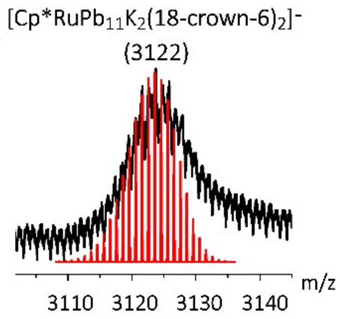

[Cp*RuPb$_{11}$K$_2$(18-crown-6)$_2$]$^-$
(3122)

Fig. S4 Enlarged isotope distributions for measured (black) and simulated (bottom, red) spectrum of the fragments [Cp*RuPb11]$^{1-}$ (m/z = 2516), [Cp*RuPb$_{11}$K]$^{1-}$ (m/z = 2555), [Cp*RuPb$_{11}$K(18-crown-6)]$^{1-}$ (m/z = 2819) and [Cp*RuPb$_{11}$K$_2$(18-crown-6)$_2$]$^{1-}$ (m/z = 3122) in {[K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$]}**1**.

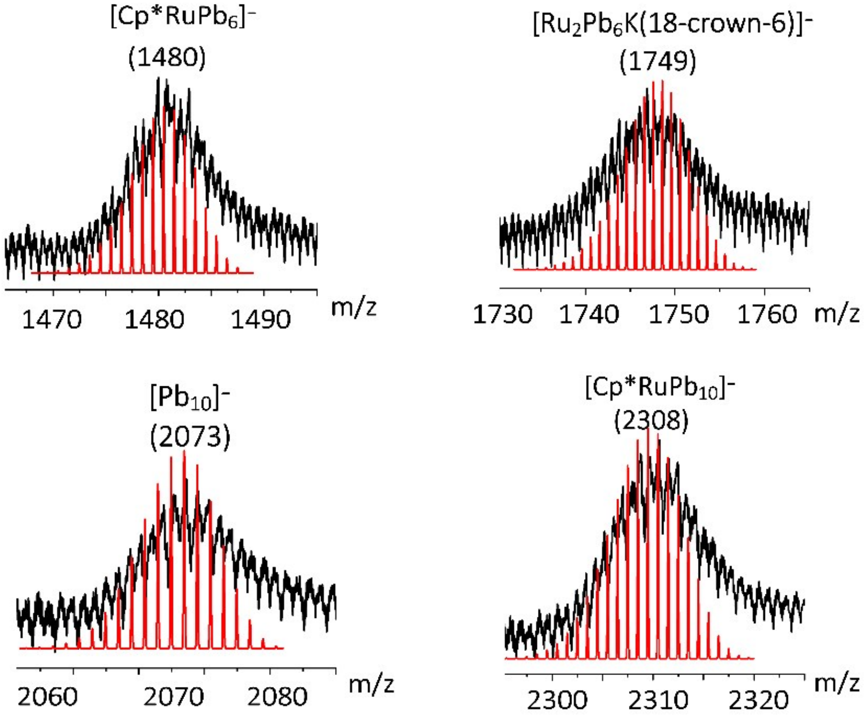


Fig. S5 Enlarged isotope distributions for measured (black) and simulated (bottom, red) spectrum of the fragments [Cp*RuPb$_6$]$^{1-}$ (m/z = 1480), [Ru$_2$Pb$_6$K(18-crown-6)]$^{1-}$ (m/z = 1749), [Pb$_{10}$]$^{1-}$ (m/z = 2073), and [Cp*RuPb$_{10}$]$^{1-}$ (m/z = 2308) in {[K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$]}**1**.

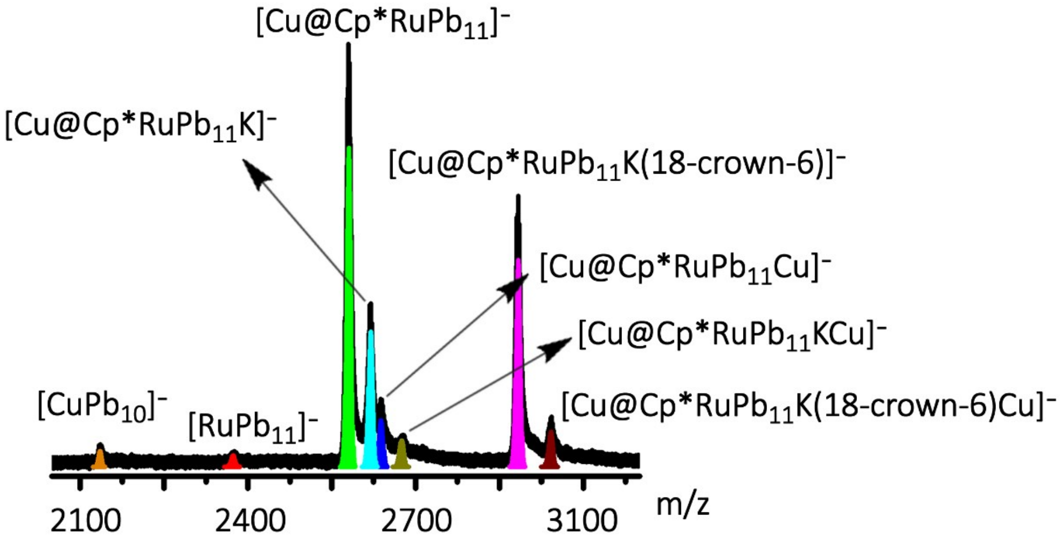


Fig. S6 Electrospray mass spectrum (negative ion mode) of {[K(18-crown-6)]$_2$(tol)$_2$}(**2**) recorded from a CH$_3$CN solution, showing a dominant peak corresponding to [Cu@Cp*RuPb$_{11}$]$^{1-}$ (m/z = 2581) along with its corresponding K/crown anions,

$[Cu@Cp^*RuPb_{11}K]^{1-}$ (m/z = 2619), $[Cu@Cp^*RuPb_{11}K(18\text{-crown-}6)]^{1-}$ (m/z = 2883), as well as some weaker peaks assigned to $[Cu@Cp^*RuPb_{11}Cu]^{1-}$ (m/z = 2645), $[Cu@Cp^*RuPb_{11}KCu]^{1-}$ (m/z = 2683), $[Cu@Cp^*RuPb_{11}K(18\text{-crown-}6)Cu]^{1-}$ (m/z = 2947), $[CuPb_{10}]^{1-}$ (m/z = 2136), and $[RuPb_{11}]^{1-}$ (m/z = 2380).

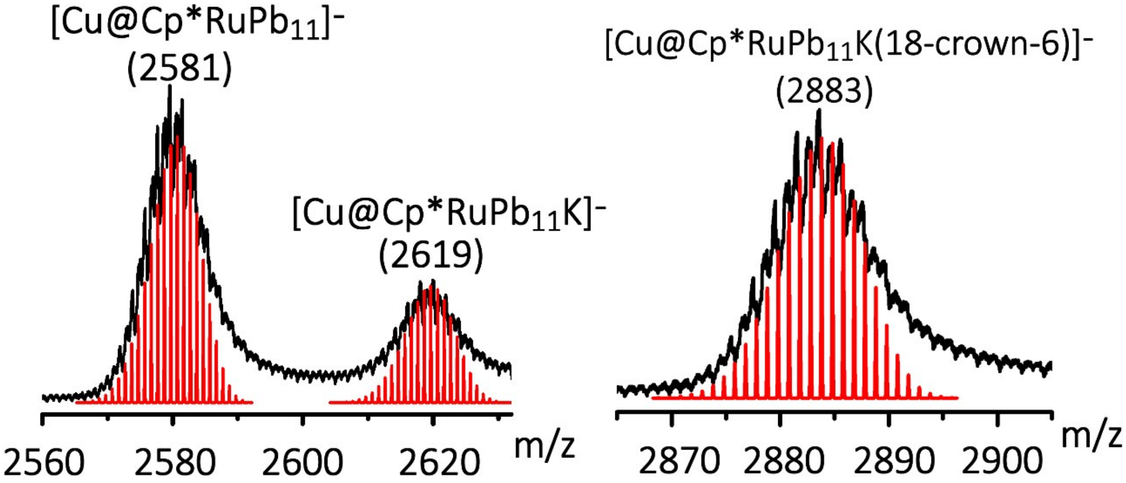


Fig. S7 Enlarged isotope distributions for measured (black) and simulated (bottom, red) spectrum of the fragments to $[Cu@Cp^*RuPb_{11}]^{1-}$ (m/z = 2581), $[Cu@Cp^*RuPb_{11}K]^{1-}$ (m/z = 2619), $[Cu@Cp^*RuPb_{11}K(18\text{-crown-}6)]^{1-}$ (m/z = 2883) in $\{[K(18\text{-crown-}6)]_2(tol)_2\}$**2**.

5. NMR Data for $[K(18\text{-crown-}6)]_2[K(18\text{-crown-}6)(en)_2]$(1) and $\{[K(18\text{-crown-}6)]_2(tol)_2\}$(2)

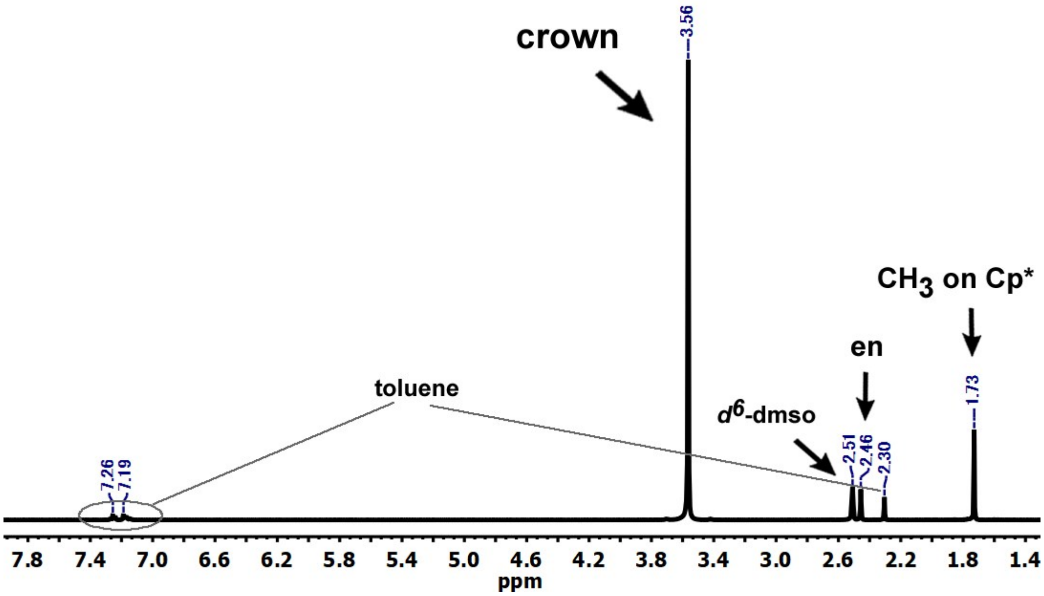


Fig. S8 ^{1}H-NMR of crystalline sample for [K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$](**1**) in *d*^{6}-DMSO. The data were collected at 104.63 MHz and room temperature.

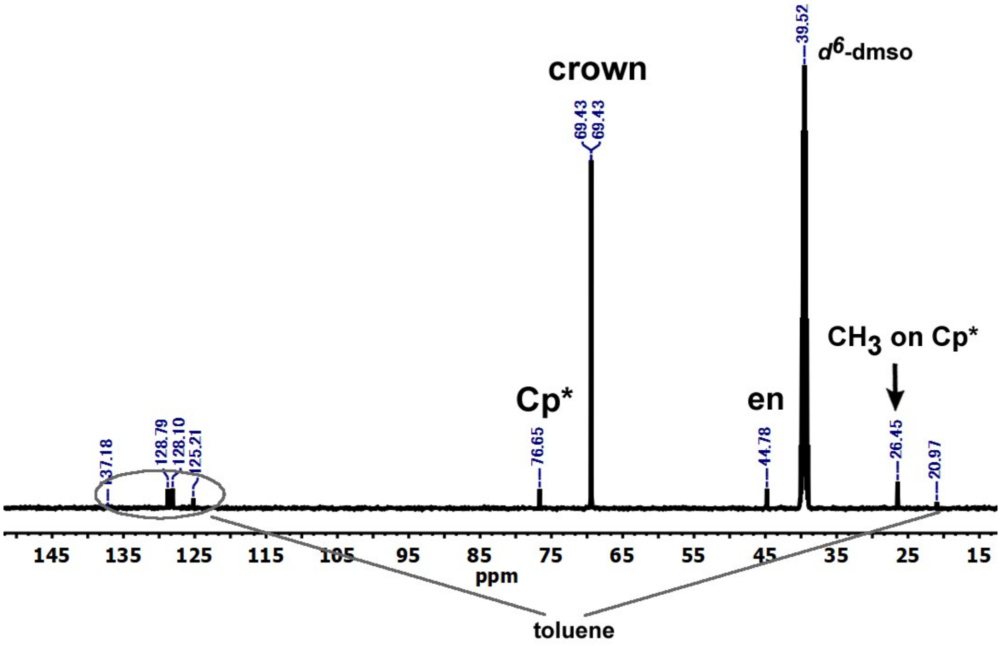


Fig. S9 ^{13}C-NMR of crystalline sample for [K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$](**1**) in *d*^{6}-DMSO. The data were collected at 104.63 MHz and room temperature.

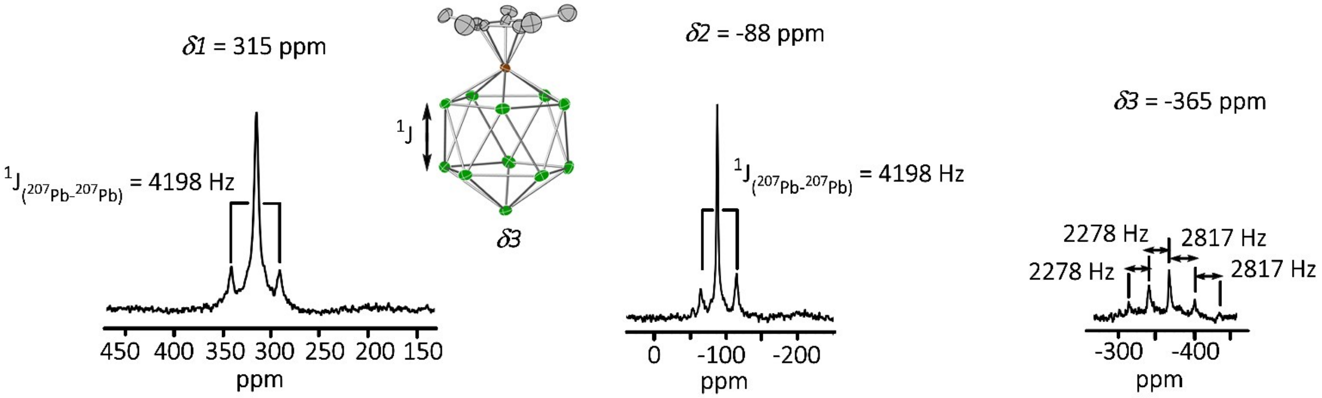


Fig. S10 207Pb-NMR of crystalline [K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$](**1**) sample in *d*^{7}-DMF. The data were collected at 83.71 MHz and room temperature.

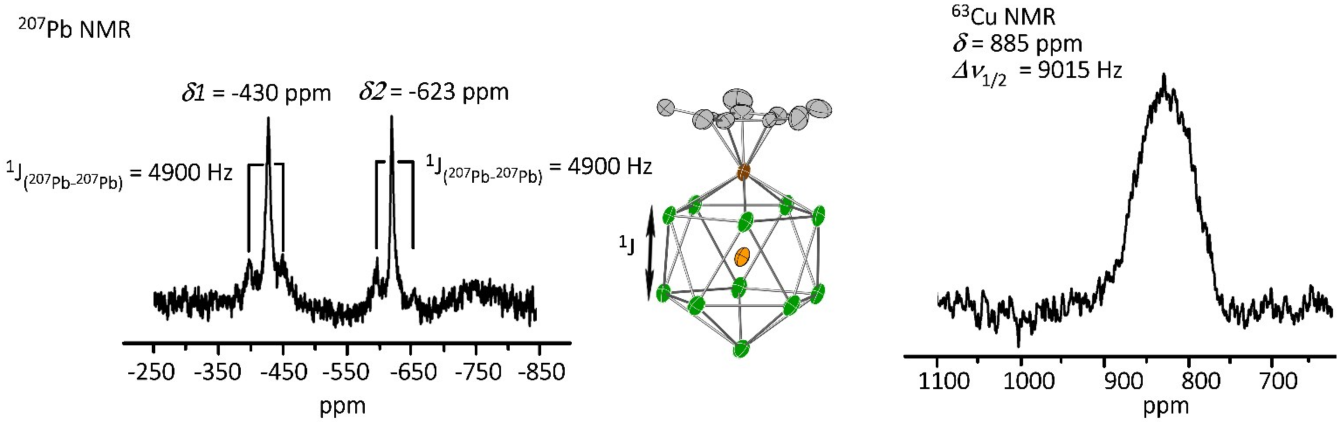


Fig. 11 ^{207}Pb-(left) and ^{63}Cu-(right) NMR of crystalline {[K(18-crown-6)]$_2$(tol)$_2$}(**2**) sample in d_6-DMSO. The data were collected at 83.71 MHz and room temperature.

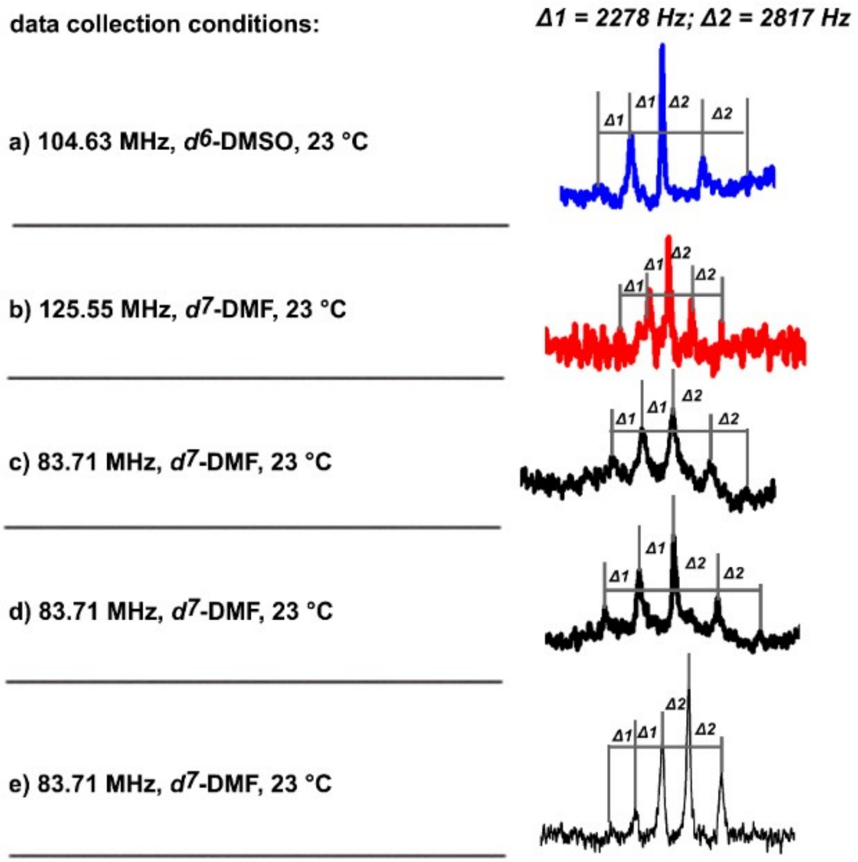


Fig. S12 ^{207}Pb-NMR of crystalline sample for [K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$](**1**) in *d*^{6}-DMSO/*d*^{7}-DMF, focusing on the apical lead atom (Pb12, $\delta 3$ = -365 ppm). The data were collected at different frequencies (83.71 MHz, 104.63 MHz and 125.55 MHz) and room temperature. This spectrum showed that under different collecting frequencies, the apical Pb12 give the same multiplet pattern with the same peak separation in Hz, indicating that the multiplet arises from second order coupling associated with the Pb12 atom.

6. Edx Data for [K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$](1) and {[K(18-crown-6)]$_2$(tol)$_2$}(2)

Table S4. EDX analysis of {[K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$]}**1**.

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%] (cal)
Carbon	6	K-series	17243	16.72	18.61	**38.77 (59.24)**
Oxygen	8	K-series	15756	30.90	34.39	**53.78 (22.67)**
Potassium	19	K-series	14973	2.69	3.00	**1.92 (3.61)**
Ruthenium	44	L-series	6978	1.54	1.71	**0.42 (1.23)**
Lead	82	L-series	18111	37.99	42.29	**5.11 (13.25)**
			Sum:	89.84	100	100

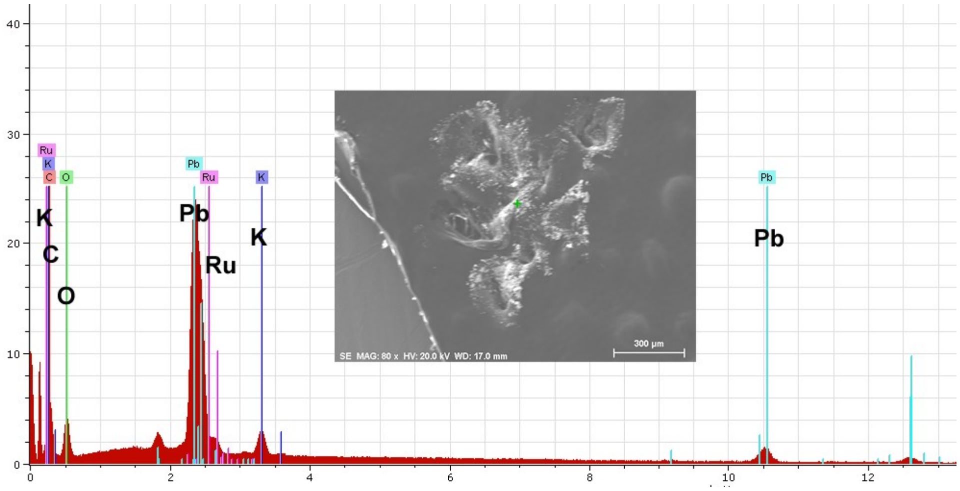


Fig. S13 SEM images and EDX analysis of {[K(18-crown-6)]$_2$[K(18-crown-6)(en)$_2$]}**1**. It shows the presence of K, Ru and Pb.

Table S5. EDX analysis of {[K(18-crown-6)]$_2$(tol)$_2$}**2**.

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%] (cal)
Oxygen	8	K-series	7641	10.06	5.29	**39.74 (44.45)**
Potassium	19	K-series	5998	3.57	2.01	**5.76 (7.41)**
Copper	29	K-series	2311	1.32	0.70	**1.32 (3.70)**
Ruthenium	44	L-series	2289	2.41	1.30	**1.51 (3.70)**
Lead	82	M-series	160092	169.38	90.70	**51.67 (40.74)**
			Sum:	186.74	100	100

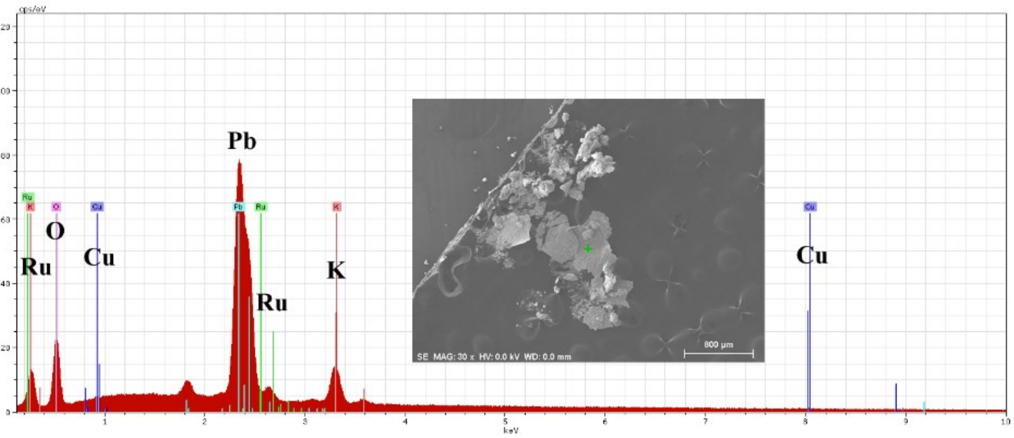


Fig. S14 SEM images and EDX analysis of $\{[K(18\text{-crown-}6)]_2(tol)_2\}$**2**. It shows the presence of K, Ru, Cu and Pb.

7. Computational Details

Theoretical calculations were carried out at the relativistic density functional level of theory[1] by using the ADF code[2], incorporating scalar corrections via the ZORA Hamiltonian.[3] Triple- Slater basis set, plus two polarization functions (STO-TZ2P) for valence electrons, were employed within the generalized gradient approximation (GGA) according to the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.[4,5] The frozen core approximation was applied to the $[1s^2\text{-}5p^6]$ shells for Pb, $[1s^2\text{-}4p^6]$ for Ru, and $[1s^2]$ for C, leaving the remaining electrons to be treated variationally. Geometry optimizations were performed without any symmetry restrain, via the analytical energy gradient method implemented by Versluis and Ziegler.[6] An energy convergence criterion of 10^{-4} Hartree, gradient convergence criteria of 10^{-3} Hartree/Å and radial convergence criteria of 10^{-2} Å were employed for the evaluation of the relaxed structures. The obtained HOMO-LUMO gaps at the TZ2P-ZORA/PBE level are -1.638 eV for $[Pb_{11}RuCp^*]^{3-}$ which contrast to the -3.412 eV calculated for Cp^*_2Ru. At the hybrid TZ2P-ZORA/PBE0 such values exhibits a similar trend with values of -2.805 and -4.628 eV, respectively. In addition, we performed the Boys–Foster localization scheme[7] of the molecular orbitals to give localized molecular orbitals (LMO's), as is implemented in the ADF code. Such LMO's correspond to Lewis-like bonds and lone pairs (2c–2e and 1c–2e), including multicenter delocalized bonds (nc–2e) which are useful for bonding patterns analysis on clusters.

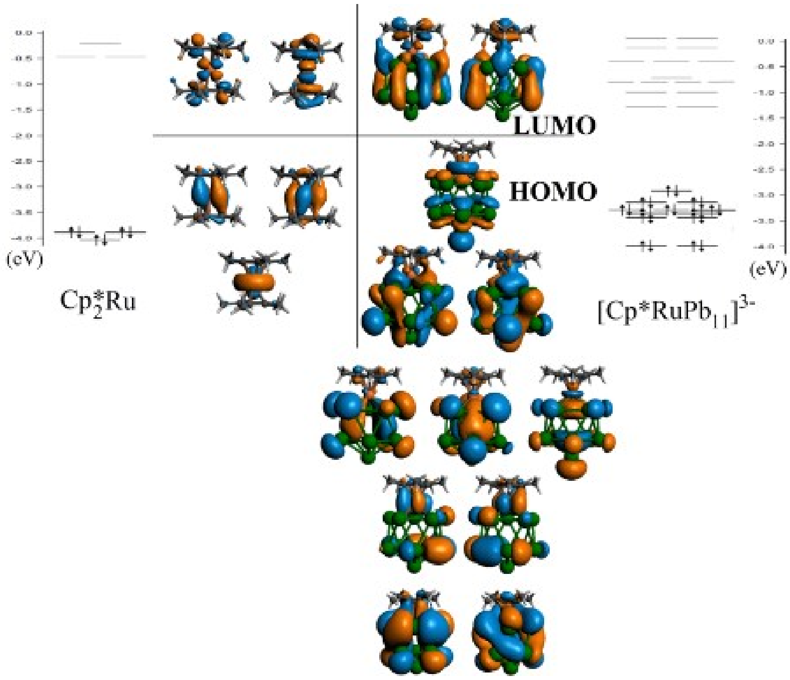


Fig. S15 Comparison between frontier orbitals of Cp^*_2Ru and $[Pb_{11}RuCp^*]^{3-}$, showing extended orbitals from HOMO to HOMO-9 orbitals for the later.

References:

[1] Dyall, K. G.; Fægri, K. *Introduction to Relativistic Quantum Chemistry*; Oxford University Press, New York, **2007**.

[2] Amsterdam Density Functional (ADF) Code, Vrije Universiteit: Amsterdam, The Netherlands. Http://Www.Scm.Com.

[3] van Lenthe, E.; Baerends, E.-J. J.; Snijders, J. G. Relativistic Total Energy Using Regular Approximations. *J. Chem. Phys.* **1994**, *101*, 9783.

[4] Perdew, J. P.; Burke, K.; Wang, Y. Generalized Gradient Approximation for the Exchange-Correlation Hole of a Many-Electron System. *Phys. Rev. B* **1996**, *54* , 16533–16539.

[5] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.

[6] Versluis, L.; Ziegler, T. The Determination of Molecular Structures by Density Functional Theory. The Evaluation of Analytical Energy Gradients by Numerical Integration. *J. Chem. Phys.* **1988**, *88*, 322–328.

[7] Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.*, **1960**, 32, 300-302.

8. Localized molecular orbitals for 1 and 2.

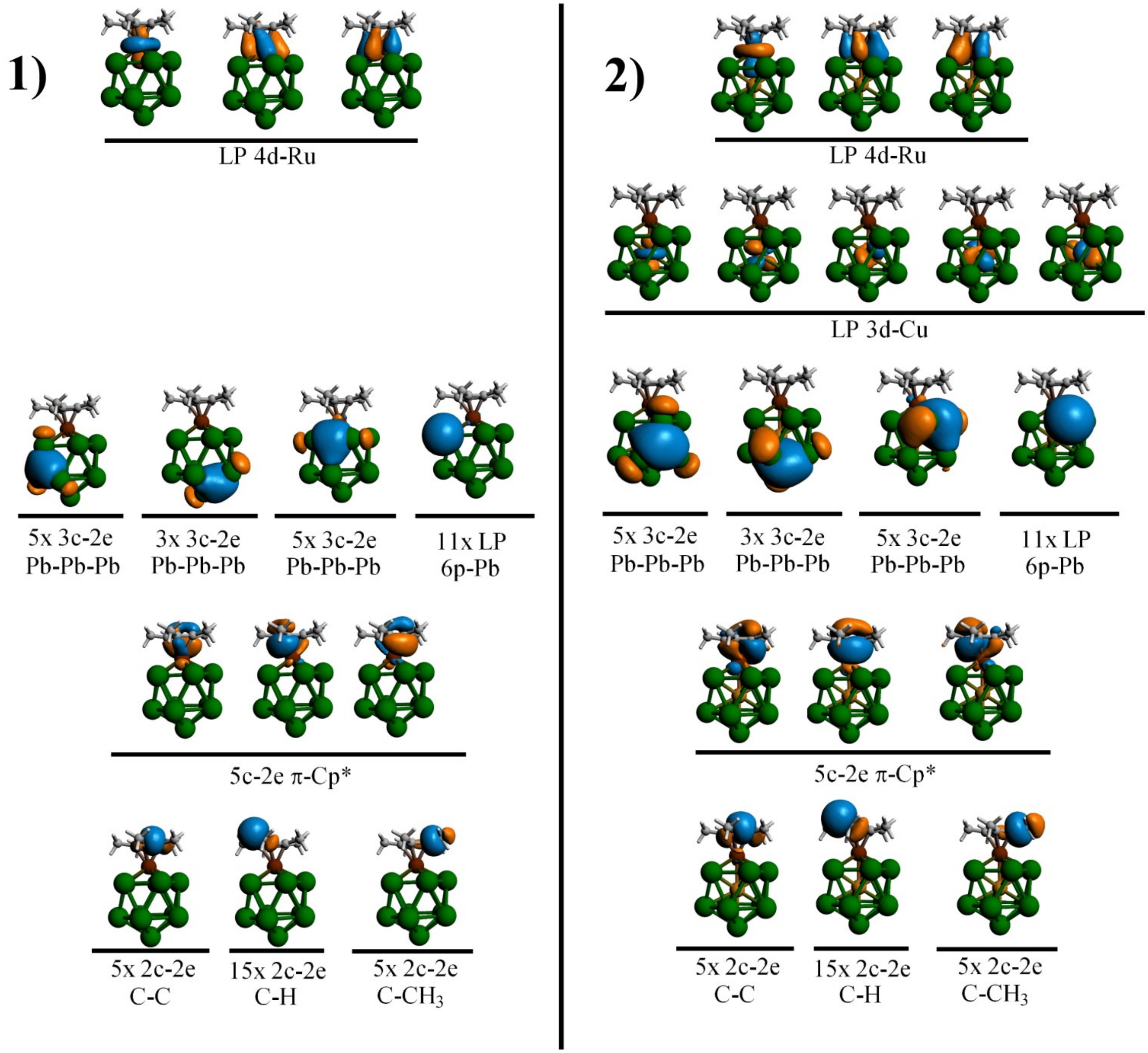


Fig. S16. Localized Molecular Orbitals (LMO) for **1** and **2**. Note the Lone-Pair (LP) character of the 3d-Cu orbitals in **2** (1c-2e 3d-Cu).

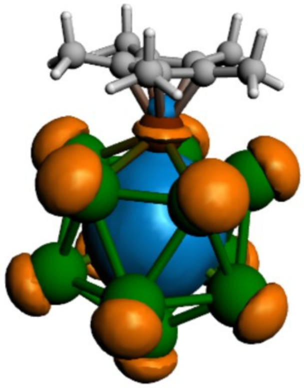


Fig. S17. Bonding interaction between 4s-Cu shell and the totally symmetric radial orbital of the $Pb_{11}Ru$ cage in **2**, supporting the bonding stabilization of the encapsulated d^{10}-Cu atom.

9. Cartesian coordinates for optimized structures (Å). In MultipleXYZ format.

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Cluster 1. [$Pb_{11}RuCp^*$]$^{3-}$

Pb	2.206555947	-1.622842599	1.439772289
Pb	0.789709347	-2.476231824	-1.427794361
Pb	2.599149447	-0.014077974	-1.427432636
Pb	-0.857708178	-2.600600874	1.441301089
Pb	0.003050097	-0.004604874	3.193146964
Pb	2.223819297	1.593455226	1.442616364
Pb	-2.094673128	1.538439876	-1.421830286
Pb	-0.829828053	2.603717076	1.446335989
Pb	-2.734339428	0.011600601	1.444838389
Pb	0.816074322	2.467064976	-1.423389311
Ru	-0.001206753	0.000381276	-2.848796411
Pb	-2.111040453	-1.516728474	-1.425014636
C	-0.367387122	1.139175324	-4.682938189
C	-1.199623722	0.005533074	-4.681348939
C	-0.377941497	-1.135918926	-4.683183889
C	0.961859628	-0.706709301	-4.686030889
C	0.968430153	0.699893949	-4.685739364
C	2.130265503	-1.567979451	-4.869482014
H	3.010527678	-1.126893351	-4.448446789
H	1.996876728	-2.520842076	-4.398465364
H	2.322567678	-1.744957551	-5.913531514
C	-0.826848072	-2.517532926	-4.861352464
H	-0.148666347	-3.209774151	-4.406563714
H	-1.788972222	-2.681469426	-4.420948864
H	-0.898796247	-2.772522726	-5.904528364
C	-2.653319472	0.018054999	-4.852809514
H	-3.102368397	0.853593924	-4.353901039
H	-2.923518297	0.077324274	-5.893502089
H	-3.101662497	-0.868578801	-4.451741314
C	-0.813778197	2.520939474	-4.863285889
H	-0.122315022	3.218612424	-4.435922914
H	-0.917019972	2.762712174	-5.906943439
H	-1.763472072	2.688889074	-4.396880989
C	2.141057778	1.557236799	-4.865960314
H	2.028436503	2.487641274	-4.346055214
H	3.031165503	1.091684049	-4.493243164
H	2.302406628	1.783913574	-5.906277514

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Cluster 2. [$CuPb_{11}RuCp^*$]$^{2-}$

Cu	0.004434300	-0.006616350	0.049369125
Pb	2.232530625	-1.667446950	1.451373300
Pb	0.792098775	-2.535534300	-1.456625625
Pb	2.653526850	-0.034657350	-1.455533625
Pb	-0.881328825	-2.639225550	1.454350950
Pb	0.009223500	-0.012900225	3.215184375
Pb	2.270579025	1.594825050	1.458253875

Pb	-2.124968625	1.580669025	-1.443217425
Pb	-0.819982800	2.639768625	1.466079225
Pb	-2.767967475	0.023373675	1.463348250
Pb	0.850372575	2.508786150	-1.447240275
Ru	-0.000290550	-0.000778050	-2.816217300
Pb	-2.161414125	-1.536974400	-1.450076550
C	-0.369299775	1.144098150	-4.639771500
C	-1.201709925	0.010230675	-4.637208225
C	-0.380820375	-1.131823875	-4.639854375
C	0.959772450	-0.704196675	-4.642305525
C	0.966515550	0.702507975	-4.640450100
C	2.127447075	-1.557388950	-4.868124300
H	3.014120850	-1.141371075	-4.434970800
H	1.994034900	-2.533693500	-4.448655900
H	2.309986575	-1.680548025	-5.920815225
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H	-0.149018025	-3.220353825	-4.452815250
H	-1.787836050	-2.685665775	-4.396572375
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H	-1.780463100	2.700844575	-4.440395700
C	2.139952425	1.548887925	-4.862145600
H	2.000963250	2.531767875	-4.462862625
H	3.018724800	1.138149675	-4.409440425
H	2.337001875	1.654278600	-5.914249575

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Ruthenocene. [Cp^*_2Ru]

Ru	0.000000000	0.000000000	0.000000000
C	0.695002000	-1.014579000	-1.851835000
C	1.179690000	0.347464000	-1.851835000
C	0.034086000	1.229324000	-1.851835000
C	-1.158623000	0.412300000	-1.851835000
C	-0.750154000	-0.974509000	-1.851835000
C	-2.569681000	0.915880000	-1.974166000
H	-3.052023000	1.081019000	-1.001579000
H	-2.600190000	1.870338000	-2.517076000
H	-3.194788000	0.202963000	-2.529344000
C	0.076979000	2.726934000	-1.974166000
H	0.084984000	3.236700000	-1.001579000
H	0.975295000	3.050894000	-2.517076000
H	-0.794214000	3.101143000	-2.529344000
C	2.617256000	0.769458000	-1.974166000
H	3.202955000	0.015218000	-2.517076000
H	2.703937000	1.713649000	-2.529344000
H	3.104546000	0.919371000	-1.001579000
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H	1.004241000	-3.041489000	-2.517076000

H	2.465339000	-2.042050000	-2.529344000
H	1.833731000	-2.668497000	-1.001579000
C	-1.665129000	-2.160889000	-1.974166000
H	-1.971238000	-2.568593000	-1.001579000
H	-2.582300000	-1.894961000	-2.517076000
H	-1.180273000	-2.975705000	-2.529344000
C	0.695002000	1.014579000	1.851835000
C	1.179690000	-0.347464000	1.851835000
C	0.034086000	-1.229324000	1.851835000
C	-1.158623000	-0.412300000	1.851835000
C	-0.750154000	0.974509000	1.851835000
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H	-3.194788000	-0.202963000	2.529344000
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H	0.975295000	-3.050894000	2.517076000
H	-0.794214000	-3.101143000	2.529344000
C	2.617256000	-0.769458000	1.974166000
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H	2.703937000	-1.713649000	2.529344000
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H	-1.971238000	2.568593000	1.001579000
H	-2.582300000	1.894961000	2.517076000
H	-1.180273000	2.975705000	2.529344000

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[Cp*RuC2B9H11]1-

B	1.224305000	-0.889510000	0.439191000
B	0.479521000	-1.475812000	-1.090572000
B	1.551761000	0.000000000	-1.090572000
B	-0.467643000	-1.439257000	0.439191000
B	0.000000000	0.000000000	1.376288000
B	1.224305000	0.889510000	0.439191000
B	-1.255401000	0.912102000	-1.090572000
B	-0.467643000	1.439257000	0.439191000
B	-1.513324000	0.000000000	0.439191000
B	0.479521000	1.475812000	-1.090572000
Ru	0.000000000	0.000000000	-2.634064000
B	-1.255401000	-0.912102000	-1.090572000
C	-0.380023000	1.169590000	-4.561162000
C	-1.229780000	0.000000000	-4.561162000
C	-0.380023000	-1.169590000	-4.561162000
C	0.994913000	-0.722846000	-4.561162000
C	0.994913000	0.722846000	-4.561162000
C	2.209558000	-1.605338000	-4.672139000
H	2.608386000	-1.895104000	-3.688094000
H	1.980069000	-2.533366000	-5.218738000

H	3.021249000	-1.100304000	-5.218738000
C	-0.843976000	-2.597491000	-4.672139000
H	-0.996315000	-3.066342000	-3.688094000
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H	-0.112834000	-3.213391000	-5.218738000
C	-2.731163000	0.000000000	-4.672139000
H	-3.090984000	0.885681000	-5.218738000
H	-3.090984000	-0.885681000	-5.218738000
H	-3.224143000	0.000000000	-3.688094000
C	-0.843976000	2.597491000	-4.672139000
H	-0.112834000	3.213391000	-5.218738000
H	-1.797499000	2.666010000	-5.218738000
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C	2.209558000	1.605338000	-4.672139000
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H	3.021249000	1.100304000	-5.218738000
H	1.980069000	2.533366000	-5.218738000
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H	0.000000000	0.000000000	2.590205000
H	-0.797205000	2.453546000	1.022277000
H	-2.193874000	1.593943000	-1.473672000
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H	2.087111000	-1.516375000	1.022277000
H	0.837985000	-2.579053000	-1.473672000
H	2.711777000	0.000000000	-1.473672000