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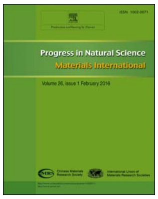

Original Research

Alternative synthetic route for the heterometallic CO-releasing $[Sb@Rh_{12}(CO)_{27}]^{3-}$ icosahedral carbonyl cluster and synthesis of its new unsaturated $[Sb@Rh_{12}(CO)_{24}]^{4-}$ and dimeric $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3]^{7-}$ derivatives

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ABSTRACT

The hetero-metallic $[Sb@Rh_{12}(CO)_{27}]^{3-}$ cluster has been known as for over three decades thanks to Vidal and co-workers, and represents the first example of an E-centered (E=heteroatom) icosahedral rhodium carbonyl cluster. However, its synthesis required high temperature (140–160 °C) and elevated CO pressure (400 atm). Applying the redox condensation method for cluster preparation, we herein report a new synthetic, high-yield route for preparing $[Sb@Rh_{12}(CO)_{27}]^{3-}$ under much milder conditions of temperature and pressure. Notably, when the same synthesis was carried out under N_2 instead of CO atmosphere, the new isostructural but unsaturated derivative $[Sb@Rh_{12}(CO)_{24}]^{4-}$ was obtained, for which we report the full X-ray structural characterization. This species represents one of the few examples of an icosahedral cluster disobeying the electron-counting Wade-Mingos rules, possessing less than the expected 170 cluster valence electrons (CVEs). Judging from IR monitoring, the two species can be obtained one from the other by switching between N_2 and CO atmosphere, making $[Sb@Rh_{12}(CO)_{27}]^{3-}$ a spontaneous CO-releasing molecule. Finally, the study of the chemical reactivity of $[Sb@Rh_{12}(CO)_{27}]^{3-}$ with PPh_3 allowed us to obtain the new $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3]^{7-}$ dimeric compound, for which we herein report the full X-ray structural and ^{31}P NMR analyses.

1. Introduction

Rhodium possesses the ability to form polynuclear carbonyl compounds with large numbers of metal atoms arranged in an extensive variety of polyhedra, thanks to the high energy of Rh-Rh and Rh-CO bonds [1]. The chemistry of rhodium carbonyl clusters has been broadly explored in the past, and several examples of homo-metallic cluster anions are present in the scientific literature [2,3]. Moreover, the ability of rhodium to accommodate main-group elements is demonstrated by the presence of many carbide and nitrite compounds [1,4,5]. Notably, heteroatoms impart extra stability to the clusters. When heavier atoms are involved, much credit is due to Vidal and his co-workers, who produced most of the reported examples of rhodium carbonyl clusters with third-row – and onwards – post-transition elements. Among them we can name $[Rh_{10}P(CO)_{22}]^{3-}$ [6], $[Rh_{17}S_2(CO)_{32}]^{3-}$ [7], $[Rh_{10}(\mu_8\text{-}As)(CO)_{22}]^{3-}$ [8] and $[Sb@Rh_{12}(CO)_{27}]^{3-}$[9]. More recently we synthetized the icosahedral $[Sn@Rh_{12}(CO)_{27}]^{4-}$ cluster anion [10], which proved to exist also in its two unsaturated $[Sn@Rh_{12}(CO)_{26}]^{4-}$ and $[Sn@Rh_{12}(CO)_{25}]^{4-}$ derivatives, both obtained from the parent compound by thermal cleavage of Rh-CO bonds [11]. All of the above species, with the exception of $[Sn@Rh_{12}(CO)_{27}]^{4-}$, were prepared under an elevated pressure of CO or CO/H_2 (250–400 atm) and at a temperatures of 140–180 °C. As our group is active in the synthesis of new icosahedral Rh carbonyl clusters, we decided to explore a different synthetic route for $[Sb@Rh_{12}(CO)_{27}]^{3-}$ by exploiting the redox condensation method, first reported by Hieber and Schubert [12], but actually coined and developed by Chini [13].

We repeated the same reaction but under N_2 instead of CO atmosphere, and discovered that the new unsaturated but isostructural $[Sb@Rh_{12}(CO)_{24}]^{4-}$ derivative could be obtained. Notably, this icosahedral cluster possesses only 165 CVEs, 5 electrons less than the ones expected for such a geometry by the Wade-Mingos rules [14]. This is a rare case for such nuclearity, as other exceptions to these rules are found in much larger clusters [15]. This result prompted us to

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investigate the stability of $[Sb@Rh_{12}(CO)_{27}]^{3-}$ under N_2 atmosphere: we discovered, by IR monitoring, that the cluster spontaneously released CO ligands. This observation is very interesting as $[Sb@Rh_{12}(CO)_{27}]^{3-}$ represents a rare example of a spontaneous CO-releasing transition-metal carbonyl cluster. Another case is represented by the $[Pt_{19}(CO)_{24}]^{4-}$ cluster anion, which under N_2 turns into $[Pt_{19}(CO)_{22}]^{4-}$ [16]. Finally, the investigation of the chemical reactivity of $[Sb@Rh_{12}(CO)_{27}]^{3-}$ with PPh_3 led us to obtain the novel $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3]^{7-}$ dimeric species. We here report the syntheses and full structural characterizations of the two new compounds, as well as the new synthesis and X-ray structure of the already known $[Sb@Rh_{12}(CO)_{27}]^{3-}$ parent cluster.

2. Experimental procedures

All reactions and compounds were handled using the standard Schlenk technique and under nitrogen or carbon monoxide atmosphere. Solvents were dried and degassed before use, tetrahydrofuran (THF) was dehydrated with Na-benzophenone and distilled under nitrogen. Ammonium salts and $SbCl_3$ reagents were commercial products. The $[Rh_7(CO)_{16}]^{3-}$ cluster precursor was prepared according to literature [17]. IR spectra were recorded on a PerkinElmer Spectrum One interferometer in CaF_2 cells. ^{31}P NMR spectra were recorded on a Varian Mercury 400 MHz Spectrometer at 298 K.

X-ray single-crystal diffraction experiments were performed at 100 K on a Bruker Apex II diffractometer, equipped with a CCD Detector, by using Kα-Mo radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS) [18]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [19]. Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, including disordered atoms. Structure drawings were made with SCHAKAL99 [20]. The crystal structure of $[Sb@Rh_{12}(CO)_{27}][NEt_4]_3$ presents some absorption issues as indicated by residual electron density within the metal frame. In the case of $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3][NEt_4]_7{\cdot}CH_3CN$, the structure presents heavy disorders on the cations and solvent molecules. For the former, atoms have been split in two parts and anisotropic-parameter and distance restraints have been applied, in order to obtain a better structural model. However, despite the numerous restraints, some anomalous distances between hydrogen atoms remained. As for the solvent molecules, after identifying one acetonitrile per cluster, there was still some random residual electron density in the unit cell, so the Platon Squeeze function was applied [21]. However, this has not impaired the correct molecular structure determination of the cluster.

2.1. Synthesis of $[Sb@Rh_{12}(CO)_{27}][NEt_4]_3$

An acetonitrile solution of $SbCl_3$ (0.131 mmol) was slowly added to a second solution of $[Rh_7(CO)_{16}][NEt_4]_3$ (0.175 mmol) in the same solvent, in a 3:4 M ratio, respectively, under 1.5 atm of CO pressure. After a few hours, the resulting brown solution was dried under vacuum, and the solid was washed with water (40 mL) in order to eliminate $[NEt_4]Cl$, then ethanol (40 mL) and tetrahydrofuran (THF) (20 mL) to separate the $[Rh(CO)_2Cl_2]^-$ by-product. The solid residue was finally extracted with about 15 mL of acetone and crystallized by slow addition of 2-propanol. After a few days, black crystals of $[Sb@Rh_{12}(CO)_{27}][NEt_4]_3$ were obtained. The reaction yield was 70% (based on Rh). The cluster was well soluble in acetone, acetonitrile and dymethylformamide. And νCO in CH_3CN was 2021(sh), 2013(vs), 1826(m) cm^{-1}.

Table 1
Interatomic Sb-Rh and Rh-Rh bond lengths for $[Sb@Rh_{12}(CO)_{27}]^{3-}$ and $[Sb@Rh_{12}(CO)_{24}]^{4-}$.

$[Sb@Rh_{12}\ (CO)_{27}]^{3-}$		$[Sb@Rh_{12}\ (CO)_{24}]^{4-}$	
Atoms	Bond length (Å)	Atoms	Bond length (Å)
Sb(1)-Rh(4)#1	2.7069(12)	Sb(1)-Rh(3)#1	2.7454(6)
Sb(1)-Rh(4)	2.7070(12)	Sb(1)-Rh(3)	2.7454(6)
Sb(1)-Rh(5)#1	2.7218(12)	Sb(1)-Rh(4)#1	2.7655(7)
Sb(1)-Rh(5)	2.7218(12)	Sb(1)-Rh(4)	2.7655(6)
Sb(1)-Rh(2)#1	2.7238(11)	Sb(1)-Rh(5)	2.7865(6)
Sb(1)-Rh(2)	2.7238(11)	Sb(1)-Rh(5)#1	2.7865(6)
Sb(1)-Rh(6)#1	2.9174(10)	Sb(1)-Rh(2)#1	2.7868(6)
Sb(1)-Rh(6)	2.9174(10)	Sb(1)-Rh(2)	2.7868(6)
Sb(1)-Rh(7)	2.9253(14)	Sb(1)-Rh(6)	2.7870(7)
Sb(1)-Rh(7)#1	2.9254(14)	Sb(1)-Rh(6)#1	2.7870(7)
Sb(1)-Rh(3)	2.9409(13)	Sb(1)-Rh(7)#1	2.8016(7)
Sb(1)-Rh(3)#1	2.9409(13)	Sb(1)-Rh(7)	2.8016(7)
Rh(2)-Rh(6)	2.8720(14)	Rh(2)-Rh(5)	2.7892(9)
Rh(2)-Rh(3)	2.8788(13)	Rh(2)-Rh(6)	2.7898(10)
Rh(2)-Rh(4)#1	3.0002(13)	Rh(2)-Rh(7)#1	3.0014(10)
Rh(2)-Rh(5)	3.0029(13)	Rh(2)-Rh(3)#1	3.0120(9)
Rh(2)-Rh(7)#1	3.0250(14)	Rh(2)-Rh(4)#1	3.0187(9)
Rh(3)-Rh(6)	2.8209(13)	Rh(3)-Rh(5)	2.7835(9)
Rh(3)-Rh(4)	2.8740(14)	Rh(3)-Rh(7)	2.7878(10)
Rh(3)-Rh(4)#1	3.0302(14)	Rh(3)-Rh(4)#1	2.9891(10)
Rh(4)-Rh(6)	2.8791(14)	Rh(3)-Rh(6)#1	3.0031(10)
Rh(4)-Rh(2)#1	3.0002(13)	Rh(3)-Rh(2)#1	3.0121(9)
Rh(4)-Rh(5)#1	3.0090(15)	Rh(4)-Rh(7)	2.7898(9)
Rh(4)-Rh(3)#1	3.0303(14)	Rh(4)-Rh(6)	2.8048(9)
Rh(5)-Rh(7)	2.8694(14)	Rh(4)-Rh(3)#1	2.9891(10)
Rh(5)-Rh(7)#1	2.8786(14)	Rh(4)-Rh(5)#1	2.9974(11)
Rh(5)-Rh(4)#1	3.0090(14)	Rh(4)-Rh(2)#1	3.0187(9)
Rh(5)-Rh(6)#1	3.0174(14)	Rh(5)-Rh(4)#1	2.9973(11)
Rh(6)-Rh(5)#1	3.0174(14)	Rh(5)-Rh(6)	3.0040(9)
Rh(7)-Rh(7)#1	2.8262(19)	Rh(5)-Rh(7)	3.0580(9)
Rh(7)-Rh(5)#1	2.8786(14)	Rh(6)-Rh(3)#1	3.0030(10)
Rh(7)-Rh(2)#1	3.0249(14)	Rh(6)-Rh(7)	3.0448(9)
Rh(6)-Rh(7)#1	3.2940(14)	Rh(7)-Rh(2)#1	3.0014(10)
Rh(3)-Rh(3)#1	3.3680(15)		

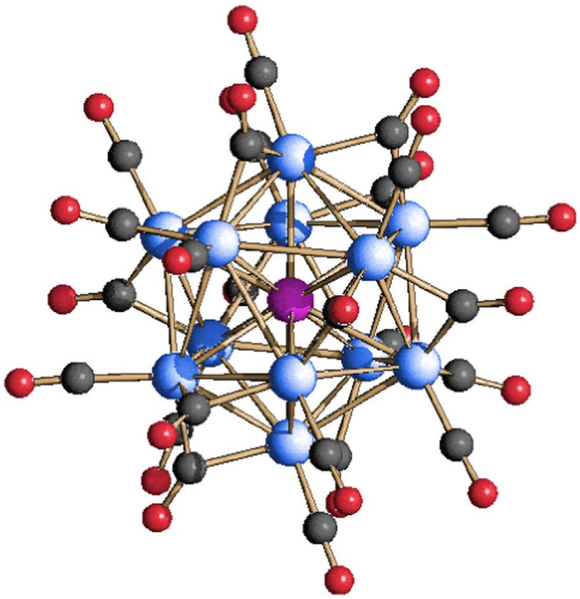

Fig. 1. Molecular structure of $[Sb@Rh_{12}(CO)_{24}]^{4-}$ (Rh: blue, Sb: pink, C: grey, O: red).

2.2. Synthesis of $[Sb@Rh_{12}(CO)_{24}][NEt_4]_4{\cdot}2CH_3CN$

An acetone solution of $SbCl_3$ (0.257 mmol) was slowly added to a solution of $[Rh_7(CO)_{16}][NEt_4]_3$ (0.321 mmol) in the same solvent, in a 4:5 M ratio, respectively, under N_2 atmosphere. After a few hours, the resulting brown solution was separated from the precipitate and dried under vacuum. The solid was washed with water (40 mL) to eliminate $[NEt_4]Cl$, ethanol (40 mL) and tetrahydrofuran (THF) (20 mL) to separate $[Rh(CO)_2Cl_2]^-$and another yet unidentified by-products. The

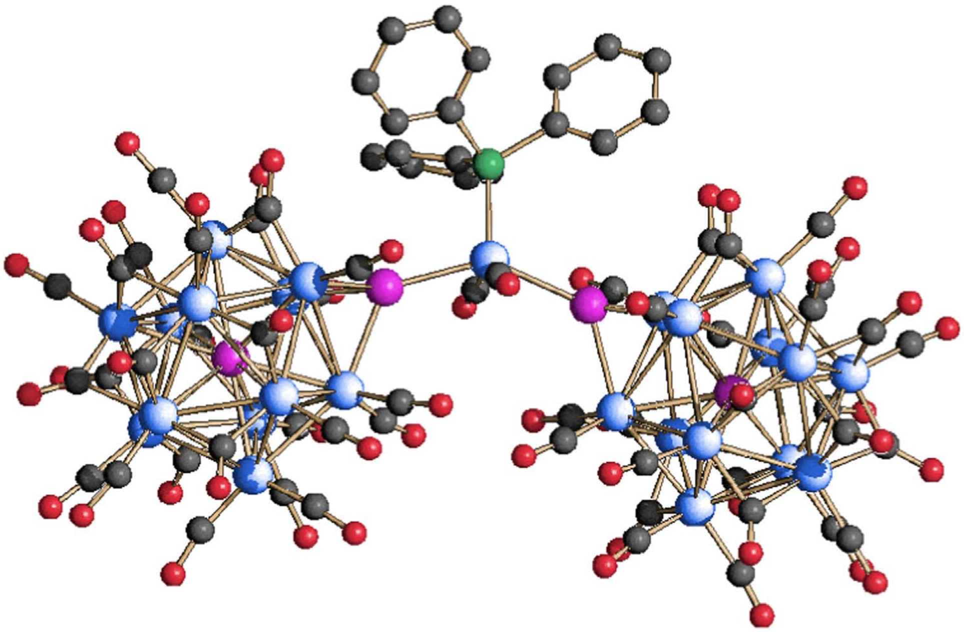

Fig. 2. Molecular structure of $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3]^{7-}$ (Rh: blue, Sb: pink, P: green, C: grey, O: red. Hydrogen atoms have been omitted for sake of clarity).

target cluster was extracted with about 20 mL of acetone but transferred to acetonitrile, where it was crystallized by layering on di-isopropyl. After a few days, black crystals of $[Sb@Rh_{12}(CO)_{24}][NEt_4]_4\cdot 2CH_3CN$ formed. Reaction yield: 22% (based on Rh). The compound is well soluble in acetone, acetonitrile and dymethylformamide. And νCO in CH_3CN was 1994(vs), 1805 (ms) cm^{-1}.

2.3. Synthesis of $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3][NEt_4]_7\cdot CH_3CN$

The cluster $[Sb@Rh_{12}(CO)_{27}][NEt_4]_3$ was prepared as described before and put in acetonitrile, then precipitated with an aqueous solution of $[NEt_4]Br$ in order to eliminate the residual acidity. A sample of such $[Sb@Rh_{12}(CO)_{27}][NEt_4]_3$ (0.112 mmol) was dissolved in acetonitrile and a second solution of PPh_3 (0.090 mmol) in the same solvent was slowly added to the first, under CO, in a 1:0.8 M ratio. After a few hours the resulting mother solution was filtered and di-isopropyl ether was layered on top, allowing to obtain $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3][NEt_4]_7\cdot CH_3CN$ in a crystalline form. The reaction yield was 43% (based on Rh). The compound is well soluble in acetone, acetonitrile and dymethylformamide. And νCO in CH_3CN was 2022(sh), 1998(vs), 1806(ms), 1767(m) $cm^{-1.}$ $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K) δ_P (ppm) was 29.9 (d, $^1J_{Rh\text{-}P}$=128 Hz).

3. Results and discussion

The previously known $[Sb@Rh_{12}(CO)_{27}]^{3-}$ cluster compound was the first reported example of an icosahedral arrangement of Rh atoms which lodged the remaining Sb inside the cavity, acting as a five-electron donor. The synthesis proposed by Vidal consisted of the reaction between $Rh(CO)_2acac$ (acac =acetylacetonate) and $SbCl_3$ in the presence of cesium benzoate, in a solution of tetraethylene glycol/dimethyl ether, under around 400 atm of carbon monoxide and hydrogen (CO/H_2=1), at 140–160 °C. The presence of CO and H_2 ensured the necessary carbonyl ligands and reductive environment, as the starting material was a Rh(I) complex and the final product presented Rh in a negative oxidation state. We adopted a completely different approach by starting from an already reduced Rh compound, the pre-formed $[Rh_7(CO)_{16}]^{3-}$ cluster, as source of both Rh and CO ligands, which we reacted with $SbCl_3$. In this way the presence of H_2 became unnecessary and the CO pressure could be reduced to just 1–1.5 atm. Furthermore, no high temperature was needed as the driving force of the reaction was the spontaneous oxidation of the Rh atoms by the Sb^{3+} species, which occurred at room temperature. We prepared a solution of $[Rh_7(CO)_{16}][NEt_4]_3$ in acetonitrile and dropwise added a second solution of $SbCl_3$, in the same solvent, under CO at room temperature. By monitoring the reaction via IR spectroscopy, we were able to observe the disappearance of the typical νCO frequencies of $[Rh_7(CO)_{16}]^{3-}$ in favor of the ones belonging to the $[Rh(CO)_2Cl_2]^-$ complex and the known $[Sb@Rh_{12}(CO)_{27}]^{3-}$. Owing to the experimental conditions and subsequent observations, we are confident that the reaction occurred according to the following equation:

$$4[Rh_7(CO)_{16}]^{3-}+3SbCl_3\rightarrow$$
$$2[Rh_{12}Sb(CO)_{27}]^{3-}+3Cl^-+3[Rh(CO)_2Cl_2]^-+Sb+Rh+4CO$$

After just a few hours the brown solution was dried under vacuum and the solid washed with water, ethanol, and tetrahydrofuran (THF) in order to eliminate $[NEt_4]Cl$ and $[Rh(CO)_2Cl_2]^-$. The residue was finally extracted with acetone and, by layering 2-propanol on the cluster solution, we were able to obtain black crystals of $[Sb@Rh_{12}(CO)_{27}][NEt_4]_3$ in fairly good yields. The X-Ray confirmed its nature and its molecular structure perfectly paralleled the one reported by Vidal, although this time we obtained a polymorphic form (see Section 4).

Once the cluster was available in reasonable quantities, its chemical reactivity was investigated. And initially its stability was tested under N_2 atmosphere in solution. By IR monitoring, we registered a progressive lowering of its νCO stretching frequencies in acetonitrile, both for terminal and bridging carbonyls. More specifically, the initial peaks at 2013(vs) and 1826(m) cm^{-1} gradually decreased down to 1995(s) and 1806(m, br) cm^{-1}, respectively, over 24 h. When the latter solution was put back into CO atmosphere, the opposite phenomenon occurred and the νCO stretching frequencies returned to their original values. Considering that the parent cluster is maintaining its metal structure throughout both processes, in the first case such lowering of CO frequencies was compatible with some ligand loss. In fact, the same negative charge has to be transferred, via π back-bonding, onto a minor number of ligands, resulting in an overall decrease of the C-O bond strength and, consequently, in a lowering of the IR frequencies. Unfortunately, the crystallization could not be confirmed, which is supposed to be an unsaturated species under nitrogen. However, this result led us to repeat the synthesis of $[Sb@Rh_{12}(CO)_{27}]^{3-}$ by using the

Table 2
Interatomic Sb-Rh and Rh-Rh bond lengths for $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3]^{7-}$.

First $[Sb@Rh_{12}\,(CO)_{24}Sb]$ unit		First $[Sb@Rh_{12}\,(CO)_{24}Sb]$ unit	
Atoms	Bond lengths (Å)	Atoms	Bond lengths (Å)
Sb(1)-Rh(7)	2.769(3)	Sb(21)-Rh(30)	2.753(3)
Sb(1)-Rh(11)	2.773(3)	Sb(21)-Rh(29)	2.766(3)
Sb(1)-Rh(4)	2.777(3)	Sb(21)-Rh(26)	2.780(3)
Sb(1)-Rh(13)	2.790(3)	Sb(21)-Rh(27)	2.787(3)
Sb(1)-Rh(8)	2.793(3)	Sb(21)-Rh(23)	2.787(3)
Sb(1)-Rh(2)	2.801(3)	Sb(21)-Rh(24)	2.789(2)
Sb(1)-Rh(10)	2.801(3)	Sb(21)-Rh(32)	2.790(3)
Sb(1)-Rh(6)	2.801(3)	Sb(21)-Rh(22)	2.802(3)
Sb(1)-Rh(12)	2.814(3)	Sb(21)-Rh(33)	2.820(3)
Sb(1)-Rh(3)	2.821(3)	Sb(21)-Rh(28)	2.888(3)
Sb(1)-Rh(9)	2.876(3)	Sb(21)-Rh(25)	2.904(3)
Sb(1)-Rh(5)	2.925(3)	Sb(21)-Rh(31)	2.916(3)
Rh(2)-Rh(7)	2.793(3)	Rh(22)-Rh(24)	2.781(3)
Rh(2)-Rh(6)	2.799(3)	Rh(22)-Rh(23)	2.806(3)
Rh(2)-Rh(4)	2.960(3)	Rh(22)-Rh(27)	2.977(3)
Rh(2)-Rh(3)	3.017(3)	Rh(22)-Rh(26)	3.005(3)
Rh(2)-Rh(5)	3.104(3)	Rh(22)-Rh(25)	3.138(3)
Rh(3)-Rh(8)	2.828(4)	Rh(23)-Rh(27)	2.912(3)
Rh(3)-Rh(7)	2.855(3)	Rh(23)-Rh(29)	2.981(3)
Rh(3)-Rh(4)	2.960(3)	Rh(23)-Rh(24)	3.073(3)
Rh(3)-Rh(12)	2.999(3)	Rh(23)-Rh(28)	3.159(3)
Rh(4)-Rh(9)	2.884(4)	Rh(24)-Rh(25)	2.920(3)
Rh(4)-Rh(5)	2.918(3)	Rh(24)-Rh(30)	2.969(3)
Rh(4)-Rh(8)	2.973(3)	Rh(24)-Rh(29)	3.120(3)
Rh(5)-Rh(9)	2.845(4)	Rh(25)-Rh(31)	2.847(3)
Rh(5)-Rh(10)	2.918(3)	Rh(25)-Rh(30)	2.884(3)
Rh(5)-Rh(6)	2.952(3)	Rh(25)-Rh(26)	2.911(3)
Rh(6)-Rh(11)	3.014(3)	Rh(26)-Rh(31)	2.914(4)
Rh(6)-Rh(10)	3.028(4)	Rh(26)-Rh(27)	2.919(3)
Rh(6)-Rh(7)	3.069(3)	Rh(26)-Rh(32)	2.979(3)
Rh(7)-Rh(11)	3.043(3)	Rh(27)-Rh(32)	2.839(3)
Rh(7)-Rh(12)	3.082(3)	Rh(27)-Rh(28)	3.053(3)
Rh(8)-Rh(12)	2.811(3)	Rh(28)-Rh(32)	2.813(3)
Rh(8)-Rh(13)	3.005(4)	Rh(28)-Rh(33)	2.831(3)
Rh(8)-Rh(9)	3.099(4)	Rh(28)-Rh(29)	2.977(3)
Rh(9)-Rh(10)	2.894(4)	Rh(29)-Rh(33)	2.900(3)
Rh(9)-Rh(13)	3.124(3)	Rh(29)-Rh(30)	3.029(3)
Rh(10)-Rh(13)	2.932(4)	Rh(30)-Rh(31)	2.903(3)
Rh(10)-Rh(11)	3.007(3)	Rh(30)-Rh(33)	2.944(3)
Rh(11)-Rh(13)	2.937(3)	Rh(31)-Rh(32)	3.103(3)
Rh(11)-Rh(12)	3.030(3)	Rh(31)-Rh(33)	3.150(3)
Rh(12)-Rh(13)	2.820(4)	Rh(32)-Rh(33)	2.975(3)
Rh(6)-Sb(14)	2.529(2)	Rh(23)-Sb(34)	2.532(2)
Rh(7)-Sb(14)	2.506(3)	Rh(24)-Sb(34)	2.504(2)
Rh(11)-Sb(14)	2.620(3)	Rh(29)-Sb(34)	2.614(3)
Sb(14)-Rh(35)	2.586(3)	Sb(34)-Rh(35)	2.582(2)

same reaction conditions as before but carrying it out under N_2 atmosphere.

The reaction path appeared more complicated than the analogous one in CO, as inferred by IR monitoring. Firstly, insoluble solid residue was found in the mother solution at the end of the reaction, making the filtration a necessary operation before the work-up. Secondly, the extraction in THF not only allowed the elimination of the $[Rh(CO)_2Cl_2]^-$ complex, but the IR spectra of this solution revealed the co-presence of an unidentified compound, whose poor yield prevented us from performing any further analysis. However, the extraction in acetone allowed to isolate a new species whose νCO stretching frequencies were compatible with those observed during the reactivity of $[Sb@Rh_{12}(CO)_{27}]^{3-}$ under N_2 (see above). The species was transferred into acetonitrile and by layering on di-isopropyl ether, we managed to obtain well-shaped crystals of the new $[Sb@Rh_{12}(CO)_{24}]^{4-}$ carbonyl cluster as $[NEt_4]^+$ salt. The reaction was later on optimized by carrying it out in acetone, which allowed a cleaner work-up of the mother solution. As expected, $[Sb@Rh_{12}(CO)_{24}]^{4-}$ presents the same metal structure of the known $[Sb@Rh_{12}(CO)_{27}]^{3-}$ but it is stabilized by just 24 CO ligands, making it electronically and coordinatively unsaturated. A full detailed description of its molecular structure is reported in Section 4. Notably, when $[Sb@Rh_{12}(CO)_{24}]^{4-}$ was exposed to CO atmosphere in solution, its IR spectrum perfectly overlaped the one of $[Sb@Rh_{12}(CO)_{27}]^{3-}$, indicating a sort of equilibrium between the two clusters driven by the presence/absence of CO atmosphere. However, it is important to underline that, despite the experimental evidence given by the IR spectroscopy, the difference in the negative charge between the two clusters makes that the equilibrium more complicated than it appears. However, this does not undermine the conclusion that $[Sb@Rh_{12}(CO)_{27}]^{3-}$ is a rare example of a CO-releasing transition-metal carbonyl cluster, which could be relevant in that field of research [22].

Because of the several by-products derived from the reaction carried out under N_2, the $[Sb@Rh_{12}(CO)_{24}]^{4-}$ yield was rather low (22% based on Rh), however we had enough sample to conduct some chemical tests, along with the ones on the parent $[Sb@Rh_{12}(CO)_{27}]^{3-}$ compound. More specifically, once we knew that the metallic $[Sb@Rh_{12}]$ core could be stable with a different number of ligands, we tried to substitute some carbonyls with other molecules such as PPh_3. The reason behind this choice was, in case of success, the future possibility of coordinating bidentate ligands allowing the building of polymeric architectures, like the ones observed in some Fe carbide clusters such as $[Fe_4Cu_2(\mu_6\text{-}C)(CO)_{12}(\mu\text{-}L\text{–}L)]\infty$[23].

We tested the reactivity of $[Sb@Rh_{12}(CO)_{24}]^{4-}$ with PPh_3 in acetonitrile firstly under N_2 atmosphere. After adding about three equivalents of the latter, we could observe the formation of a new compound with the main νCO stretching frequencies at 1991(vs), 1804(m), 1793(m), cm^{-1}. Unfortunately, we could not obtain good-quality crystals of this new species for an X-ray diffraction analysis. The same reaction carried out under CO atmospheric pressure led to another unidentified compound, with νCO stretching frequencies at 1996(s), 1806(m), cm^{-1}, not related to any known species. As for $[Sb@Rh_{12}(CO)_{27}]^{3-}$, the reaction with PPh_3 under N_2 atmosphere allowed us to obtain a new species with νCO stretching frequencies at 1985(s), 1826(m), 1779(m) cm^{-1}, by adding just one PPh_3 equivalent. But it was not possible to obtain crystals for X-ray diffraction analysis. All these above reactions and their relative products are currently under investigation. Conversely, the reaction between $[Sb@Rh_{12}(CO)_{27}]^{3-}$ and PPh_3 carried out under CO atmospheric pressure led to a new species which we were able to identify as the dimeric $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3][NEt_4]_7{\cdot}1CH_3CN$ carbonyl cluster, after an X-ray diffraction analysis. To our surprise, the phosphine ligand did not directly coordinate onto the original cluster but, after partly decomposing the starting material into smaller Rh complexes, it was the newly formed $Rh(CO)_2PPh_3$ fragment which coordinated onto two $\{Sb@Rh_{12}(CO)_{25}Sb\}$ units.

This cluster was also characterized by NMR spectroscopy. $^{31}P\{1H\}$ NMR spectrum of crystals recorded in CD_3CN at 298 K shows a doublet centered at δ_P 29.9 ppm with $^1J_{Rh\text{-}P}$=128 Hz, as previously found in analogous Rh(I) compounds [24–27]. The ^{31}P NMR spectrum of $[(Sb@Rh_{12}Sb(CO)_{25})_2Rh(CO)_2PPh_3][NEt_4]_7$ is fully consistent with its solid state structure, which contains just one PPh_3 bonded to a single rhodium atom. Furthermore, the diagnostic signal was detected as the major one in the crude, along with other signals of unidentified by-products.

4. X-Ray crystal structures

All three clusters reported in this work were analyzed by X-ray diffraction in order to determine their molecular structures. The $[Sb@Rh_{12}(CO)_{27}][NEt_4]_3$ salt was reported by Vidal to be crystallized in the rhombohedral R-3c space group, while we found that polymorphic crystals crystallized in the C2/c space group. However, the molecular structure of the trianion is equivalent to the one originally reported, and consists of a distorted icosahedron made of Rh atoms centered by the unique Sb, stabilized by 27 carbonyl ligands: 12 terminal (one for

Table 3
Crystal data and experimental details for $[Sb@Rh_{12}(CO)_{27}]^{3-}$ (1), $[Sb@Rh_{12}(CO)_{24}]^{4-}$ and $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3]^{7-}$ (3).

Formula	**1**	**2**	**3**
	$C_{51}H_{60}N_3O_{27}Rh_{12}Sb$	$C_{60}H_{86}N_6O_{24}Rh_{12}Sb$	$C_{128}H_{158}N_8O_{52}PRh_{25}Sb_4$
Fw	2503.69	2632.01	5731.33
T, K	77(2)	77(2)	77(2)
λ, Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/c	*P*−1	*C*/2c
a, Å	20.020(5)	12.9368(3)	42.0905(12)
b, Å	22.608(6)	13.6048(3)	24.2781(7)
c, Å	15.786(4)	14.0893(3)	34.1882(9)
α, deg	90	61.9360(10)	90
β, deg	102.489(3)	67.1360(10)	104.912(2)
γ, deg	90	70.8180(10)	90
Cell volume, $Å^3$	6976(3)	1983.59(8)	33759.6(17)
Z	4	1	8
D_c, g cm^3	2.384	2.203	2.255
μ, mm^{-1}	3.214	2.830	3.082
F(000)	4776	1271	21936
Crystal size, mm	0.220×0.180×0.160	0.250×0.150×0.120	0.200×0.180×0.120
θ limits, deg	1.377 to 25.995	1.707 to 25.000	1.468 to 25.000
Index ranges	−24 < =h < =24, −27 < =k < =27, −19 < =l < =19	−15 < =h < =15, −16 < =k < =16, −16 < =l < =16	−50 < =h < =50, −27 < =k < =28, −40 < =l < =40
Reflections collected	20859	27980	139944
Independent reflections	6770 [R_{int}=0.0647	6969 [R_{int}=0.0676	29699 [R_{int}=0.0987]
Completeness to *θ* max	98.8%	99.8	99.9%
Data/restraints/parameters	6770/12/432	6969/609/632	29699/1777/2257
Goodness off fit on F^2	1.039	1.007	1.067
R_1 (I > 2σ(I))	0.0604	0.0424	0.1026
wR_2 (all data)	0.1822	0.1109	0.2557
Largest diff. peak and hole, e·$Å^3$	2.987 and −1.559	1.678 and −1.141	2.231 and −2.248

each Rh) and 15 edge-bridging COs. The distortion is reflected in the Rh-Rh distances, reported in Table 1, spanning from 2.8720(14) to 3.3680 (15) Å (average 2.9821 Å), while the Rh-Sb bond lengths vary from 2.7069(12) to 2.9409(13), with an average value of 2.8227 Å, analogous to the bond distances found by Vidal. Note that Rh-Rh bonding interactions usually fall within 2.60–3.20 Å range, making the longer distance in the cluster a clear sign of the deviation from an ideal icosahedral geometry. Furthermore, no edge-bridging COs have been found on the two longest bond interactions.

The molecular structure of $[Sb@Rh_{12}(CO)_{24}]^{4-}$, illustrated in Fig. 1, is very similar to the one of the parent compound as far as the metal framework is concerned: the twelve Rh atoms are again vertexes of an icosahedron centered by the Sb atom..

However the metal core is rather more regular and compact, as inferred by the Rh-Rh and Rh-Sb bond distances, reported in Table 1. In fact, although the former distances present an average value of 2.974 Å, very similar to the one of $[Sb@Rh_{12}(CO)_{27}]^{3-}$ they span from 2.7835(9) to 3.0448(9) Å and no longer bonds are present. The shrinking of the icosahedron is also reflected in the Rh-Sb bond lengths, whose average is 2.7788 Å, going from 2.7454(6) to 2.8016(7) Å. The metal core is stabilized by 24 CO ligands, of which 12 are terminally bonded to the polyhedron vertexes and the remaining 12 are edge-bridged. The $[Sb@Rh_{12}(CO)_{24}][NEt_4]_4 \cdot 2CH_3CN$ crystallized in the *P*−1 space group and the Sb atom lays on the inversion center, so the asymmetric unit only contains half a cluster, two cations and one solvent molecule (Z=1).

The molecular structure of $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3]^{7-}$ is illustrated in Fig. 2. The cluster is made by two slightly distorted icosahedral heteroleptic $[Sb@Rh_{12}Sb(CO)_{25}]$ units, with the second Sb atom on the surface capping a triangular face and acting as a ligand, joined by a $\{Rh(CO)_2PPh_3\}$ fragment. The Sb-Rh and Rh-Rh bond distances are reported in Table 2. As illustrated, the Sb-Rh bond lengths vary from 2.769(3) to 2.925(3) Å for the first unit (average 2.812 Å) and from 2.753(3) to 2.916(3) Å (average 2.815 Å) for the second one. Their values are higher than the ones observed for $[Sb@Rh_{12}(CO)_{24}]^{4-}$ but lower than those found in $[Sb@Rh_{12}(CO)_{27}]^{3-}$. Note that the Sb-Rh bonds for the Sb atom coordinated on the cluster surface of each unit are shorter, with the values of 2.552 Å and 2.550 Å (average values), respectively. The Rh-Rh distances for the first unit span from 2.793(3) to 3.124(3) (average 2.957 Å), similar to the ones in the second unit which are in the range of 2.781(3)–3.150(3) Å (average 2.960 Å). Again, these values are in between the ones of the $[Sb@Rh_{12}(CO)_{27}]^{3-}$ and $[Sb@Rh_{12}(CO)_{24}]^{4-}$ homoleptic clusters, indicating a similar intermediate deviation from the regular icosahedral geometry. The bond lengths between the two surface Sb atoms and the central Rh coordinated to the PPh_3 are 2.586(3) Å and 2.852(2) Å. As for the carbonyl ligands of the two icosahedral units, in both cases 12 out of 25 are terminally bonded to the Rh atoms, while the remaining 13 are edge-bridged. The compound crystallized in the C2/c space group and the unit cell is very big, containing eight cluster compounds, fifty-six ammonium cations and eight acetonitrile solvent molecules. The independent unit is also large as it comprises the whole dimeric species along with the seven cations and the acetonitrile molecule (Z=8)..

Crystal data and experimental details for the three clusters are reported in Table 3.

The icosahedral arrangement is not new for clusters of such nuclearity, and can be found not only with Rh but often with heteroatomic Ni carbonyl clusters, including $[Ni_{12}M(CO)_{22}]^{2-}$ (M=Ge, Sn) [28]. When moving to higher nuclearity, icosahedral-based architectures become more common. This can be observed, for instance, in $Pd_{145}(CO)_x(PEt_3)_{30}$ [29], $Pd_{55}L_{12}(CO)_{20}$ (L=PR$_3$, R=isopropyl) [30], $[Au_{25}(SCH_2CH_2Ph)_{18}]^-$ [31], $Au_{38}(SC_2H_4Ph)_{24}$ [32] and $[Ag_{44}(p\text{-}MBA)_{44}]^{4-}$ [33]. Notably, the latter is the only one having an empty icosahedral core.

5. Conclusions

In this work an alternative synthesis has been developed, for the previously known $[Sb@Rh_{12}(CO)_{27}]^{3-}$ icosahedral carbonyl cluster in much milder reaction conditions, which became the starting point allowing to isolate and characterize two new heterometallic Rh carbonyl clusters, namely $[Sb@Rh_{12}(CO)_{24}]^{4-}$ and $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3]^{7-}$. These results pointed out that $[Sb@Rh_{12}(CO)_{27}]^{3-}$ could serve as a spontaneous CO-releasing molecule in the appropriate atmosphere. In addition, this compound showed a very rich chemical reactivity, which is currently under investigation. Furthermore, the electronically and coordinatively unsaturated $[Sb@Rh_{12}(CO)_{24}]^{4-}$ species is very interesting as it represents one of the rare cases in which a carbonyl cluster compound of such nuclearity is stable with less electrons than those predicted by the cluster-borane analogy. The achieved results are encouraging and could be very useful for the study of other heterometallic Rh systems.

Further informations

CIF data for $[Sb@Rh_{12}(CO)_{27}]^{3-}$, $[Sb@Rh_{12}(CO)_{24}]^{4-}$ and $[\{Sb@Rh_{12}Sb(CO)_{25}\}_2Rh(CO)_2PPh_3]^{7-}$ have been deposited in the CCDC database. The deposition numbers are 1496973, 1496973 and 1496975, respectively.

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