Journal of Organometallic Chemistry, 213 (1981) 351—363
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

$[Rh_{12}Sb(CO)_{27}]^{3-}$. AN EXAMPLE OF ENCAPSULATION OF ANTIMONY BY A TRANSITION METAL CARBONYL CLUSTER *

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(Received December 3rd, 1980)

Summary

The reaction of $Rh(CO)_2acac$ with triphenylantimony in the presence of cesium benzoate in tetraethylene glycol/dimethyl ether solution resulted in the selective formation of $[Rh_{12}Sb(CO)_{27}]^{3-}$ (66% yield) after 3 h of contact time under ~400 atm of carbon monoxide and hydrogen ($CO/H_2 = 1$) at 140—160°C. The cluster has been isolated as the $[Cs(18\text{-Crown-}6)_2]^+$, $[(CH_3)_4N]^+$, $[(C_2H_5)_4N]^+$, $[(Ph_3P)_2N]^+$ and $[PhCH_2N(C_2H_5)_3]^+$ salts. The $[(C_2H_5)_4N]_3[Rh_{12}Sb(CO)_{27}]$ complex has been characterized via a complete three-dimensional X-ray diffraction study. The complex crystallizes in the space group $R\bar{3}c$ with $a = 23.258(13)$ Å, $c = 22.811(4)$ Å, $V = 10\,686$ Å^3 and $\rho(calcd.) = 2.334$ g cm^{-3} for mol.wt. 2503.66 and $Z = 6$. Diffraction data were collected with an Enraf-Nonius CAD 4 automated diffractometer using graphite-monochromatized Mo-K_α radiation. The structure was solved by direct methods and refined by difference-Fourier and least-squares techniques. All non-hydrogen atoms have been located and refined: final discrepancy indices are $R_f = 3.5\%$ and $R_{wf} = 4.6\%$ for 3011 reflections. The anion's structure consists of twelve rhodium atoms situated at the corners of a distorted icosahedron with contacts of 2.807(1), 2.861(1), 2.874(1), 2.999(1), 3.017(1) and 3.334(1) Å and rhodium—antimony contacts of 2.712(0) and 2.922(0) Å. Rhodium—rhodium bond distances of 2.807 and 3.017 Å are in the range usually found for these complexes although a distance of 3.334 Å may be longer than expected from bonding interactions. The sum of the covalent radii of antimony and rhodium, 2.80 Å, is intermediate between the two observed Rh—Sb contacts. The anion cluster structure is that of a distorted icosahedron. This polyhedron has previously been found in $[B_{12}H_{12}]^{2-}$ but not with transition metal clusters. A comparison between the structures of rhodium carbonyl clusters and boranes shows the occurrence of similar structural features. Applications of bonding theories

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* Dedicated to the memory of Professor Paolo Chini.

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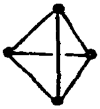
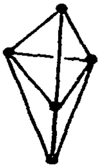
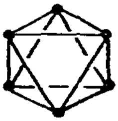
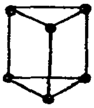
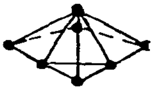
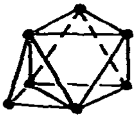
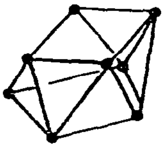
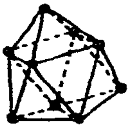
based on the boranes, such as Wade's rules, to rhodium carbonyl clusters shows the extent in which these rules are obeyed.

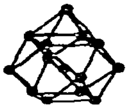
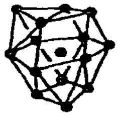
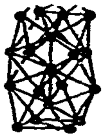
Introduction

Rhodium has been mentioned to be unique among transition metals in its ability to form polynuclear carbonyl complexes containing an unusually large number of metal atoms arranged in a wide variety of polyhedra [1]. This is evident from a comparative review of the clusters characteristic for these elements [2]. Polynuclear M_9^{n-} ($n = 2, 4$) complexes are formed by some non-metallic elements such as Sn, Pb and Ge, while other clusters are known for bismuth [3]. The tendency to form clusters with incorporated heteroatoms is more common in the case of boron, than for other non-metallic elements. Borane clusters have been shown to exhibit structures based on the same polyhedra as those of some rhodium carbonyl clusters [4]. Boron and rhodium form clusters which range in size from less than twelve atoms to the largest aggregate known to date (Scheme 1). The analogies between boron and rhodium are important because the theories that allow us to understand the bonding in boranes have been extended to the metal clusters in an attempt to rationalize their structures with respect to the number of skeletal electrons [5]. The recent characterization of $[Rh_9P(CO)_{21}]^{2-}$ and $[Rh_{10}E(CO)_{22}]^{3-}$ (E = P, As) [6] shown in the case of rhodium the existence of polyhedra expected or previously found for the boranes. Other rhodium carbonyl clusters with encapsulated carbon or nitrogen, $[Rh_6(CO)_{15}C]^{2-}$ and $[Rh_6(CO)_{15}N]^{-}$, have also been shown to have structures [2,7] previously reported for the boranes.

Rhodium carbonyl clusters with encapsulated main-group atoms were known prior to this work for carbon [2], nitrogen [7], phosphorus [6], arsenic [6] and sulfur [8]. It was of interest to us in the view of the results with phosphorus and arsenic to test the ability of rhodium carbonyl clusters to encapsulate antimony because of the isoelectronic character of these atoms and to study how the increase in the size of the encapsulated atom could affect the structures of the resulting clusters. Steric effects [2] had to be considered when determining whether the interstitial atoms would fit the polyhedral cavities. These considerations suggested that antimony, with a covalent radius similar to that of rhodium, 1.41 vs. 1.39 Å, respectively [9,1], could form clusters based on the icosahedron, the twinned-cuboctahedron and the cuboctahedron. The latter two polyhedra forms for rhodium are present in $[Rh_{13}(CO)_{24}H_2]^{3-}$ and $[Rh_{14}(CO)_{25}]^{4-}$ [10a—c].

We report now the synthesis, structure and some chemical reactions of $[Rh_{12}Sb(CO)_{27}]^{3-}$. This cluster contains a naked antimony atom in the cavity of the polyhedron. It represents the first example of a coordination complex in which antimony is acting as a five-electron donor center. This can be contrasted with another reported complex formed between atomic antimony and a cobalt carbonyl moiety, $CO_4(CO)_{12}Sb_4$, in which the antimony ligand is apparently donating only three electrons [11].

Rhodium Carbonyl Cluster	Polyhedron	Borane
$Rh_4(CO)_{12}$		B_4Cl_4
$Rh_5(CO)_{15}^-$		
$Rh_6(CO)_{16}$		$B_6H_6^{2-}$
$Rh_6(CO)_{15}C^{2-}$		$B_6H_6^{6-}$
		$B_7H_7^{2-}$
$Rh_7(CO)_{16}^{3-}$		
		$B_8H_8^{2-}$
		$B_9H_9^{2-}$

Rhodium Carbonyl Cluster	Polyhedron	Borane
$Rh_9P(CO)_{21}^{2-}$ $Rh_9As(CO)_{21}^{2-}$		
$Rh_{10}P(CO)_{22}^{3-}$ $Rh_{10}As(CO)_{22}^{3-}$		$B_{10}H_{10}^{2-}$
$Rh_{12}Sb(CO)_{27}^{3-}$		$B_{12}H_{12}^{2-}$
$Rh_{13}(CO)_{24}H_3^{2-}$		
$Rh_{14}(CO)_{25}^{4-}$		
$Rh_{15}(CO)_{27}^{3-}$		
$Rh_{17}S_2(CO)_{32}^{3-}$		
$Rh_{22}(CO)_{35}H_x^{4.5-}$		

Experimental section

The reagents used in this work have been obtained and handled as previously described [6,8] with the exception of triphenylantimony and tetraethylammonium chloride that were obtained from Aldrich Chemical Co.

The experimental procedures, equipment and analysis were conducted as in previous reports [6,8,10c]. The crystals used in the study were obtained by the slow diffusion method using acetone-2-propanol.

Synthesis of $[Rh_{12}Sb(CO)_{27}]^{3-}$ salts

$Rh(CO)_2acac$ (17.086 g, 67.25 mmol), cesium benzoate (3.310 g, 11.26 mmol) and triphenylantimony (3.800 g, 10.77 mmole) were mixed as previously described for Ph_3P and Ph_3As [6]. The same manipulations and conditions used in these cases were followed in the isolation of the product; tetraethylammonium chloride (1 g in 15 ml) was used to carry out the methathesis reaction. The amount of final product (9.25 g) corresponded to a yield of 66% based on the initial rhodium compound. The analysis of the tetraethylammonium salt is that expected for the characterized compound. Found: C, 24.20; H, 2.73; N, 1.58; Rh, 49.21; Sb, 4.77. Calcd. for $Rh_{12}SbO_{27}N_3C_{51}H_{60}$: C, 24.47; H, 2.42; N, 1.68; Rh, 49.32; Sb, 4.86%. Other salts of the anion were also prepared such as $[Cs(18\text{-Crown-}6)_2]^+$, $[(CH_3)_4N]^+$, $[(Ph_3P)_2N]^+$ and $[PhCH_2N(C_2H_5)_3]^+$. These compounds are soluble in acetone, acetonitrile, methanol, sulfolane and other polar organic solvents. The cesium salt is also soluble in glymes and tetrahydrofuran.

X-ray data collection

The first crystal selected for the study was a black prismatic crystal with dimensions of 0.2 × 0.2 × 0.1 mm, which decayed relatively quickly during our studies. Another similar crystal, 0.2 × 0.2 × 0.3 mm, was used in the determination of the structure. The manipulations of the crystal, the instrumentation, the software and the instrumental settings not mentioned below were similar to those previously used by us [6,8,10c].

In the present study, we have used an incident-beam collimator diameter of 0.7 mm, and a variable scan rate of 2—20°/min in omega. This technique as well as moving-crystal background counting methods have been already discussed [6,8]. Intensity data was collected via ω—θ scans with an ω—θ scan speed ratio of 1 over a range of data of $0.4° < 2\theta$ (Mo-K_α) $< 55°$, with a scan range in degrees of ω (width) $= 0.7° + 0.35$ (Tan(θ)). The scan width was increased as a function of θ to correct for the separation of the $K_{\alpha1}$, $K_{\alpha2}$ doublet. The calculations of the intensities and standard derivations followed previous procedures [6,8]. The stabilities of the crystal and the electronics were checked by measuring periodically three strong representative reflections. No significant changes were observed. Lorentz and polarization corrections were applied to the data. Corrections for extinction were not required. An absorption correction was made using the psi scan method. The variation in transmission was from 91.9% to 99.8%. Two space groups were initially possible, $R\bar{3}c$ and $R3c$; however, the former one was confirmed by refinement. Twenty-five reflections were used in the determination of the unit cell dimensions and

TABLE 1

DATA FOR THE X-RAY DIFFRACTION STUDY OF $[(C_2H_5)_4N]_3[Rh_{12}Sb(CO)_{27}]$

(A) Crystal data
Crystal System: Rhombohedral
Space group: $R\bar{3}c$
$a = 23.258(13)$ Å
$c = 22.811(4)$ Å
$V = 10868$ Å^3
$T = 23°$C
$Z = 6$
mol. wt. = 2503.66
ρ(calcd.) = 2.334 g cm^{-3}
$F(000) = 7164$
$\mu = 30.703$ cm^{-1}
extinctions = $h0ll \neq 2n$

(B) Intensity data
Radiation: Mo-K_α
monochromator: graphite-crystalline incident beam
max 2θ: 55°
min 2θ: 0.4°
scan type: $\omega - \theta$
scan speed ratio: $\omega/\theta = 1$
scan speed: 2° to 20°/min in omega
scan range: ω(width) = 0.7° + 0.35(tan θ)
θ(width) = 1 (ω(width))
reflections collected: 3101 total; 3011 independent
linear absorption coeff: 30.703 cm^{-1}

orientation matrix for data collection. Numerical information on data collection is given in Table 1.

Solution and refinement of the structure

The computer software, the scattering factors, the function minimized during least-squares refinement and the calculation of the discrepancy indices have been previously described [6,8].

The structure was solved by direct methods. A total of 16 phase sets were produced using 500 reflections with $|E_{\min}| = 1.85$ and 2000 phase relationships. An E map prepared from the phase set showing the best probability statistics (absolute figure of merit = 1.25, residual = 19.1) resulted in the determination of the position of the three rhodium atoms. These atoms were included in a full-matrix least-squares refinement resulting in agreement factors of $R_f = 18\%$ and $R_{wf} = 27\%$. The remaining non-hydrogen atoms were located in the succeeding difference Fourier maps. All non-hydrogen atoms were refined anisotropically using only 1717 reflections having $|F_o|^2 > 3\sigma(|F_o|^2)$. Refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms led to convergence with $R_f = 3.5\%$ and $R_{wf} = 4.6\%$ for a total of 18 non-hydrogen atoms. The value of an e.s.d. of an observation of unit weight was 1.304 and the maximum parameter shift was 0.02 times its e.s.d. The function $\Sigma\, w(|F_o| - |F_c|)^2$ showed no appreciable dependence on $\lambda^{-1} \sin\theta$ or upon $|F_o|$. The final difference-Fourier map showed no residual electron density as high as carbon atoms on a previous difference-Fourier map.

A table of observed and calculated structure factor amplitudes is available from the authors as supplementary material together with the positional parameters and full tables of interatomic distances and angles.

Results and discussion

Triphenylantimony reacts with Rh(CO)$_2$acac in presence of cesium benzoate upon mixing these reagents at ambient conditions, giving a complex mixture after several hours at 80° C under ~3 atm of carbon monoxide and hydrogen. The relative strengths of the aryl carbon bonds to Group V elements [9], together with our previous observations concerning the easy cleavage of this bond in Ph$_3$E (E = P, As) with the resulting formation of $[Rh_9E(CO)_{21}]^{2-}$ and $[Rh_{10}E(CO)_{22}]^{3-}$ [6], indicated that formation of clusters containing atomic antimony was a distinct possibility when operating under the conditions used in those studies. In agreement with these expectations, it was noted that the infrared spectra of the mixture during and after reaction (Fig. 1) are the same as that of $[Rh_{12}Sb(CO)_{27}]^{3-}$. These results indicate the high selectivity of this system. Similar high preference for the formation of a specific compound has also been observed during the high pressure synthesis [6,8,10c] of $[Rh_{17}Sb_2(CO)_{32}]^{3-}$, $[Rh_9E(CO)_{21}]^{2-}$, $[Rh_{10}E(CO)_{22}]^{3-}$ and $[Rh_{14}(CO)_{25}]^{4-}$. This appears to indicate the convenience of using high pressure techniques for the synthesis of some transition metal carbonyl clusters, as a probable way of

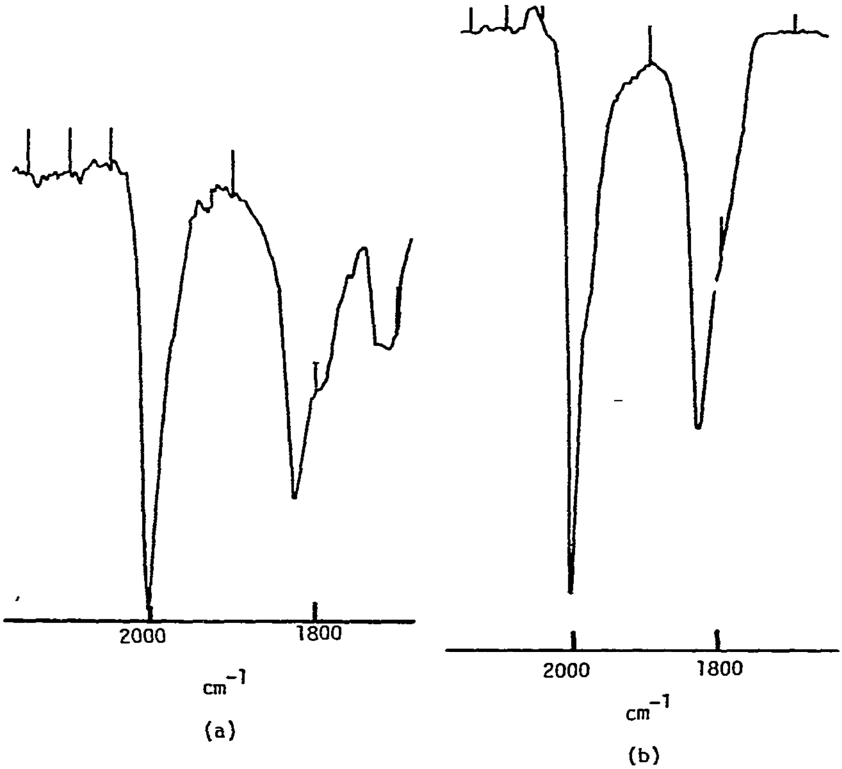


Fig. 1. Infrared spectra of: a) Synthetic mixture after 12 hours at 150° C under 500 atm of carbon monoxide and hydrogen. The same spectrum is observed with solutions of salts of $[Rh_{12}Sb(CO)_{27}]^{3-}$ after 1 hour at 260° C, under 800 atm of carbon monoxide and hydrogen, either in presence or absence of n-methylmorpholine. b) $[(C_2H_5)_4N]_3$ $[Rh_{12}Sb(CO)_{27}]$ in acetone solution under ambient conditions.

avoiding the involved, low-yield preparations required under ambient conditions in some cases.

The formation of a cluster containing an interstitial antimony atom shows the ability of this element to parallel the behavior previously observed for phosphorus and arsenic, with respect to the loss of the three phenyl radicals coordinated to these atoms, as well as its ability to form complexes in which the atomic ligand shares its five outer-shell electrons. This behavior has been found for the first time for antimony in $[Rh_{12}Sb(CO)_{27}]^{3-}$. This atom shares only three outer-shell electrons in the other known transition metal complex obtaining atomic antimony as a ligand, $Co_4(CO)_{12}Sb_4$ [11].

Structure of $[Rh_{12}Sb(CO)_{27}]^{3-}$

The structure of the cluster consists of a distorted icosahedron with the twelve rhodium atoms located at the corners and the antimony atom placed in the cavity of the polyhedron (Fig. 2). The carbonyl ligands are distributed with one terminally bonded to each rhodium atom, CO(1) and CO(2), three edge-bridged around each of the two capping metal atoms, CO(3), CO(4) and CO(5), two intra-planer edge-bridged on each of the basal sections, CO(4), CO(5) and three inter-planer edge-bridged connecting some of the atoms on these two layers, CO(3), CO(5).

The distortion of the basic icosahedron is reflected in the rhodium—rhodium distances (Table 2). The pentagonal planes of the icosahedron are folded in the cluster with the three Rh(2) atoms located in a coplanar position and the two remaining Rh(1) atoms out of the plane. This distortion results in rhodium—rhodium contacts of 2.874 and 2.999 Å between Rh(1)—Rh(1) and Rh(1)—Rh(2), respectively. The apical rhodium atoms, Rh(1), that in a regular icosahedron should be equidistant from the surrounding atoms, are separated by 2.874 Å from Rh(2), and are closer to the rhodium atoms, Rh(1), that are above the plane than to those Rh(1) below it as shown by contacts of 2.807 and 3.334 Å, respectively. Bonding interactions between two rhodium atoms in this type of complex are usually in the range of 2.60—3.20 Å [2,10]. These

TABLE 2

INTERATOMIC DISTANCES AND e.s.d.'s FOR $[Rh_{12}Sb(CO)_{27}]^{3-}$

(a) Rhodium—rhodium and rhodium—antimony distances			
Rh(1)—Rh(1)	3.334(1)	Rh(1)—Sb	2.922(1)
Rh(1)—Rh(1)	2.807(1)	Rh(2)—Sb	2.712(1)
Rh(1)—Rh(2)	2.874(1)		
Rh(1)—Rh(2)	3.017(1)		
Rh(1)—Rh(2)	2.861(1)		
Rh(2)—Rh(2)	2.999(1)		
(b) Rhodium—carbon and carbon—oxygen distances			
Rh(1)—C(1)	1.893(7)	C(1)—O(1)	1.114(8)
Rh(1)—C(3)	2.026(15)	C(2)—O(2)	1.110(8)
Rh(1)—C(3)	2.026(3)	C(3)—O(3)	1.152(9)
Rh(1)—C(4)	2.159(7)	C(4)—O(4)	1.179(7)
Rh(1)—C(5)	2.091(6)	C(5)—O(5)	1.190(7)
Rh(2)—C(2)	1.895(7)		
Rh(2)—C(4)	1.955(7)		
Rh(2)—C(5)	1.964(6)		

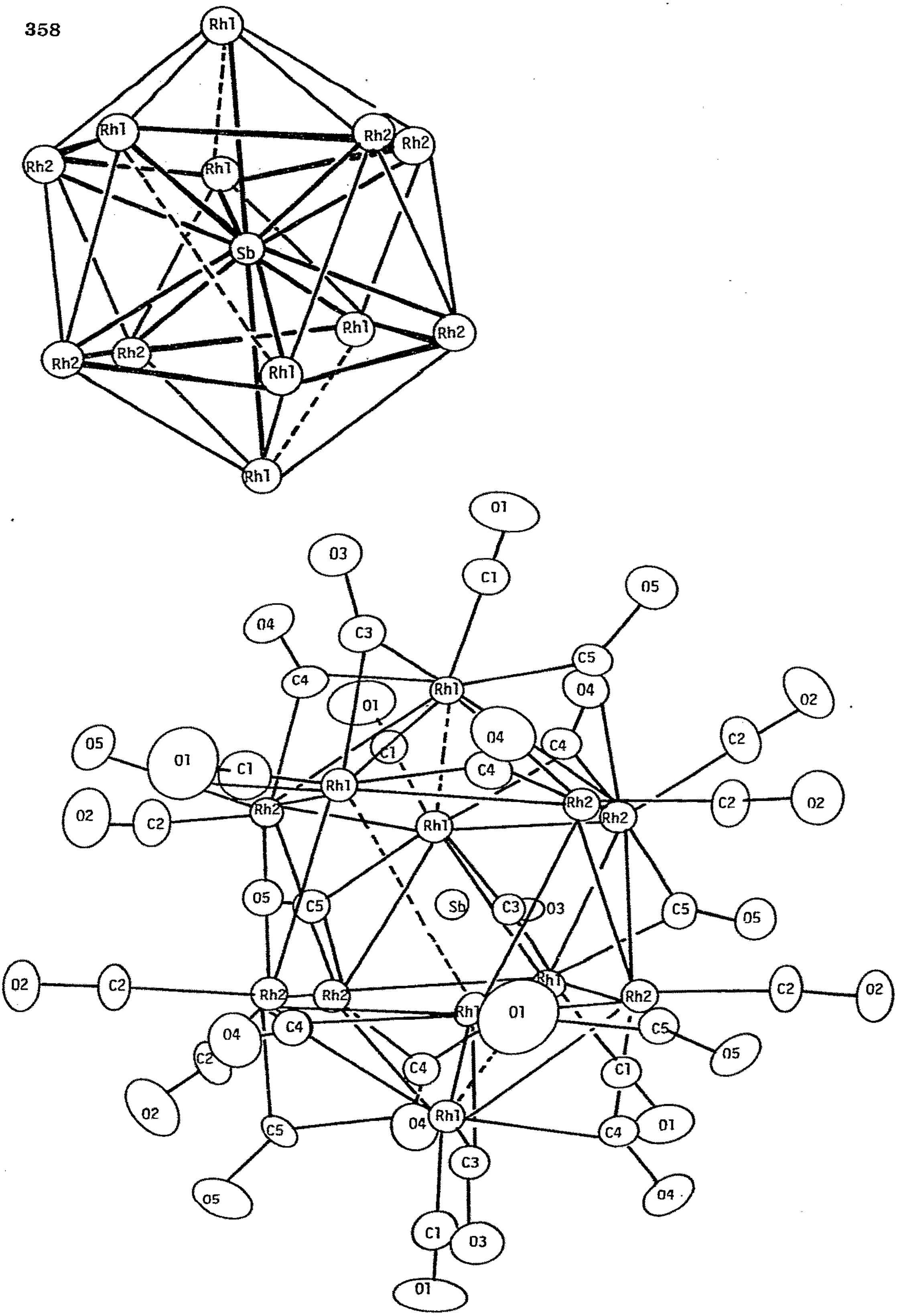
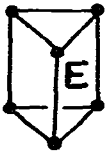
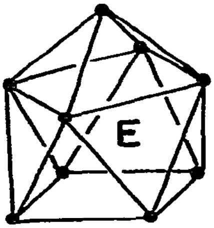
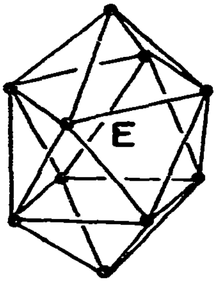
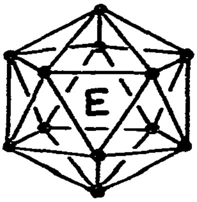


Fig. 2. ORTEP of $[Rh_{12}Sb(CO)_{27}]^{3-}$: a) With the carbonyl ligands omitted. b) Showing these ligands.

longer intraatomic rhodium contacts in $[Rh_{12}Sb(CO)_{27}]^{3-}$ result in the presence of three pseudo-square faces defined by two Rh(2) and two Rh(1) atoms. The two distinct sets of antimony—rhodium distances are also a consequence of this distortion. The antimony atom is in a linear arrangement with the two capping Rh(1) atoms as shown by a Rh(1)—Sb—Rh(1) angle of 173.0° and is equidistant from all the Rh(1) atoms with an interatomic distance of 2.922 Å, but it is closer to the Rh(2) atoms as indicated by Sb—Rh(2) contacts of 2.712 Å. Both

TABLE 3

RHODIUM CARBONYL CLUSTERS WITH ENCAPSULATED MAIN GROUP ATOMS (E = C, N, P, As, Sb)

		Covalent radius of main-group atom (Å)	Radius of polyhedral cavity, (Å) [a]
$Rh_6(CO)_{15}C^{2-}$ $Rh_6(CO)_{15}N^{-}$		0.77 0.70	0.735
$Rh_9P(CO)_{21}{}^{2-}$ $Rh_9As(CO)_{21}{}^{2-}$		1.10 1.21	0.900
$Rh_{10}P(CO)_{22}{}^{3-}$ $Rh_{10}As(CO)_{22}{}^{3-}$		1.10 1.21	0.900
$Rh_{12}Sb(CO)_{27}{}^{3-}$		1.41	2.085

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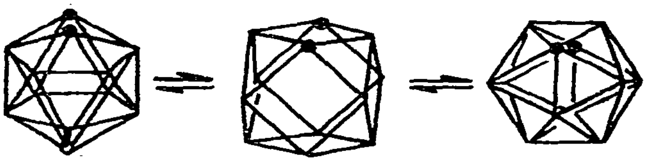
[a] The radii of the polyhedra's cavities have been taken from ref. 2 for the three first clusters using for the capped square antisprism the same radius as for the uncapped polyhedron, while it has been calculated by us in the case of the icosahedron using the same criteria as Chini, et al. [2].

of these lengths correspond to bonding interactions as suggested by comparison with the sum of the covalent radii of antimony and rhodium, 1.41 and 1.39 Å, respectively [9,1].

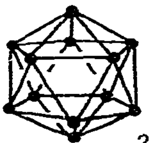
The average Rh—C and C—O distances in the case of the terminally bonded ligands are 1.894 and 1.112 Å, respectively. There are two symmetrical bridging carbonyls CO(5), each being between one of the two capping Rh(1) atoms and the closest of the surrounding Rh(1) atoms, with Rh—C and C—O distances of 2.026 and 1.152 Å, respectively. The remaining carbonyls are all asymmetric bridges with Rh(1)—C(4) and Rh(1)—C(5) distances of 2.159 and 2.091 Å, respectively, and average Rh(2) distances to C(4) and C(5) of 1.959 Å, with C—O lengths of 1.185 Å. These interatomic distances are normal for this type of complex [2,6].

The structures of the rhodium clusters with encapsulated phosphorus and arsenic show the pervasiveness of the square antiprism as the basic building block for these species [6], as well as for the cluster containing encapsulated sulfur [8]. By contrast, the structures of the clusters containing interstitial carbon or nitrogen atoms (Table 3) shows the presence of the trigonal prism in these instances and suggests the persistence of this arrangement with the smaller interstitial atoms. This is a probable consequence of the steric demands of the encapsulated atoms and the ability of the cavity of the respective polyhedra to accommodate them. The presence of a larger polyhedron in the case of the antimony-containing cluster is in agreement with these steric ideas.

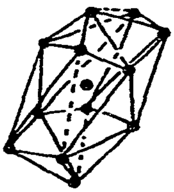
A comparison of the structure of $[Rh_{12}Sb(CO)_{27}]^{3-}$ with those of other rhodium carbonyl clusters showing related polyhedra, e.g., the cuboctahedron, the twinned cuboctahedron or the regular icosahedron in $[B_{12}H_{12}]^{2-}$, could model the structural changes that may occur during interconversions of surfaces with these arrangements of metal atoms. The rearrangement between the icosahedral and cuboctahedral conformations of a cluster has previously been involved to explain the isomerization of 1,2-dicarbaclosododecaborane, 1-2-$C_2B_{10}H_{12}$, into the 1,7-isomer [12].



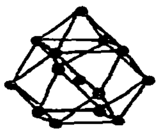
The departure from the regular icosahedron found in $[B_{12}H_{12}]^{2-}$ may occur in $[Rh_{12}Sb(CO)_{27}]^{3-}$ by the formal elongation of three edges, and this generates the three rhombohedral faces present in the solid state structure of this cluster.



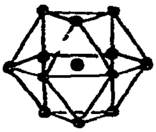
$[B_{12}H_{12}]^{2-}$
Regular
Icosahedron



$[Rh_{12}(CO)_{27}Sb]^{3-}$
Distorted Icosahedron



$[Rh_{14}(CO)_{25}]^{4-}$
Capped
Cuboctahedron



$[Rh_{13}(CO)_{24}H_3]^{2-}$
Twinned
Cuboctahedron

TABLE 4

APPLICATION OF WADE'S RULES TO RHODIUM CARBONYLCLUSTERS

Cluster	Number of electrons	Number of electrons calculated by Wade's rules	Ref.
$Rh_6(CO)_{16}$	86	86	2
$[Rh_6(CO)_{15}C]^{2-}$	90	86	2
$[Rh_7(CO)_{16}]^{2-}$	98	98	2
$[Rh_7(CO)_{16}I]^{2-}$	100	98	2
$[Rh_8(CO)_{19}C]$	114	114	2
$[Rh_9E(CO)_{21}]^{2-}$	130	130	
$[Rh_{10}E(CO)_{22}]^{3-}$	142	170	
$[Rh_{12}Sb(CO)_{27}]^{2-}$	170	170	
$[Rh_{12}(CO)_{30}]^{2-}$	170	170	2
$[Rh_{13}(CO)_{24}H_3]^{2-}$	170	170	2, 15
$[Rh_{12}(CO)_{25}C_2]$	164	170	2
$[Rh_{15}(CO)_{28}C_2]^-$	200	198	2
$[Rh_{14}(CO)_{25}]^{4-}$	180	186	2, 15
$[Rh_{15}(CO)_{27}]^{3-}$	192	192	2, 15
$[Rh_{17}S_2(CO)_{32}]^{3-}$	232	232	[a]

[a] $[Rh_{17}S_2(CO)_{32}]^{3-}$ obeys Wade's rules if it is considered a bis-nido cluster.

Further elongation of the longest Rh(1)—Rh(1) edges followed by minor changes in the positions of the remaining rhodium atoms could lead to either the twinned cuboctahedron, or more likely to the cuboctahedron.

An extension of these arguments may indicate that the rhodium skeleton of $[Rh_{12}Sb(CO)_{27}]^{3-}$ may be able to undergo a ready rearrangement in solution that could result in the fluxionality of the rhodium cage. This possibility is now under study [13].

The analogies between the structures of $[Rh_9E(CO)_{21}]^{2-}$, $[Rh_{10}E(CO)_{22}]^{3-}$ and $[Rh_{12}Sb(CO)_{27}]^{3-}$ and those of the boranes of similar nuclearity may be relevant with respect to the extension of borane bonding theories [5] to transition metal carbonyl clusters. It appears that the phosphido and arsenido clusters follow Wade's rules [5] (Table 4). However, the antimonido species only obeys these rules if it is accepted that its structure corresponds to a closo polyhedron. For this argument the presence of rhodium—rhodium bonding interactions between Rh(1)—Rh(1), with a interatomic bonding of 3.334 Å, has to be accepted. It appears then that these rules are not followed mostly when encapsulated carbon or rhodium atoms are present.

Reactivity

Rhodium carbonyl clusters usually get transformed into $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ when placed under high pressures of carbon monoxide and hydrogen unless atoms of the main-group elements are located in the cluster's cavity [14]. As a result of this, it was expected that the infrared spectra of $[Rh_{12}Sb(CO)_{27}]^{3-}$ would be the same under either ambient or high pressure conditions. This was confirmed subsequently (Fig. 1).

^{13}C NMR studies conducted with an enriched sample of the anion show the fluxional character of the carbonyl ligands of the cluster as concluded from the presence of a sharp multiplet at 216.9 ppm (Fig. 3). A full study of the car-

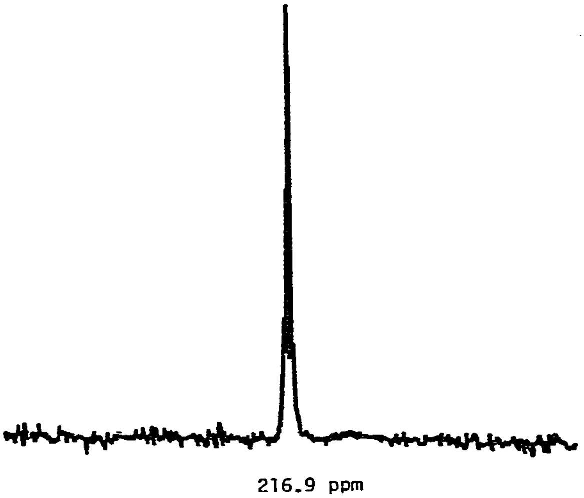


Fig. 3. ^{13}C NMR spectrum of $[PhCH_2N(C_2H_5)_3]_3$ $[Rh_{12}Sb(CO)_{27}]$ in acetone-d_6 at 40°C. The compound was enriched for 5 hours under 4 atm of 50% ^{13}CO at 25°C. Chemical shifts are reported downfield from tetramethylsilane used as external standard.

bonyl scrambling properties of this and related rhodium carbonyl clusters is under way and it will be reported elsewhere [13].

Acknowledgement

The authors appreciate the authorization for the publication of this work extended by Union Carbide Corporation, and the contribution of Drs. R.C. Schoening and W.E. Walker (the late) to the NMR and high pressure infrared studies.

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