

Insertion of germanium atoms in high-nuclearity rhodium carbonyl compounds: synthesis, characterization and preliminary biological activity of the heterometallic $[\text{Rh}_{13}\text{Ge}(\text{CO})_{25}]^{3-}$, $[\text{Rh}_{14}\text{Ge}_2(\text{CO})_{30}]^{2-}$ and $[\text{Rh}_{12}\text{Ge}(\text{CO})_{27}]^{4-}$ cluster anions.

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Supporting Information

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1. IR spectra for clusters **1**, **2** and **3**;
2. ESI-MS spectra for clusters **1**, **2** and **3**;
3. IR and ESI-MS spectra of $[\text{HRh}_{14}(\text{CO})_{25}]^{3-}$;
4. Crystallographic data for clusters **1**, **2** and **3**;
5. Most relevant bond lengths for clusters **1**, **2** and **3**.

IR and ESI mass spectra for $[\text{Rh}_{13}\text{Ge}(\text{CO})_{25}]^{3-}$ (1).

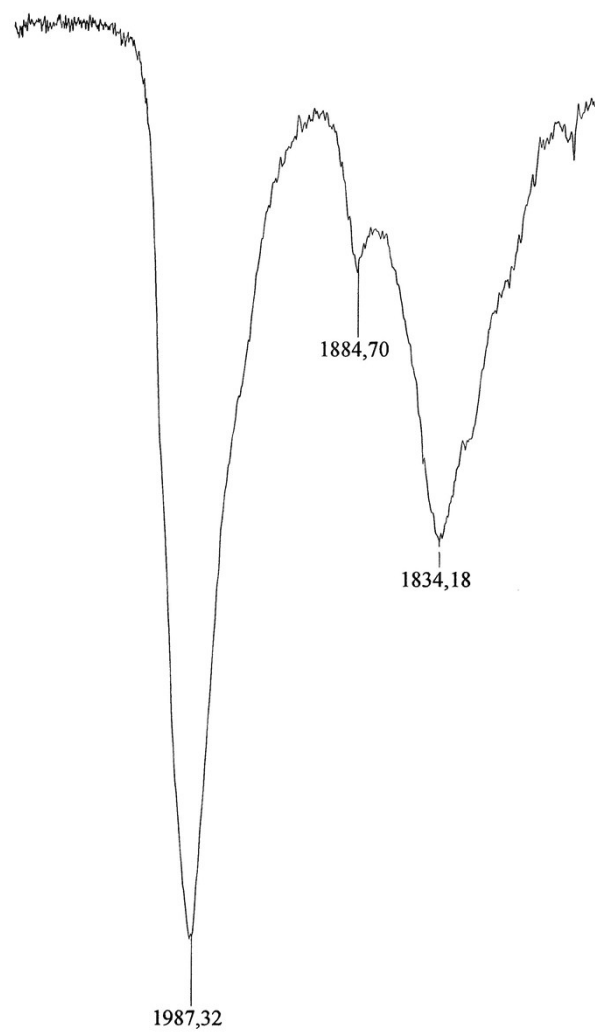


Figure 1Sa. IR spectrum of $[\text{Rh}_{13}\text{Ge}(\text{CO})_{25}][\text{NEt}_4]_3 \cdot [\text{NEt}_4]\text{Br}$ registered in CH_3CN solution.

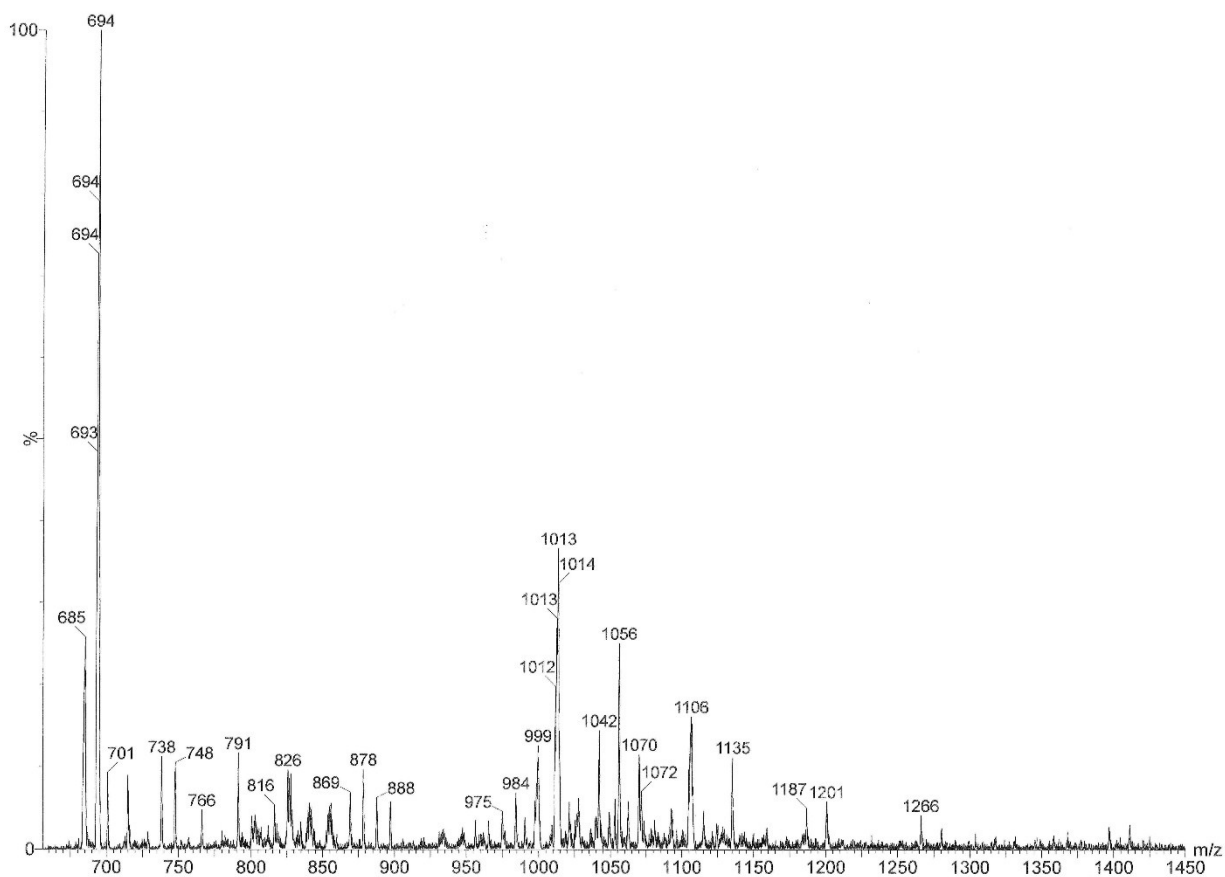


Figure 1Sb. ESI-MS of $[\text{Rh}_{13}\text{Ge}(\text{CO})_{25}][\text{NEt}_4]_3 \cdot [\text{NEt}_4]\text{Br}$ registered in CH_3CN solution.

Peaks or groups of peaks (m/z)	Corresponding Ions
1106	$\{[\text{Rh}_{13}\text{Ge}(\text{CO})_{24}][\text{NEt}_4]\}^{2-}$
1056-1042-1013-999-984	$[\text{Rh}_{13}\text{Ge}(\text{CO})_{25-24-22-21-20}]^{2-}$
694-685	$[\text{Rh}_{13}\text{Ge}(\text{CO})_{24-23}]^{3-}$

Table 1S. ESI-MS peak assignments for $[\text{Rh}_{13}\text{Ge}(\text{CO})_{25}][\text{NEt}_4]_3 \cdot [\text{NEt}_4]\text{Br}$.

IR and ESI mass spectra for compound $[\text{Rh}_{12}\text{Ge}(\text{CO})_{27}]^{4-}$ (2).

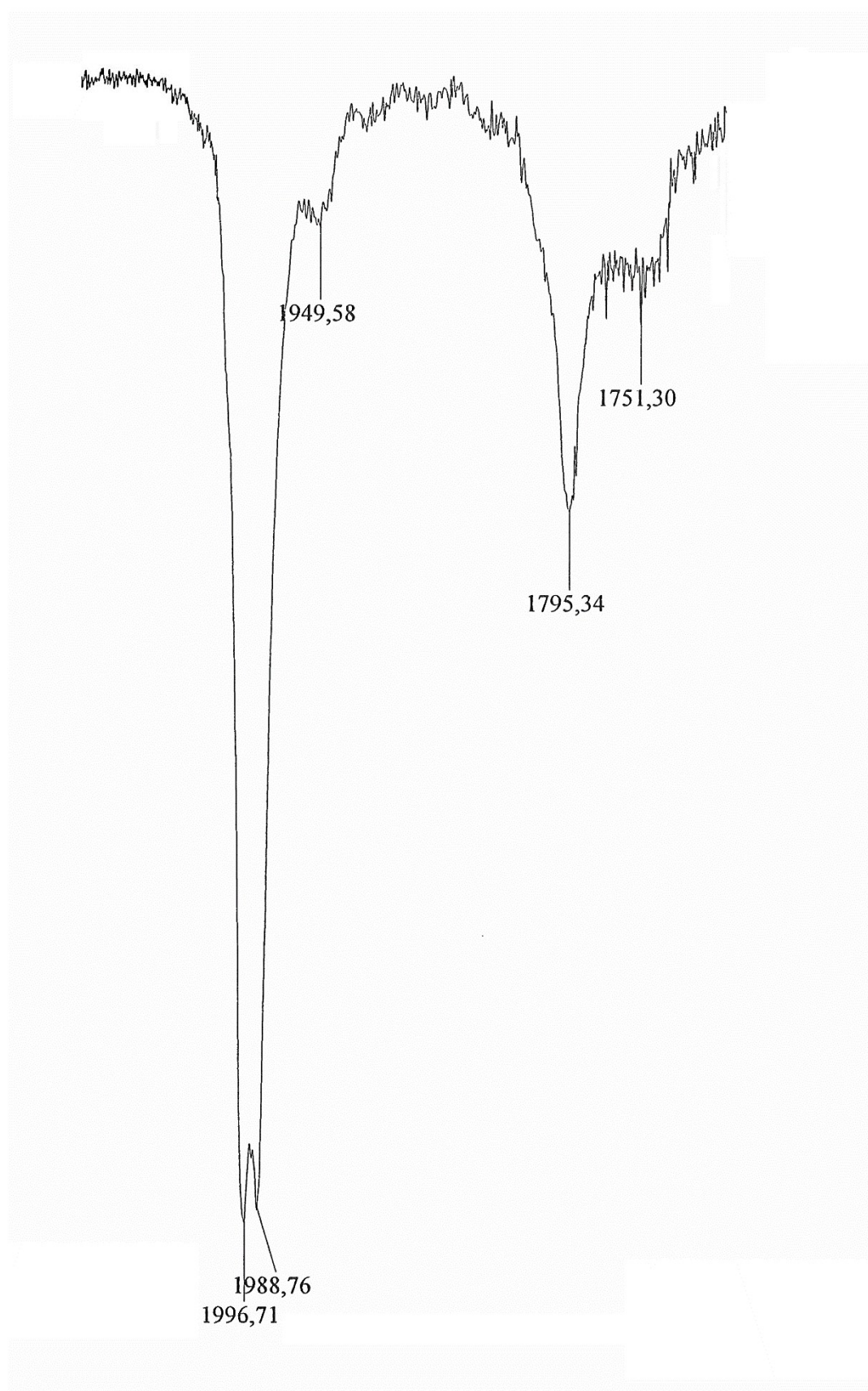


Figure 2Sa. IR spectrum of $[\text{Rh}_{12}\text{Ge}(\text{CO})_{27}][\text{NEt}_4]_4 \cdot 2\text{CH}_3\text{CN}$ registered in CH_3CN solution under CO.

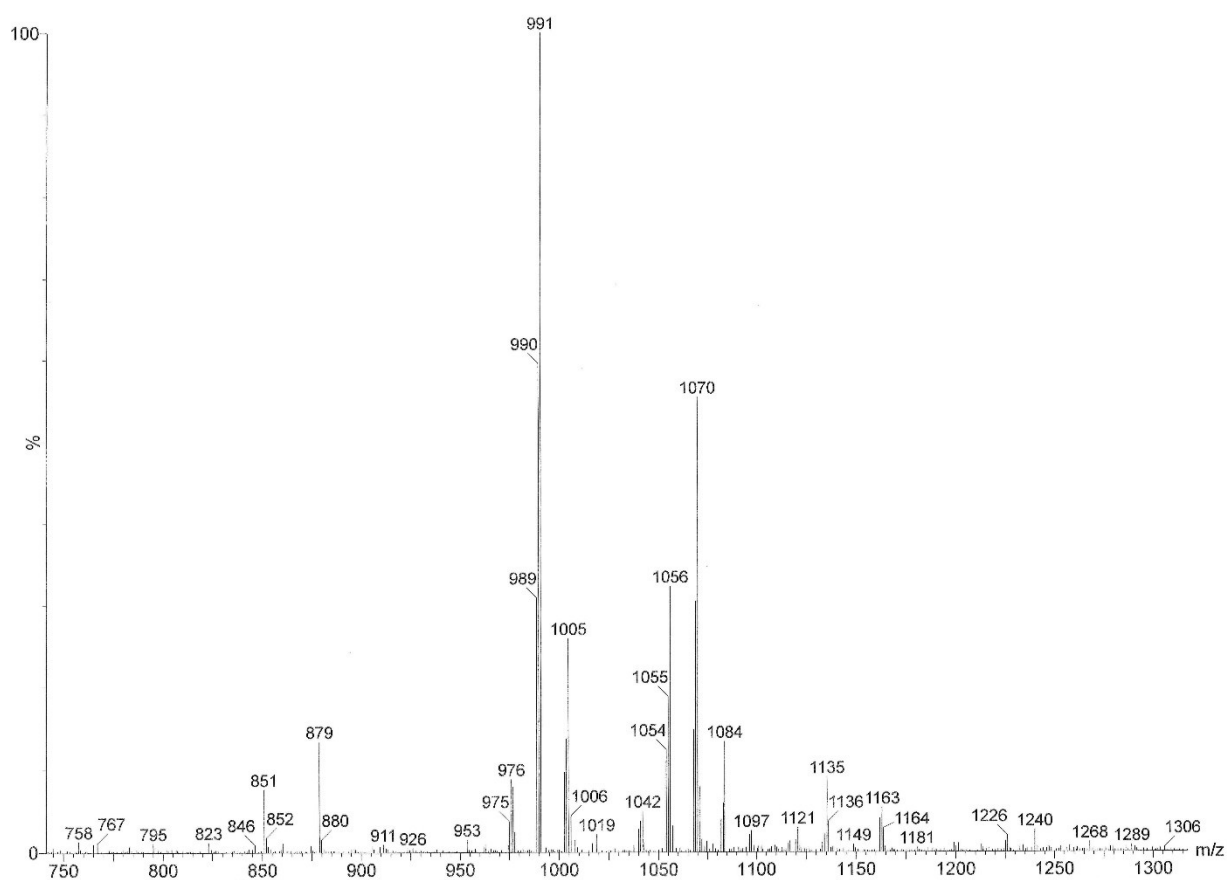


Figure 2Sb. ESI-MS of $[\text{Rh}_{12}\text{Ge}(\text{CO})_{27}][\text{NEt}_4]_4 \cdot 2\text{CH}_3\text{CN}$ registered in CH_3CN solution.

Peaks or groups of peaks (m/z)	Corresponding Ions
1163-1149-1135-1121	$[\text{Rh}_{12}\text{Ge}(\text{CO})_{26-25-24-23}]^{2-}$
1097-1084-1070-1056-1042	$\{[\text{Rh}_{12}\text{Ge}(\text{CO})_{27-26-25-24-23}][\text{NEt}_4]\}^{2-}$
1019-1005-991-976	$[\text{Rh}_{12}\text{Ge}(\text{CO})_{26-25-24-23}]^{2-}$
879-851	$[\text{Rh}_5(\text{CO})_{13-12}]^-$

Table 2S. ESI-MS peak assignments for $[\text{Rh}_{12}\text{Ge}(\text{CO})_{27}][\text{NEt}_4]_4 \cdot 2\text{CH}_3\text{CN}$.

ESI-MS and IR spectra for $[\text{Rh}_{14}\text{Ge}_2(\text{CO})_{30}]^{2-}$ (3).

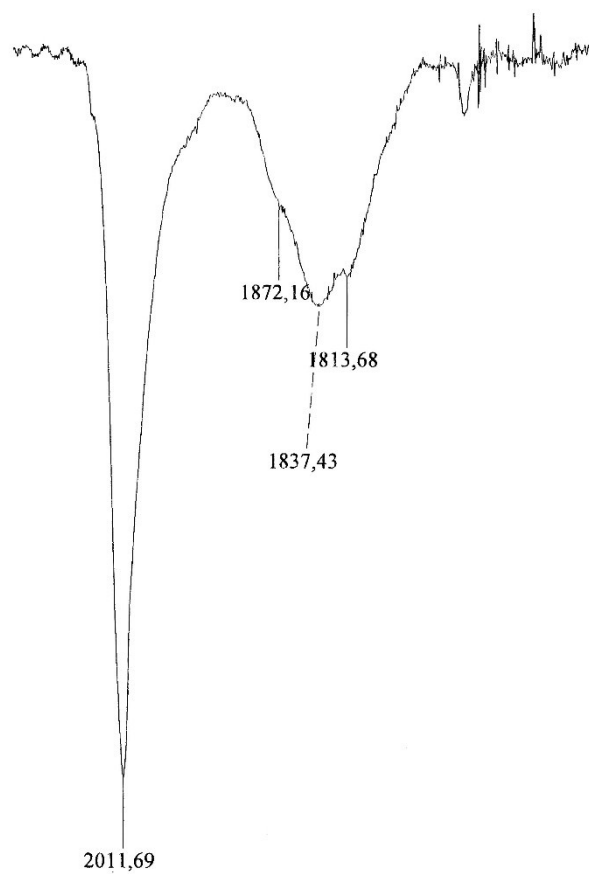


Figure 3Sa. IR spectrum of $[\text{Rh}_{14}\text{Ge}_2(\text{CO})_{30}][\text{NEt}_4]_2$ registered in CH_3CN solution.

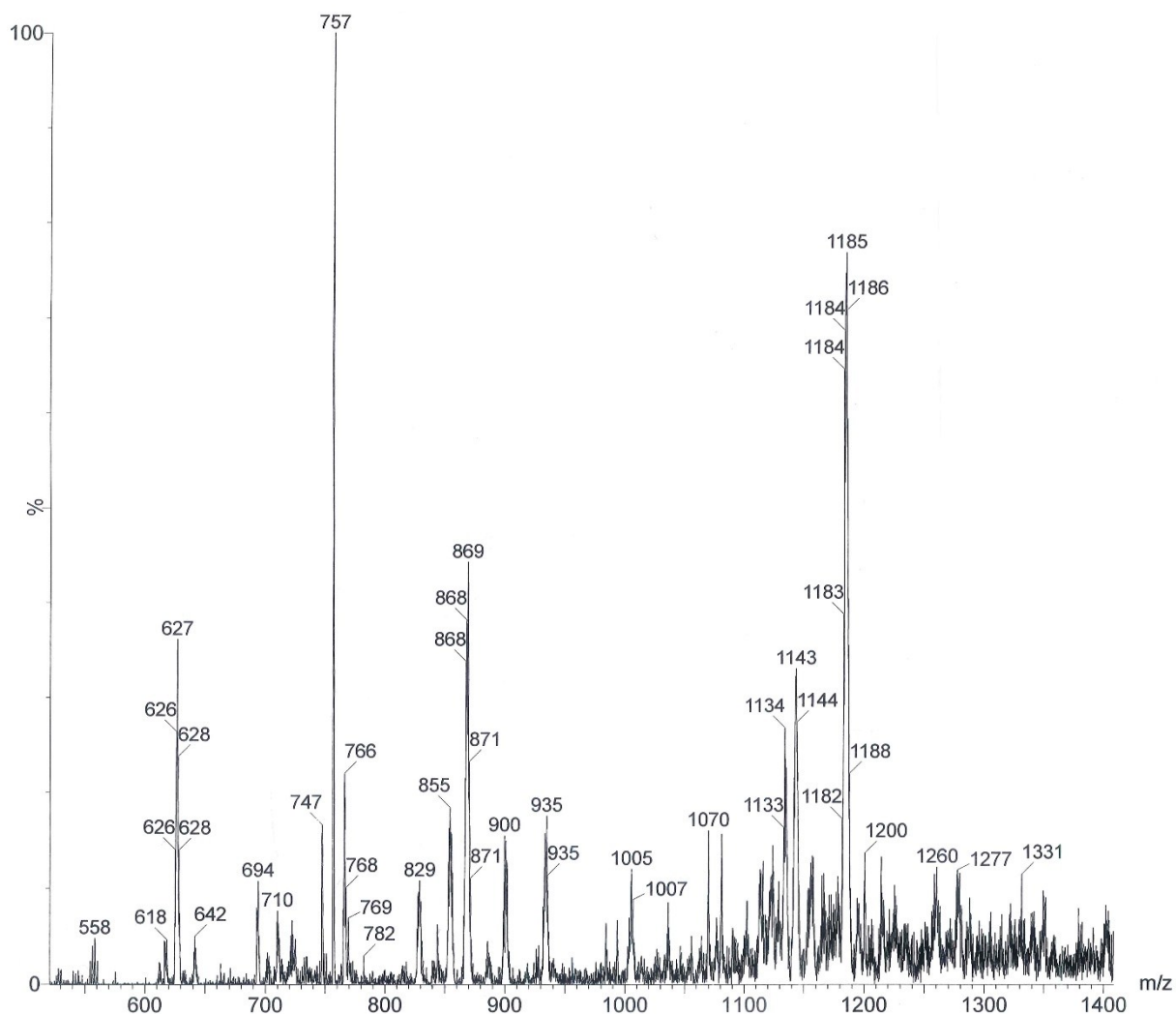


Figure 3Sb. ESI-MS of $[\text{Rh}_{14}\text{Ge}_2(\text{CO})_{30}][\text{NEt}_4]_2$ registered in CH_3CN solution.

Peaks or groups of peaks (m/z)	Corresponding Ions
1185-1143	$[\text{Rh}_{14}\text{Ge}_2(\text{CO})_{28-25}]^{2-}$
1134	$[\text{Rh}_{13}\text{Ge}_2(\text{CO})_{28}]^{2-}$
869-855	$\{[\text{Rh}_9\text{Ge}(\text{CO})_{17-16}][\text{NEt}_4]_2\}^{2-}$
766-757-747	$[\text{Rh}_{13}\text{Ge}_2(\text{CO})_{29-28-27}]^{3-}$
627-618	$[\text{Rh}_{11}\text{Ge}(\text{CO})_{24-23}]^{3-}$

Table 3S. ESI-MS peak assignments for $[\text{Rh}_{14}\text{Ge}_2(\text{CO})_{30}][\text{NEt}_4]_2$.

ESI-MS and IR spectra for $[\text{HRh}_{14}(\text{CO})_{25}]^{3-}$.

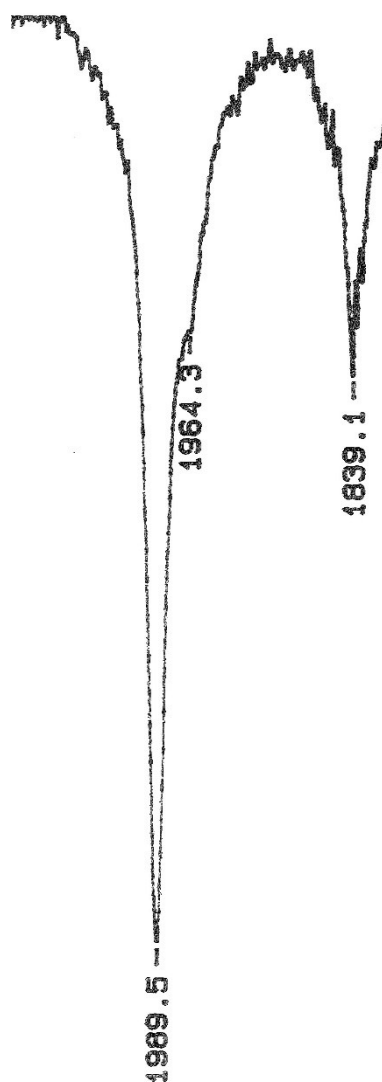


Figure 4Sa. IR spectrum of $[\text{HRh}_{14}(\text{CO})_{25}]^{3-}$ registered in CH_3CN solution.

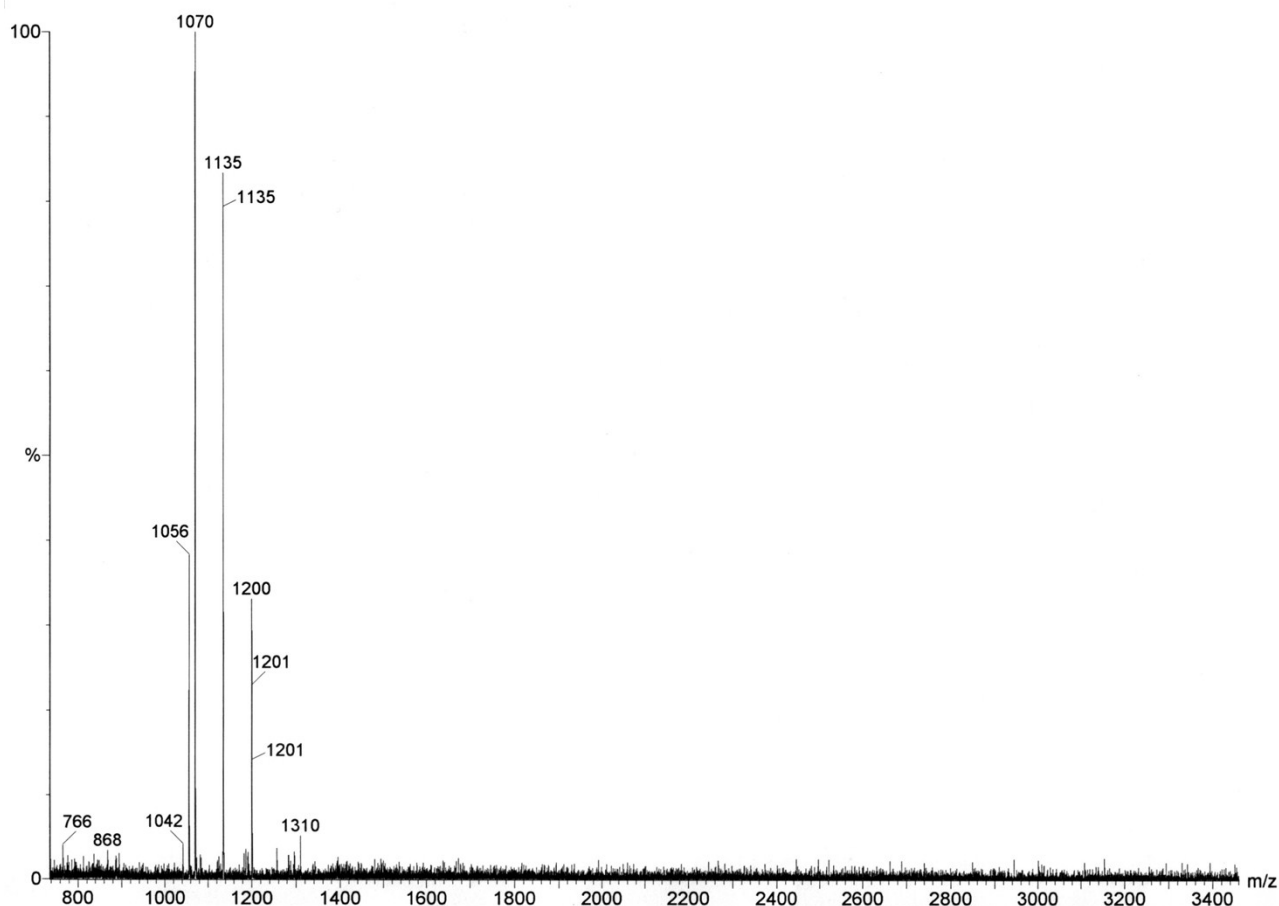


Figure 4Sb. ESI-MS of $[\text{HRh}_{14}(\text{CO})_{25}]^{3-}$ registered in CH_3CN solution.

Peaks or groups of peaks (m/z)	Corresponding Ions
1070-1057	$[\text{HRh}_{14}(\text{CO})_{25-24}]^{2-}$
1135	$\{[\text{HRh}_{14}(\text{CO})_{25}][\text{NEt}_4]\}^{2-}$
1200	$\{[\text{HRh}_{14}(\text{CO})_{25}][\text{NEt}_4]_2\}^{2-}$

Table 4S. ESI-MS signal assignments for $[\text{HRh}_{14}(\text{CO})_{25}]^{3-}$.

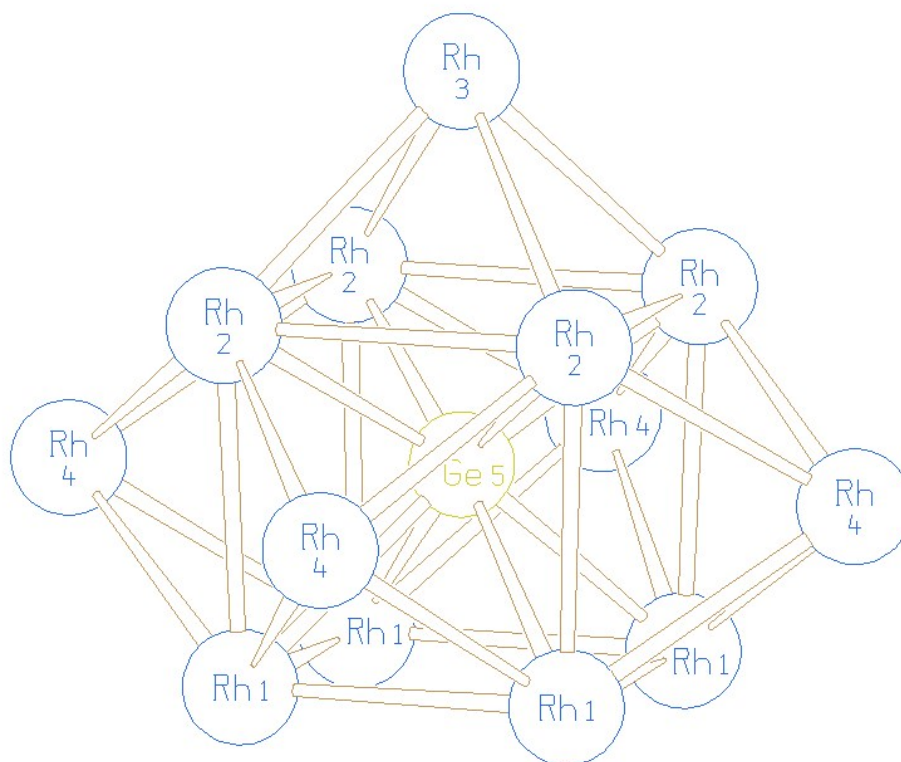
Table 1S. Crystallographic data for clusters 1, 2 and 3.

Compound	1[NEt ₄] ₃ ·[NEt ₄]Br	2[NEt ₄] ₄ ·2CH ₃ CN	3[NEt ₄] ₂
Formula	C ₅₇ H ₈₀ BrGeN ₄ O ₂₅ Rh ₁₃	C ₆₃ H ₈₆ GeN ₆ O ₂₇ Rh ₁₂	C ₄₆ H ₄₀ Ge ₂ N ₂ O ₃₀ Rh ₁₄
Fw	2711.57	2666.88	2686.72
Crystal system	Tetragonal	Triclinic	Triclinic
Space group	<i>P</i> 4/ncc	<i>P</i> -1	<i>P</i> -1
a (Å)	18.5028(6)	13.279(3)	11.4246(4)
b (Å)	18.5028(6)	26.614(5)	11.5375(4)
c (Å)	22.8486(11)	27.049(5)	13.4617(5)
α (deg)	90	119.285(3)	112.059(2)
β (deg)	90	98.012(4)	98.082(2)
γ (deg)	90	95.078(4)	94.045(3)
Cell volume (Å ³)	7822.3(6)	8119(3)	1613.40(10)
Z	4	4	1
D (g/cm ³)	2.302	2.182	2.765
μ (mm ⁻¹)	3.623	2.810	4.474
F(000)	5208	5176	1264
θ limits (deg)	1.783 to 24.998	1.521 to 24.999	1.660 to 24.997
Index ranges	-22 ≤ h ≤ 22, - 21 ≤ k ≤ 22, - 27 ≤ l ≤ 27	-15 ≤ h ≤ 15, -31 ≤ k ≤ 31, - 32 ≤ l ≤ 32	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	89494	76284	23355
Independent reflections	3455 [R(int) = 0.1077]	27668 [R(int) = 0.0543]	5690 [R(int) = 0.1320]
Completeness to θ max	100.0 %	99.8 %	99.9 %
Data/restraints/parameters	3455 / 0 / 231	27668 / 658 / 2029	5690 / 90 / 429
Goodness of fit	1.146	1.088	0.990
R ₁ (I > 2σ(I))	0.0482	0.0726	0.0550
wR ₂ (all data)	0.1035	0.2114	0.1445
Largest diff. peak and hole, e Å ⁻³	1.383 and -1.338	2.892 and -2.092	2.397 and -1.639

Most relevant bond distances for $[\text{Rh}_{13}\text{Ge}(\text{CO})_{25}]^{3-}$ (1).

Rh(1)-Ge(5)	2.5565(10)
Rh(2)-Ge(5)	2.4548(9)
Ge(5)-Rh(2)#1	2.4549(9)
Ge(5)-Rh(2)#3	2.4549(9)
Ge(5)-Rh(2)#2	2.4549(9)
Ge(5)-Rh(1)#1	2.5565(10)
Ge(5)-Rh(1)#3	2.5565(10)
Ge(5)-Rh(1)#2	2.5565(10)
Rh(1)-Rh(1)#1	2.7597(8)
Rh(1)-Rh(1)#2	2.7597(8)
Rh(1)-Rh(4)#3	2.8191(8)
Rh(1)-Rh(4)#1	2.8261(8)
Rh(1)-Rh(2)#1	2.9335(8)

Rh(2)-Rh(4)#1	2.7576(8)
Rh(2)-Rh(4)	2.7632(8)
Rh(2)-Rh(3)	2.8273(10)
Rh(2)-Rh(1)#2	2.9335(8)
Rh(2)-Rh(2)#2	2.9638(8)
Rh(2)-Rh(2)#1	2.9638(8)
Rh(3)-Rh(2)#3	2.8273(10)
Rh(3)-Rh(2)#2	2.8273(10)
Rh(3)-Rh(2)#1	2.8273(10)
Rh(4)-Rh(2)#2	2.7576(8)
Rh(4)-Rh(1)#3	2.8192(8)
Rh(4)-Rh(1)#2	2.8261(8)

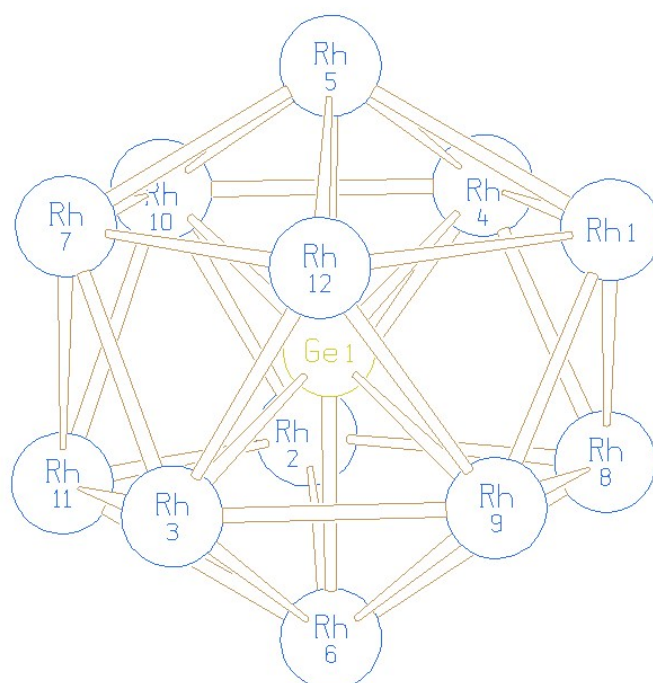


Most relevant bond distances for [Rh₁₂Ge(CO)₂₇]⁴⁻ (2).

First isomer

Ge(1)-Rh(10)	2,645(2)
Ge(1)-Rh(9)	2,656(2)
Ge(1)-Rh(5)	2,6666(19)
Ge(1)-Rh(3)	2,6677(19)
Ge(1)-Rh(4)	2,6751(19)
Ge(1)-Rh(6)	2,6924(19)
Ge(1)-Rh(2)	2,882(2)
Ge(1)-Rh(8)	2,893(2)
Ge(1)-Rh(12)	2,907(2)
Ge(1)-Rh(7)	2,918(2)
Ge(1)-Rh(1)	2,922(2)
Ge(1)-Rh(11)	2,929(2)
Rh(1)-Rh(8)	2,8244(17)
Rh(1)-Rh(9)	2,8429(17)
Rh(1)-Rh(4)	2,8633(18)
Rh(1)-Rh(5)	2,9657(18)
Rh(2)-Rh(11)	2,8078(17)
Rh(2)-Rh(10)	2,8506(17)
Rh(2)-Rh(6)	2,8544(18)
Rh(2)-Rh(4)	2,9764(18)
Rh(3)-Rh(7)	2,8438(18)

Rh(3)-Rh(12)	2,8650(18)
Rh(3)-Rh(6)	2,9158(17)
Rh(3)-Rh(9)	2,9493(18)
Rh(3)-Rh(11)	2,9677(18)
Rh(4)-Rh(8)	2,8392(18)
Rh(4)-Rh(10)	2,9320(18)
Rh(4)-Rh(5)	2,9452(17)
Rh(5)-Rh(12)	2,8435(18)
Rh(5)-Rh(7)	2,8763(17)
Rh(5)-Rh(10)	2,9372(17)
Rh(6)-Rh(11)	2,8675(18)
Rh(6)-Rh(9)	2,9505(18)
Rh(6)-Rh(8)	2,9979(17)
Rh(7)-Rh(12)	2,8208(18)
Rh(7)-Rh(10)	2,9715(18)
Rh(8)-Rh(9)	2,8573(18)
Rh(9)-Rh(12)	2,9512(18)
Rh(10)-Rh(11)	2,8595(18)
Rh(1)-Rh(12)	3.301
Rh(2)-Rh(8)	3.250
Rh(7)-Rh(11)	3.307



Second isomer

Ge(2)-Rh(23)	2,647(2)
Ge(2)-Rh(27)	2,647(2)
Ge(2)-Rh(31)	2,6499(19)
Ge(2)-Rh(22)	2,6647(19)
Ge(2)-Rh(26)	2,6849(19)
Ge(2)-Rh(24)	2,706(2)
Ge(2)-Rh(28)	2,898(2)
Ge(2)-Rh(32)	2,899(2)
Ge(2)-Rh(30)	2,899(2)
Ge(2)-Rh(21)	2,909(2)
Ge(2)-Rh(25)	2,915(2)
Ge(2)-Rh(29)	2,937(2)
Rh(21)-Rh(32)	2,8079(17)
Rh(21)-Rh(23)	2,8303(17)
Rh(21)-Rh(26)	2,8727(17)
Rh(21)-Rh(22)	2,9784(18)
Rh(22)-Rh(30)	2,8397(18)
Rh(22)-Rh(28)	2,8514(18)
Rh(22)-Rh(26)	2,9296(18)
Rh(22)-Rh(27)	2,9755(17)
Rh(23)-Rh(32)	2,8716(17)

Rh(23)-Rh(24)	2,9280(17)
Rh(23)-Rh(31)	2,9474(18)
Rh(23)-Rh(28)	2,9708(17)
Rh(24)-Rh(25)	2,8560(18)
Rh(24)-Rh(29)	2,8576(18)
Rh(24)-Rh(31)	2,9321(18)
Rh(24)-Rh(32)	2,9963(18)
Rh(25)-Rh(29)	2,8120(17)
Rh(25)-Rh(27)	2,8684(17)
Rh(25)-Rh(26)	2,9842(17)
Rh(25)-Rh(32)	3,1970(18)
Rh(26)-Rh(32)	2,8435(18)
Rh(26)-Rh(27)	2,9225(18)
Rh(27)-Rh(29)	2,8360(17)
Rh(27)-Rh(30)	2,9573(17)
Rh(28)-Rh(30)	2,8072(18)
Rh(28)-Rh(31)	2,8419(17)
Rh(29)-Rh(31)	2,9888(17)
Rh(30)-Rh(31)	2,8562(18)
Rh(21)-Rh(28)	3,321
Rh(29)-Rh(30)	3,366

Most relevant bond distances $[\text{Rh}_{14}\text{Ge}_2(\text{CO})_{30}]^{2-}$ (3).

Rh(1)-Ge(8)	2.4796(19)
Rh(2)-Ge(8)	2.4711(19)
Rh(3)-Ge(8)	2.4862(19)
Rh(4)-Ge(8)	2.4829(18)
Rh(5)-Ge(8)	2.8119(18)
Rh(6)-Ge(8)#1	2.6009(19)
Rh(6)-Ge(8)	2.6166(18)
Rh(7)-Ge(8)#1	2.6097(19)
Rh(7)-Ge(8)	2.6114(19)
Ge(8)-Rh(6)#1	2.6009(19)
Ge(8)-Rh(7)#1	2.6097(19)
Ge(8)-Ge(8)#1	2.678(3)
Rh(1)-Rh(5)	2.8790(16)
Rh(1)-Rh(7)	2.8811(16)
Rh(1)-Rh(6)	2.9724(16)
Rh(1)-Rh(4)	3.1913(17)
Rh(1)-Rh(3)	3.1975(17)

Rh(2)-Rh(5)	2.8823(17)
Rh(2)-Rh(7)#1	2.8854(15)
Rh(2)-Rh(6)#1	2.9820(16)
Rh(2)-Rh(3)	3.1694(17)
Rh(3)-Rh(5)	2.8668(16)
Rh(3)-Rh(6)	2.8946(16)
Rh(3)-Rh(7)#1	2.9660(16)
Rh(4)-Rh(5)	2.8740(17)
Rh(4)-Rh(6)#1	2.8785(16)
Rh(4)-Rh(7)	2.9625(15)
Rh(6)-Rh(4)#1	2.8785(16)
Rh(6)-Rh(2)#1	2.9820(16)
Rh(6)-Rh(7)#1	3.1415(17)
Rh(6)-Rh(7)	3.1938(16)
Rh(7)-Rh(2)#1	2.8854(15)
Rh(7)-Rh(3)#1	2.9659(16)
Rh(7)-Rh(6)#1	3.1415(17)

