Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

$[Bi_7M_3(CO)_3]^{2-}$ (M = Co, Rh): A New Architype of 10-vertex Deltahedral Hybrids From Unprecedented Polycyclic η^5–coordination addition of Bi_7^{3-} and trimetallic fragments†

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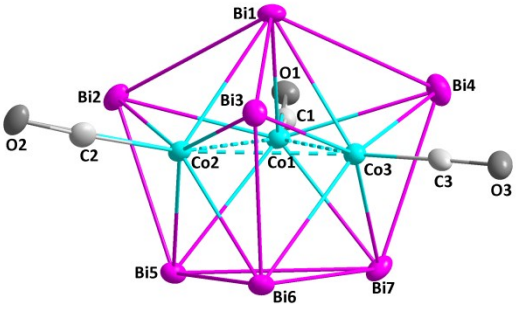
S1 Experimental Details

All manipulations were carried out under argon using standard Schlenk-line and glovebox techniques. Ethylenediamine (Acros, 99%) was distilled over sodium metal and stored in a gastight Schlenk under argon in the glovebox. Toluene was dried with potassium-sodium alloy and then stored in the glovebox. Precursors with nominal composition K_5Bi_4 [1] was synthesized by heating the corresponding mixtures of elements (K: +99%; Bi: 99.999 %, all from Strem) at 800℃ for two days in sealed niobium containers that were jacketed in evacuated fused-silica ampoules. 2,2,2-cryptand(TCI, 99%), $CpCo(CO)_2$ (Tansoole-Alfa) and $Rh(CO)_2(acac)$ (acac = acetylacetonate) (Aladdin, 99%) were used as received.

Synthesis of $[K(2,2,2\text{-ccrypt})]_2[Bi_7(CoCO)_3]$ ·Toluene (**1**): The binary alloy with the nominal composition K_5Bi_4 (51 mg, 0.388 mmol) and 2,2,2-cryptand(90 mg, 0.236 mmol) were dissolved in 2 mL ethylenediamine and stirred for 0.5 hours at room temperature, resulting in a dark green solution, to which $CpCo(CO)_2$ (5 mg, 0.028 mmol) was added. The resulting solution was stirred for 10 minutes at room temperature and turned red-brown. The resulting red-brown solution was filtered *via* a glass fiber pipette and the filtrate was layered with toluene (8 ml). Black, rod crystals of **1**(3 mg, 12.1% based on Co) were obtained after two weeks.

Synthesis of $[K(2,2,2\text{-ccrypt})]_2[Bi_7(RhCO)_3]$ ·Toluene (**2**): The binary alloy with the nominal composition K_5Bi_4 (51 mg, 0.388 mmol) and 2,2,2-cryptand(90 mg, 0.236 mmol) were dissolved in 2 mL ethylenediamine and stirred for 0.5 hours at room temperature, resulting in a dark green solution, to which $Rh(CO)_2(acac)$ (acac = acetylacetonate) (8 mg, 0.031 mmol) was added. The resulting solution was stirred for 10 minutes at room temperature and turned red-brown. The resulting red-brown solution was filtered *via* a glass fiber pipette and the filtrate was layered with toluene (8 ml). Black, rod crystals of **2**(8 mg, 27.8% based on Rh) were obtained after two weeks.

S2 Molecular and Crystal structures



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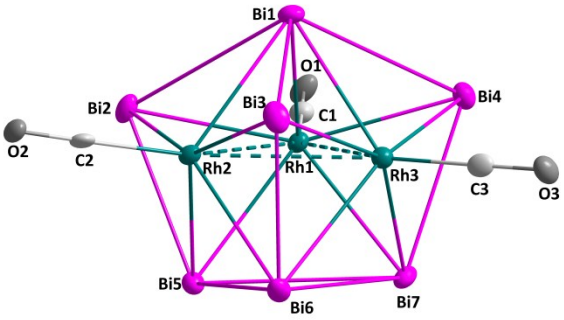

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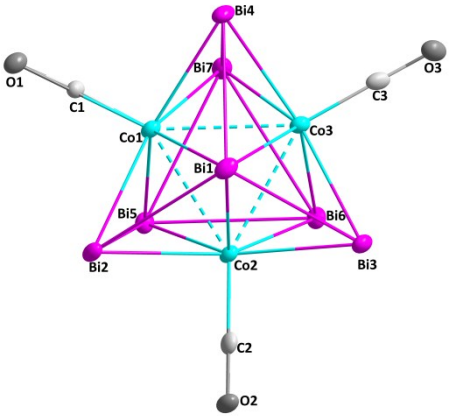

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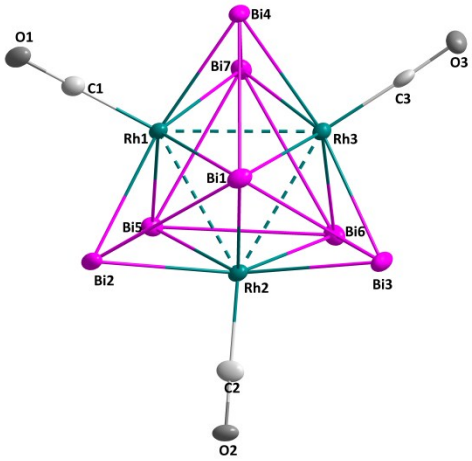

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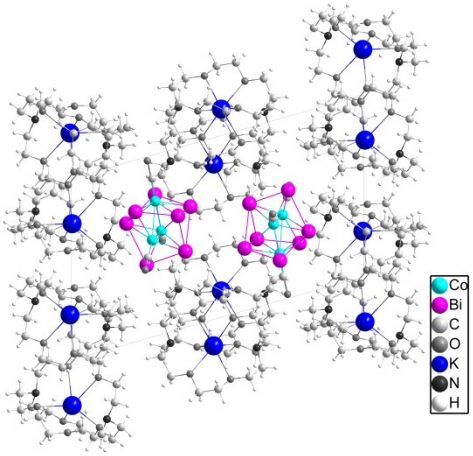
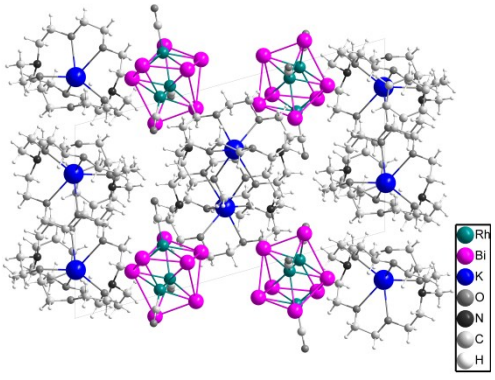




(e) **(f)**

Figure S2.1 (a)(b) Crystallographic molecular structure of **1a** and **2a** with 30% probability thermal ellipsoids. (c)(d) The molecular structure view of **1a** and **2a** along ideal 3-fold axis. (e)(f) The crystal structure of **1** and **2** down *a* axis.

Table S2.1 Bonding lengths comparison.

	Bi-Bi (Å)	Bi-Rh/Bi-Co (Å)	Rh-Rh/Co-Co (Å)	Rh-C/Co-C (Å)
Bi_7^{3-} [a]	2.882(4) - 3.100(5) *av.* 2.967(5)	-	-	-
$[Bi_7(RhCO)_3]^{2-}$	2.9687(9) - 3.5291(10) *av.* 3.2599(11)	2.7379(14) - 2.8194(14) *av.* 2.7704(14)	2.9925(16) - 3.0318(16) *av.* 3.0093(17)	1.714(10) - 1.791(15) *av.* 1.790(17)
$Rh_3(CO)_5(\mu_2\text{-}PPh_2)_3$ [b]	-	-	2.698(1) - 2.806(1) *av.* 2.765(1)	1.804(8) - 1.933(7) *av.* 1.875(9)
$Rh_3(CO)_7(\mu_2\text{-}PPh_2)_3$ [b]	-	-	3.084(11) - 3.223(12) *av.* 3.143(12) Å	1.851(16) - 1.875(22) *av.* 1.858(22)
$[Bi@Rh_{14}(CO)_{27}Bi_2]^{3-}$ [c]	-	2.656(3) - 3.008(4) *av.* 2.731	-	-
$[Bi_7(CoCO)_3]^{2-}$	2.9527(5) - 3.3346(6) *av.* 3.1745(6)	2.6418(14) – 2.7282(13) *av.* 2.6798(14)	2.7760(18) – 2.810(2) *av.* 2.788(2)	1.612(10) – 1.711(10) *av.* 1.1.670(11)
$Cp_3Co_3(CO)_3$ [d]	-	-	2.440(4) - 2.521(4) *av.* 2.473(4)	1.75(4) – 2.11(4) *av.* 1.90(4)
$Co_3(CO)_7(PPh_2)_2$ [e]	-	-	2.482(3) - 2.584(3) *av.* 2.546(3)	1.729(19) - 1.824(17) *av.* 1.782(19)
$[Bi_4Co_9(CO)_{16}]^{2-}$ [f]	-	2.709(1) - 2.757(2) *av.* 2.734(2)	-	-

a, ref. 5a; b, ref. 14; c, ref. 17; d, ref. 16b; e, ref. 16a; f, ref. 18a.

S3 Mass spectrum of 1 and 2

LDI-TOF mass spectrum of 1 and 2 were recorded on a rapifleX MALDI Tissuetyper (Bruker Daltonics, Germany) in negative-ion mode.

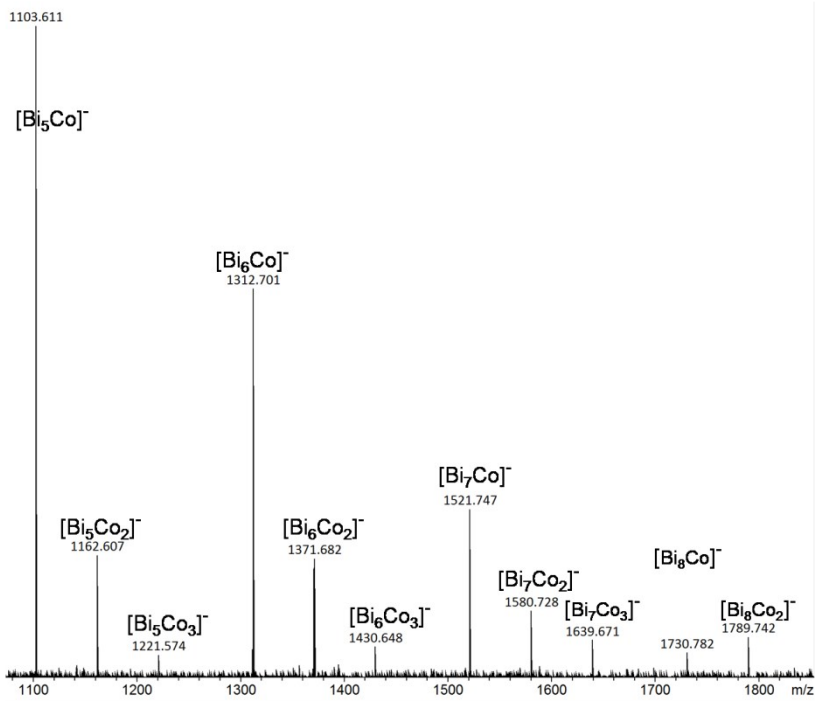


Fig. S3.1. LDI-TOF mass spectrum of 1.

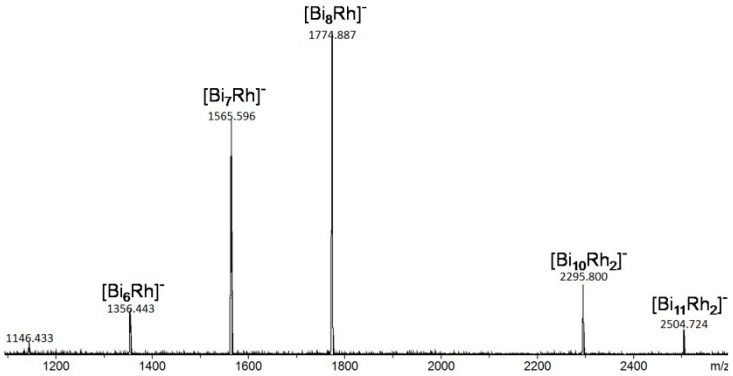
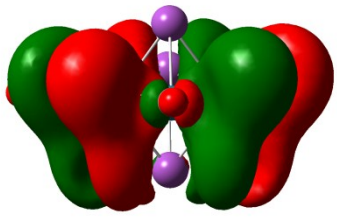
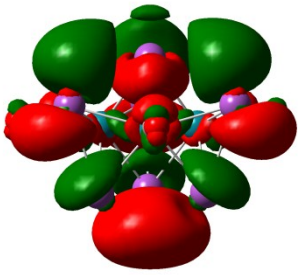


Fig. S3.2. LDI-TOF mass spectrum of 2.

S4 Computational Methods and Details

DFT calculations were performed using the GAUSSIAN 09(Revision D.01) [2] program package on the PBE0/def2-TZVP level.[3, 4] In these calculations, the solvent effects were taken into account by the conductor-like polarizable contiuum model (C-PCM).[5] The geometric and electronic structure for **2a** was optimized and the final Cartesian coordinates were provided in Table S4.2. The natural atomic orbital(NAO) analyses were calculated by the NBO 3.1 module embedded in Gaussian 09 program. The analyses of frontier molecular orbitals and adaptive natural density portioning (AdNDP) were performed by Multiwfn, [6] which is a multifunctional wavefunction analysis program developed by Lu *et. al.* and can be freely downloaded.

Table S4.1 Molecular orbital composition analysis by the natural atomic orbital (NAO) method for **2a**.

HOMO		**LUMO**	
			
Atoms	**Composition %**	**Atoms**	**Composition %**
1(Bi)	5.30	1(Bi)	7.59
2(Bi)	5.30	2(Bi)	7.59
3(Bi)	17.00	3(Bi)	18.16
4(Bi)	5.33	4(Bi)	7.58
5(Bi)	17.00	5(Bi)	18.16

6(Bi)	0	6(Bi)	11.83
7(Bi)	16.96	7(Bi)	18.16
8(Rh)	10.64	8(Rh)	1.12
9(Rh)	10.64	9(Rh)	1.12
10(Rh)	10.64	10(Rh)	1.12
11(C)	0.06	11(C)	1.17
12(C)	0.06	12(C)	1.17
13(C)	0.06	13(C)	1.17
14(O)	0.13	14(O)	0.43
15(O)	0.13	15(O)	0.44
16(O)	0.13	16(O)	0.44

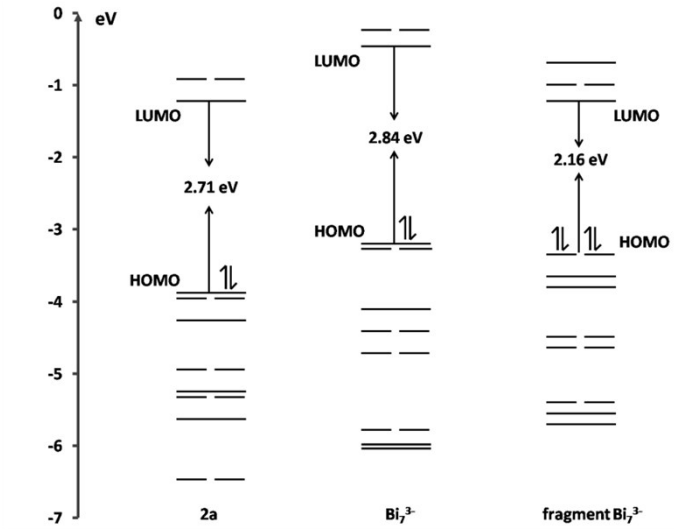
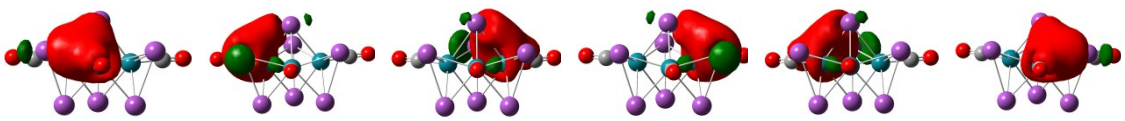


Figure S4.1 Molecular orbital energy levels of **2a**, Bi_7^{3-} and fragment Bi_7^{3-}.

(a) basal-basal Bi_2Rh *3c-2e* bonding in 2a.



(b) Bi_2Ir *3c-2e* bonding

Figure S4.2 ***3c-2e***-AdNDP orbital for **2a** (Bi: purple; Rh: blue; C: grey; O: red)

Table S4.2 Cartesian Coordinates of optimized **2a**.

Bi	1.71494604	-0.99012456	1.85343936
Bi	-0.00000000	1.98024912	1.85343936
Bi	2.63712931	-1.52254732	-0.91493956
Bi	-1.71494604	-0.99012456	1.85343936
Bi	-0.00000000	3.04509463	-0.91493956
Bi	0.00000000	0.00000000	-2.34711693
Bi	-2.63712931	-1.52254732	-0.91493956
Rh	1.53030230	0.88352044	-0.19108890
Rh	-0.00000000	-1.76704088	-0.19108890
Rh	-1.53030230	0.88352044	-0.19108890
C	3.09245995	1.78543259	-0.29735478
C	0.00000000	-3.57086517	-0.29735478
C	-3.09245995	1.78543259	-0.29735478
O	4.10381545	2.36933895	-0.34888855
O	0.00000000	-4.73867791	-0.34888855
O	-4.10381545	2.36933895	-0.34888855

S5 IR spectrum of 1 and 2

IR data were recorded as KBr pellets in Nujol mulls on a Magna 750 FT-IR spectrometer photometer.

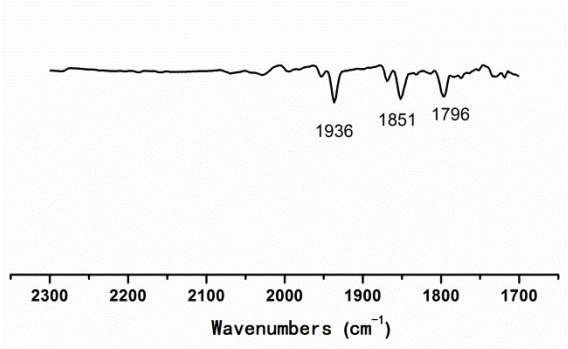


Fig. S5.1. The IR spectrum of **1**.

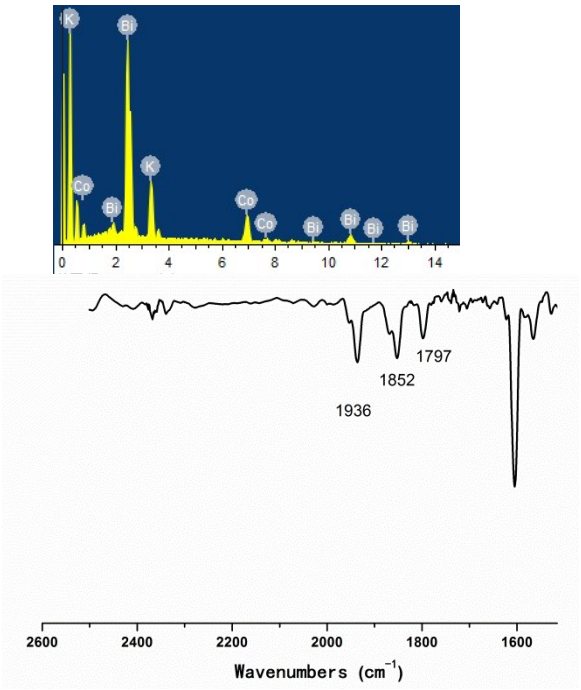


Fig. S5.2. The IR spectrum of **2**.

S6 EDX spectroscopy and ICP results for 1 and 2

Fig. S6.1 and Table S6.1 (Fig. S6.2 and Table S6.2) gave the energy-dispersive X-ray spectroscopy (EDX, JEOL-SEM, JSM-6700F) analyses of the single crystals of **1** (**2**), which indicate the presence of K, Co(Rh) and Bi in an approximate atomic ratio of 2:3:7. Combustion analyses, namely Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analyses of the crystalline samples of **1** (**2**) were also carried on Ultima 2 as indicated in Tables S6.1 and 6.2. The ICP results are close to both calculated and EDX values and hence provide additional evidence of the sample purity in addition to X-ray analyses.

Fig. S6.1. EDX spectroscopy of **1**.

Table S6.1 EDX and ICP results of **1**.

	EDX			ICP		
Element	Weight	Atom	Ratio	Measured	Weight	Cal. Weight
	%	%		mg/L	%	%
K	4.51	16.74	2	8.00	4.86	4.54

Co	9.60	23.63	2.82	16.74	10.18	10.29
Bi	85.89	59.62	7.12	139.75	84.96	85.17

Fig. S6.2. EDX spectroscopy of **2**.

Table S6.2 EDX and ICP results of **2**.

	EDX			ICP		
Element	Weight	Atom	Ratio	Measured	Weight	Cal. Weight
	%	%		mg/L	%	%
K	4.22	16.57	2	1.43	4.33	4.22
Rh	17.26	25.75	3.11	5.78	17.50	16.69
Bi	78.52	57.68	6.96	25.81	78.16	79.12

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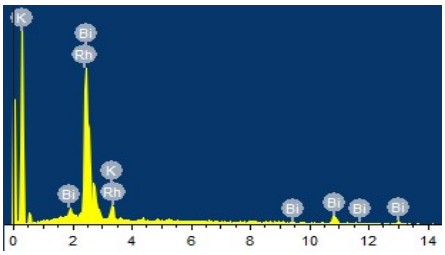

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