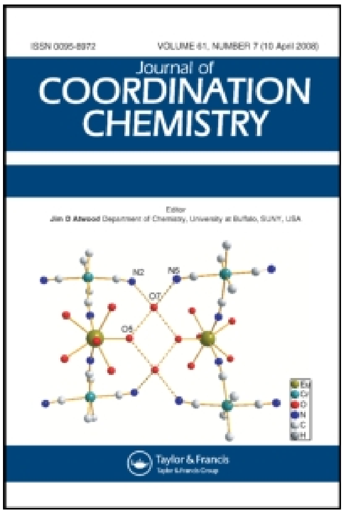

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ELECTROPHILIC ADDITION TO $[Rh_{17}S_2(CO)_{32}]^{3-}$

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Reactions of electrophiles with $[Rh_{17}S_2(CO)_{32}]^{3-}$ produce the adducts $[Rh_{17}S_2(CO)_{32}E]^{2-}$, E = Au(PPh$_3$), Au(PPh$_2$Me), Ag, Rh(COD), Pt(COD)Cl, and Pd(COD)Cl, characterized by spectroscopic methods. The ^{13}C NMR spectrum of $[Rh_{17}S_2(CO)_{32}Au(PPh_3)]^{2-}$ suggests that addition of the electrophile occurs at a Rh-Rh edge between the basal and internal Rh_4 planes. Cyclic voltammograms for $[Rh_{17}S_2(CO)_{32}]^{3-}$ and $[Rh_{17}S_2(CO)_{32}AuL]^{2-}$ show several irreversible oxidation processes but two 1-electron reductions, the first of which is nearly reversible.

KEYWORDS: high nuclearity metal clusters, Rh_{17}, electrophilic addition

INTRODUCTION

High nuclearity metal carbonyl clusters are considered to be better models for metal surfaces than are small clusters.[1,2]. These very large clusters present a variety of face geometries, including triangular, square, and "butterfly" arrangements of metal atoms. Yet little has been established concerning the chemical reactivities of different face geometries. A difficulty has been the syntheses of significant amounts of these large clusters, most of which are anions, and the necessity to rely upon X-ray crystallography for product characterization.

The cluster $[Rh_{17}S_2(CO)_{32}]^{3-}$ was first synthesized by Vidal and co-workers in 1978.[3] This anion is an attractive target for further studies because it is available in excellent yield, has good thermal and air stability, and presents a variety of face arrangements of metal atoms. Vidal and co-workers reported that the cluster was relatively inert to ^{13}CO exchange even at high temperatures, but that it could be reversibly protonated. Our initial thought was that chemical methods, such as electron-transfer catalyzed substitution,[4] might allow us to induce reactions of this cluster with Lewis bases and unsaturated hydrocarbons. Although no ligand substitutions were achieved, we were able to add several other Lewis acids, some containing cyclooctadiene ligands, to the cluster framework. We also report here on the electrochemistry of $[Rh_{17}S_2(CO)_{32}]^{3-}$ and its adducts with $Au(PR_3)^{1+}$.

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EXPERIMENTAL

All reactions were initially carried out under nitrogen using standard Schlenk techniques, or in a Vacuum Atmospheres glovebox under argon. IR spectra between 2150 and 1800 cm^{-1} were recorded on a Beckman 4250 or a Mattson Alpha Centari spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained on a Varian 300 or 400 MHz spectrometers. ^{31}P NMR spectra were recorded on a Varian 400 MHz instrument. UV/Vis spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

High pressure syntheses were performed in Autoclave Engineers Inc. 300-cc or 1-L MagneDrive autoclaves (rated to 6000 psi). $AuPPh_3Cl$,[5] $[Rh(COD)Cl]_2$,[6] $Pt(COD)Cl_2$,[7] and $Pd(COD)Cl_2$[7] were prepared according to literature procedures. $Au(PPh_2Me)Cl$ was prepared using a procedure analogous to that for $AuPPh_3Cl$.

Syntheses

$[Bu_4N]_3[Rh_{17}S_2(CO)_{32}]$

This cluster was synthesized using a modification of the procedure of Vidal and co-workers.[3] $Rh(CO)_2(acac)$ (1.1022 g) was dissolved in 150 mL of tetraglyme. Cesium benzoate (0.275 g) was added and the solution stirred for 0.5 h. The solution was then transferred to the 300 cc autoclave, and 125 μL of thiophenol was added. The autoclave was charged with 80 atm of a 1:1 mixture of $CO:H_2$, and was heated overnight at 160°C. The solution was then removed from the autoclave, mixed with 1 L of toluene, and refrigerated at −15°C. A precipitate formed overnight which was filtered and washed with isopropanol. The tetrabutylammonium salt was recrystallized from an acetone/isopropanol solution. Yield 0.6640 g (85%). The IR and ^{13}C NMR spectra were found to be as reported.[3] Other cations, such as $PPh_4{}^{1+}$ and PPN^{1+} were also used in the recrystallization of the cluster.

$[PPh_4]_2[Rh_{17}S_2(CO)_{32}AuPPh_3]$

To a 100-mL, three-necked flask fitted with a reflux condenser was added $[NBu_4]_3[Rh_{17}S_2(CO)_{32}]$ (433 mg) in 20 mL of acetone. In a separate flask 62 mg (1 equiv) of $AuPPh_3Cl$ and 32 mg (1 equiv) of $AgCF_3SO_3$ were mixed in 10 mL of acetone, and the AgCl precipitate was filtered off. This solution was added dropwise to the cluster solution *via* an addition funnel, and the mixture was allowed to reflux for one hour. The solution was cooled, and then evaporated to dryness, and the residue was washed with isopropanol. Yield of $[NBu_4]_2[Rh_{17}S_2(CO)_{32}AuPPh_3]$, 400 mg (87%) *Anal.* Calcd. for $AuC_{82}H_{87}N_2O_{32}PRh_{17}S_2$: C, 26.95; H, 2.40; Au, 5.39; Rh, 47.88. Found: C, 27.88; H, 3.10; Au, 4.32; Rh, 52.63. The $NBu_4{}^+$ cation was exchanged with $PPh_4{}^+$, and the cluster was recrystallized from acetone/isopropanol.

$[PPh_4]_2[Rh_{17}S_2(CO)_{32}AuPPh_3]$. IR ($CH_2Cl_2$):2028(vs), 1858(m), 1820(m) cm^{-1}. ^{31}P NMR ($CDCl_3$, 25°C): 50.23(1P), 22.16(2P) ppm. *Anal.* Calcd. for $AuC_{98}H_{55}P_3S_2O_{32}Rh_{17}$: C, 30.39; H, 1.44; Found: C, 30.86; H, 1.37.

$[PPh_4]_2[Rh_{17}S_2(CO)_{32}Au(PPh_2Me)]$

To a 100-mL, three-necked flask fitted with a reflux condenser was added $[PPh_4]_3[Rh_{17}S_2(CO)_{32}]$ (297 mg) in 20 mL of acetone. Previously, 42 mg (1 equiv) of $Au(PPh_2Me)Cl$ and 21 mg (1 equiv.) of $AgCF_3SO_3$ were mixed in 10 mL of acetone in a separate flask and the precipitate was filtered off. This solution was added dropwise to the cluster solution *via* an addition funnel, and the mixture was allowed to reflux for one hour. The solution was cooled, and then evaporated to dryness, and the residue was washed with isopropanol. Yield of $[PPh_4]_2[Rh_{17}S_2(CO)_{32}Au(PPh_2Me)]$, 270 mg (88%) IR ($CH_2Cl_2$): 2027(vs), 1857(m), 1819(m) cm^{-1}. ^{31}P NMR ($CDCl_3$, 25°C): 37.32(1P), 22.16(2P) ppm. *Anal.* Calcd. for $C_{93}H_{50}P_3S_2O_{32}Rh_{17}Au$: C, 29.95; H, 1.40; Found: C, 25.79; H, 1.26.

$[PPN]_2[Rh_{17}S_2(CO)_{32}E]$, E = Ag, Rh(COD), Pt(COD)Cl, Pd(COD)Cl

These adducts were prepared *in situ* but proved to be too unstable for purification. The electrophilic reagent was $AgSO_3CF_3$ or was prepared by addition of 1 equiv of $AgSO_3CF_3$ to $[Rh(COD)Cl]_2$, $Pt(COD)Cl_2$, or $Pd(COD)Cl_2$, followed by removal of the AgCl precipitate. In each case 1 equiv of the electrophilic reagent was added to an acetone solution of $[PPN]_3[Rh_{17}S_2(CO)_{32}]$ and the resulting solution was stirred under nitrogen for 2 h. IR analyses showed that no starting cluster remained, although no pure, crystalline solids could be isolated. The products were characterized by spectroscopic methods.

$[PPN]_2[Rh_{17}S_2(CO)_{32}Ag]$. IR (acetone): 2026(vs), 1860(m), 1823(m) cm^{-1}.

$[PPN]_2[Rh_{17}S_2(CO)_{32}Rh(COD)]$. IR ($CH_2Cl_2$): 2086(w), 2035(vs), 1867(m), 1832(m) cm^{-1}. ^1H NMR ($CDCl_3$, 25°C, COD resonances only): 4.13(br s, 4H), 2.48 (br s, 4H), 1.66(br s, 4H) ppm.

$[PPN]_2[Rh_{17}S_2(CO)_{32}Pt(COD)Cl]$. IR ($CH_2Cl_2$): 2091(w), 2034(vs), 1865(m), 1830(m) cm^{-1}. ^1H NMR ($CDCl_3$, 25°C, COD resonances only): 4.23(br, s, 4H), 2.49(br s, 4H), 1.79(br s, 4H) ppm.

$[PPN]_2[Rh_{17}S_2(CO)_{32}Pd(COD)Cl]$. IR ($CH_2Cl_2$): 2084(w), 2034(vs), 1868(m), 1830(m) cm^{-1}. ^1H NMR ($CDCl_3$, 25°C, COD resonances only)): 4.22(br s, 4H), 2.49 (br s, 4H), 1.73 (br s, 4H) ppm.

Electrochemistry

All electrochemical measurements were performed with a BAS 100 electrochemical analyzer. Tetrabutylammonium tetrafluoroborate, TBATFB, was recrystallized three times from an ethanol solution. Acetronitrile was freshly distilled over calcium hydride and stored under nitrogen. Silver nitrate was used as received. The reference electrode was a Ag/Ag^+ (0.01 M $AgNO_3$, 0.25 M TBATFB in acetonitrile) reference,[8] separated from the cell by a Vicor tip. The working electrode was a 2 mm diameter platinum disk electrode, and the auxiliary electrode was a platinum wire. The concentration of cluster was 10^{-3} M, with 0.1 M TBATFB as supporting electrolyte. Under these conditions, ferrocene exhibited a reversible couple at $E_{1/2}$ = 0.140 V (ΔE_p 74 mV).

RESULTS AND DISCUSSION

The structure of the cluster core of $[Rh_{17}S_2(CO)_{32}]^{3-}$ is shown in Figure 1.[3] It consists of four parallel squares of rhodium atoms with the squares staggered by 45°, so that the core has three square antiprismatic cavities. The two outer cavities contain one sulfur atom each, and the internal cavity contains an encapsulated rhodium atom. The outer planes will be referred to as the basal planes, and the inner planes as the internal planes. Each of the sixteen external rhodium atoms has one terminal carbonyl ligand and two symmetrically bridging carbonyls. Four of the carbonyls bridge between adjacent atoms on each basal plane (intraplanar), for a total of eight carbonyls. The remaining eight carbonyls bridge between the two internal planes of atoms (interplanar). No carbonyl groups bridge from the basal to internal planes. The cluster has idealized D_{4d} symmetry, and offers a variety of

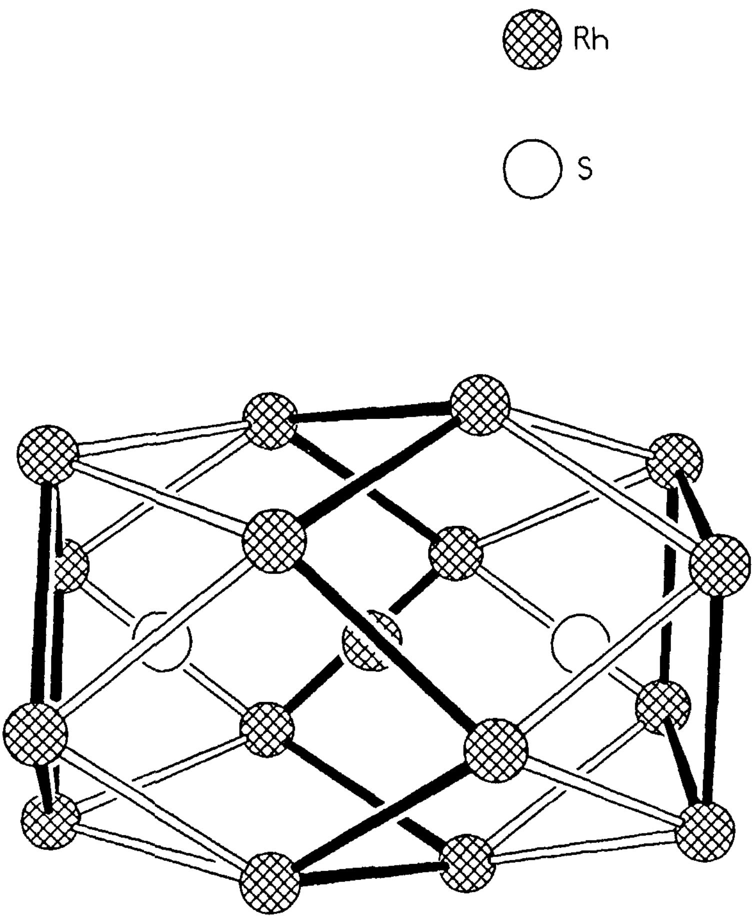

Figure 1 Structure of $[Rh_{17}S_2(CO)_{32}]^{3-}$. A terminal CO is bonded to each external Rh. Shaded bonds are bridged by μ-CO ligands.

different coordination sites, from the typical metal-metal edge, to a variety of triangular faces, "butterfly" and square faces. This feature makes this cluster particularly interesting, but little has been reported in terms of the reactivity of this cluster or other important features such as its electrochemical properties.

The original synthesis of $[Rh_{17}S_2(CO)_{32}]^{3-}$ was performed at a pressure of 300 atm of a 50:50 mixture $CO{:}H_2$ at 160°C, with H_2S or SO_2 used as the source of the encapsulated sulfur atoms.[3] We found it convenient to modify the procedure, using thiophenol as the sulfur source and reducing the CO/H_2 pressure to 80 atm; the yield (85%) under these conditions was essentially the same as that reported by Vidal and coworkers.

The first reactions attempted with this cluster were ligand substitution reactions. However, $[Rh_{17}S_2(CO)_{32}]^{3-}$ proved to be inert to substitution by a variety of ligands, including triphenylphosphine, trimethylphosphite and diphenylacetylene, under a variety of thermal, photolytic and chemical conditions ($ONMe_3$ and Na/benzophenone were both attempted as agents to induce ligand substitution) to the point of cluster decomposition. This is not surprising in light of ^{13}CO exchange reactions reported for this cluster.[9] At 40°C under 1 atm of ^{13}CO, no exchange occurs even after 72 hours. At 125°C, the extent of exchange was only 20-30% even after 168 hours.

While $[Rh_{17}S_2(CO)_{32}]^{3-}$ proved to be inert to substitution reactions, Vidal and co-workers had reported[3] that it could be doubly protonated with strong acid, and subsequently deprotonated. This result suggested that the cluster might also be susceptible to attack by other electrophiles and that this route might provide an avenue to introduce hydrocarbon ligands into the cluster coordination sphere.

Electrophilic addition is a common reaction for cluster anions, with examples in the chemistry of large rhenium and large osmium clusters, among others.[2] A large number of adducts involving Group 11 metals have been prepared, with addition of the Group 11 atom to edges or triangular faces (*e.g.* $[Rh_6C(CO)_{15}(\mu_3\text{-}AuPPh_3)]^{-1}$ [10]) of the transition metal clusters. While many of the common electrophiles do not change the electron count of the cluster, structural changes can accompany the addition.[2] This could result in a cluster whose properties are quite different from those of the original cluster.

Reaction of $AuPPh_3^+$ with $[Rh_{17}S_2(CO)_{32}]^{3-}$ produced the adduct $[Rh_{17}S_2(CO)_{32}AuPPh_3]^{2-}$. Adducts were also formed with the electrophiles $AuPPh_2Me^+$, Ag^+, $Rh(COD)^+$, $Pt(COD)Cl^+$, and $Pd(COD)Cl^+$. These products were characterized spectroscopically. The IR data for $[Rh_{17}S_2(CO)_{32}]^{3-}$ and its electrophilic adducts are given in Table 1. The addition of the electrophile to the cluster decreases the overall electron density of the Rh_{17} core, which results in a

Table 1 IR data from 2150 to 1800 cm^{-1}

Cluster	CO stretching frequences (cm^{-1})
$[Rh_{17}S_2(CO)_{32}]^{3-}$	2012(vs), 1847(m), 1810(m)[a]
$[Rh_{17}S_2(CO)_{32}AuPPh_3]^{2-}$	2028(vs), 1858(m), 1820(m)[b]
$[Rh_{17}S_2(CO)_{32}AuPPh_2Me]^{2-}$	2027(vs), 1857(m), 1819(m)[b]
$[Rh_{17}S_2(CO)_{32}Ag]^{2-}$	2026(vs), 1860(m), 1823(m)[a]
$[Rh_{17}S_2(CO)_{32}Rh(COD)]^{2-}$	2086(w), 2035(vs), 1867(m), 1832(m)[b]
$[Rh_{17}S_2(CO)_{32}Pt(COD)Cl]^{2-}$	2091(w), 2034(vs), 1865(m), 1830(m)[b]
$[Rh_{17}S_2(CO)_{32}Pd(COD)Cl]^{2-}$	2084(w), 2034(vs), 1868(m), 1830(m)[b]

[a] In acetone solution. [b] In dichloromethane solution.

shift to higher frequencies for the carbonyl stretches. This shift is similar to that caused by protonation of the cluster.[3] However, all spectra are very similar in the numbers and relative intensities of bridging and terminal CO stretches, suggesting no major changes in the $[Rh_{17}S_2(CO)_{32}]$ portion of the framework.

Each of the clusters studied is similar in color, a very dark brown/purple. As expected, the UV/visible spectra are all very similar, each with a large absorption around 335 nm (ε *ca.* 1150000), a medium band around 490 nm ($\varepsilon = 644000$) and a smaller band around 650 nm ($\varepsilon = 168000$). The UV/visible spectral data are reported in Table 3.

The close resemblance for the IR and UV/visible spectra for all the adducts $[Rh_{17}S_2(CO)_{32}E]^{2-}$, E = $AuPPh_3$, $AuPPh_2Me$, Ag, Rh(COD), Pt(COD)Cl, and Pd(COD)Cl suggests that all are structurally analogous. Only the gold adducts proved sufficiently robust to allow for the repeated crystallizations required for purification, but despite extraordinary efforts we were unable to obtain crystals of sufficient size for X-ray structural characterization. However, analysis of the ^{13}C NMR spectra for $[Rh_{17}S_2(CO)_{32}(AuPPh_3)]^{2-}$ allows us to propose the likely structure adopted.

The ^{13}C NMR spectrum of $[Rh_{17}S_2(CO)_{32}]^{3-}$ has been previously reported.[3,9] It consists of a pair of doublets, each of weight 8, at 195.8 ppm and 194.1 ppm ($J_{Rh\text{-}C} = 83.9$ Hz and 97.3 Hz respectively), which correspond to the terminal carbonyls on the internal and basal planes, respectively, and a pair of triplets, each of weight 8, at 252.7 ppm and 231.8 ppm ($J_{Rh\text{-}C} = 40.9$ Hz and 44.5 Hz) which correspond to bridging carbonyls on the basal and internal planes respectively. The static spectrum was obtained at 40°C, however, fluxional exchange specifically between bridging and terminal carbonyls located on the Rh atoms of the internal planes was noted at 60° with coalescence at 120°C.

The ^{13}C NMR spectrum of $[Rh_{17}S_2(CO)_{32}(AuPPh_3)]^{2-}$ displays a very low molecular symmetry. The room temperature spectrum, shown in Figure 2(a), indicates that the molecule is fluxional, with broad lines at 226.2 and 217.8 ppm. At −60°C the limiting slow exchange spectrum was obtained (Figure 2(b)). In the region from 190 ppm to 205 ppm, there are a number of overlapping doublets, with coupling constants of *ca.* 90 Hz. This region integrates to 16 carbons, and is consistent with assignment to terminal carbonyls. The region between 215 ppm and 255 ppm consists of a number of overlapping triplets, with coupling constants of *ca.* 40 Hz. Again this region integrates to 16 carbons, and is consistent with assignment to the bridging carbonyls. Chemical shifts for the cluster carbonyls are reported in Table 3, as well as the rhodium-carbon coupling constants. The number of terminal

Table 2 UV visible spectral data for cluster anions

Cluster	Maxima(nm)		
	[a]in Acetone		
$[Rh_{17}S_2(CO)_{32}]^{3-}$	338	486	594
$[Rh_{17}S_2(CO)_{32}AuPPh_3]^{2-}$	332	492	624
	[b]in dichloromethane		
$[Rh_{17}S_2(CO)_{32}AuPPh_3]^{2-}$	336	494	624
$[Rh_{17}S_2(CO)_{32}Ag]^{2-}$	340	490	658
$[Rh_{17}S_2(CO)_{32}Rh(COD)]^{2-}$	338	488	658
$[Rh_{17}S_2(CO)_{32}Pt(COD)Cl]^{2-}$	326	488	658

Table 3 ^{13}C NMR data[a,d] for the carbonyls of $[Rh_{17}S_2(CO)_{32}AuPPh_3]^{2-}$ at 25° and -60°C in $(CD_3)_2CO$.

-60°C[b]		25°C[c]
	Bridging carbonyl region	
250.29 (t,1C, J 37 Hz)		249.4 (t, 1C, J 40 Hz)
249.4 (t, 1C, J 37 Hz)		247.5 (t, 1 C, J ca. 40 Hz)[e]
247.8 (t, 2C, J 37 Hz)		248.0 (t, 2C, J 40 Hz)
246.8 (t, 2C J 44 Hz)		247.0 (t, 2C, J 41 Hz)
241.2 (t, 2C, J 40 Hz)		241.5 (t, 2C, J 41 Hz)
231.6 (br t, 2C, J indeterminant)		
228.5 (t, 1C, J 40 Hz)		226.2 (v br)
225.9 (br t, 3C, J indeterminant)		
217.1 (br t, 2 C, J indeterminant)		217.8 (v br)
	Terminal carbony region	
197.85 (d, 1 C, J 88 Hz)		199.48 (dd, 1C, J 90, 10 Hz)
194.60 (d 1C, J 81 Hz)		
193.85 (d, 1 C, J ca. 80 Hz)[e]		
191.95 (br d, 4 C, J 80 Hz)		192.54 (d, 2C, J 97 Hz)
191.00 (br d, 3 C, J 79 Hz)		190.75 (d, 1 C, J 98 Hz)
189.62 (d, 2 C, J 95 Hz)		191.16 (d, 2C, J 95 Hz)
188.89 (d, 2C, J 95 Hz)		190.54 (d, 2C, J 96 Hz)

[a] Chemical shifts referenced to the carbonyl of acetone as 205.1 ppm.

[b] Recorded on a 300 MHz spectrometer.

[c] Recorded on a 400 MHz spectrometer.

[d] Two carbonyls are unaccounted for. These are believed to be two 1-C resonances in the region of 192-190 ppm which are obscurred by other, larger resonances. The total integral for the terminal carbonyl region is identical to that of the bridging carbonyl region.

[e] This signal overlaps with other resonances.

and μ_2-CO resonances in the ^{13}C spectrum suggests that the general arrangement of bridging and terminal CO ligands in the adduct $[Rh_{17}S_2(CO)_{32}(AuPPh_3)]^{2-}$ is similar to that in $[Rh_{17}S_2(CO)_{32}]^{3-}$. The fluxional process noted at room temperature for $[Rh_{17}S_2(CO)_{32}(AuPPh_3)]^{2-}$ seems identical to that observed at higher temperatures for $[Rh_{17}S_2(CO)_{32}]^{3-}$. The resonances between 240 and 255 ppm due to carbonyls bridging the basal Rh atoms (*cf.* 252.7 ppm for $[Rh_{17}S_2(CO)_{32}]^{3-}$) remain sharp, while those between 215 and 235 ppm due to carbonyls bridging the internal Rh atoms (*cf.* 231.8 ppm for $[Rh_{17}S_2(CO)_{32}]^{3-}$) are broadened. Thus, the sharp resonances observed in the terminal carbonyl region at room temperature are assigned to carbonyls attached to basal Rh atoms; this assignment is consistent with the larger Rh-C coupling constants for these resonances (*cf.* $J_{Rh\text{-}C}$ 97 Hz for basal CO's of $[Rh_{17}S_2(CO)_{32}]^{3-}$). The small coupling of 10 Hz to the resonance at 199.48 ppm is attributed to coupling to the ^{31}P nucleus of the $AuPPh_3$ moiety; for comparison, the "transoid" $^{31}P-^{13}CO$ coupling for $H_2Ru_3(\mu_3-COMe)(CO)_9(\mu-AuPPh_3)$ is 15 Hz.[11] This coupling suggests that the $AuPPh_3$ unit bridges to one of the basal Rh atoms. The low symmetry of the molecule rules out a structure resulting from addition of the gold moiety to either a square face (C_{4v}) or any of the "butterfly" faces as a μ_3- or μ_4-moiety (C_s) or as a doubly bridging group across the Rh-Rh edge between the two internal Rh_4 planes (C_2) or along the edge of the basal plane (C_s). Addition as a terminally bound unit is unlikely, as the symmetry would be expected to be higher than that observed (C_s) and as this is not a common

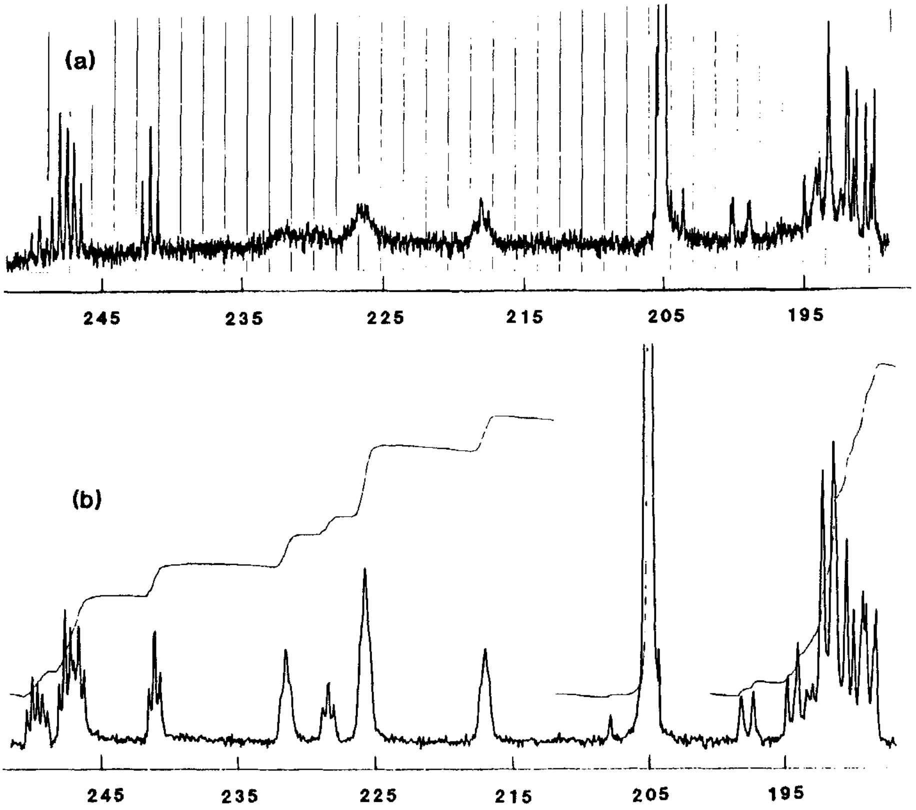

Figure 2 ^{13}C NMR spectra of $[PPN]_2[Rh_{17}S_2(CO)_{32}(AuPPh_3)]$ in d_6-acetone at (a) 25°C and 300 MHz and (b) -60°C and 400 MHz.

coordination mode for Au-cluster complexes. We propose the structure shown in Figure 3, in which the $Au(PPh_3)$ moiety bridges a Rh-Rh edge between basal and internal planes. This structure is consistent with the ^{13}C NMR spectrum (with the assumption of coincidental overlaps, most likely for resonances of carbonyls furthest from the $Au(PPh_3)$ group), and by addition of the $Au(PPh_3)$ unit to this edge the arrangement of the bridging carbonyls is relatively unaffected. Presumably a similar ^{31}P- ^{13}C coupling constant would be noted to a terminal carbonyl bound to the internal Rh atom, but we were unable to observe this in the low temperature spectrum, and in fact the resolution was insufficient to observe the small coupling for the resonance at 197.85 ppm.

It is interesting that the adduct $[Rh_{17}S_2(CO)_{32}AuPPh_3]^{2-}$ exhibits a lower barrier for fluxionality of carbonyls between the internal planes than does $[Rh_{17}S_2(CO)_{32}]^{3-}$. Vidal *et al.* inferred that the higher mobility of the carbonyls of the internal planes was due to a greater negative charge on these Rh atoms.[9] However, our results show that *decreasing* the negative charge on the cluster *accelerates* the rate of carbonyl fluxionality.

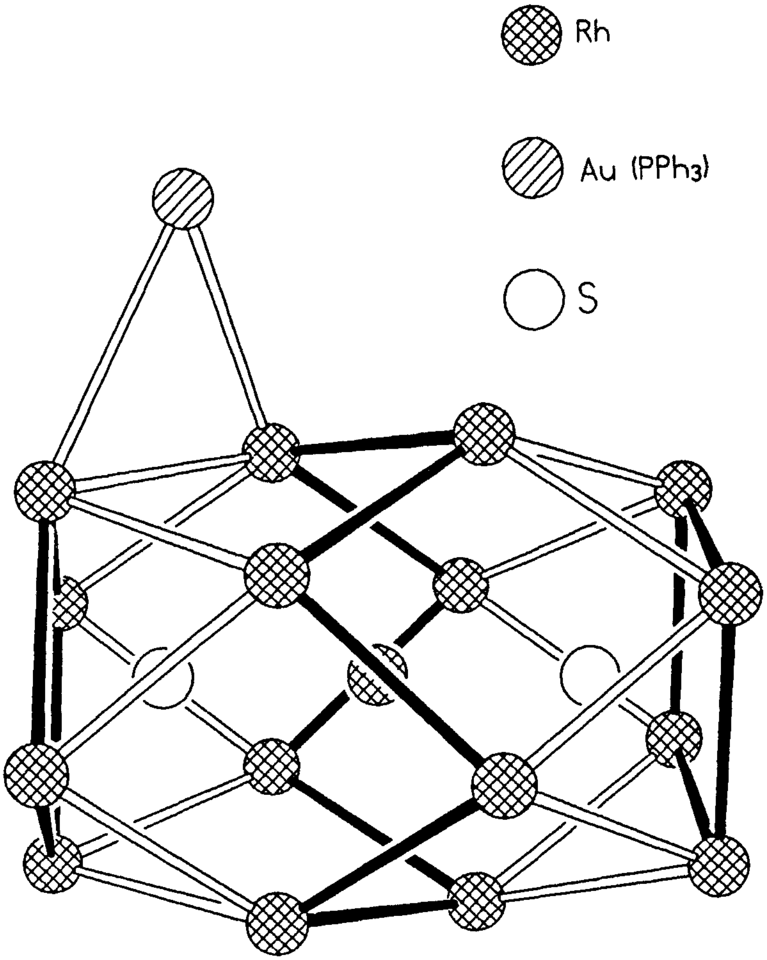

Figure 3 Proposed structure for $[Rh_{17}S_2(CO)_{32}(AuPPh_3)]^{2-}$. A terminal CO is bonded to each external Rh. Shaded bonds are bridged by μ-CO ligands.

Electrochemistry of $[Rh_{17}S_2(CO)_{32}]^{3-}$ *and* $[Rh_{17}S_2(CO)_{32}AuL]^{2-}$ *(L = PPh_3, PPh_2Me)*

Initially we had hoped that ETC promoted substitution might allow us to induce nucleophilic substitution on $[Rh_{17}S_2(CO)_{32}]^{3-}$. Although this did not prove to be the case, the electrochemistry of this cluster and its adducts is of interest. The number of studies of the electrochemistry of metal clusters is rapidly increasing, but as yet no general conclusions have been reached.[2,16]

All of the cyclic voltammetric measurements reported for $[Rh_{17}S_2(CO)_{32}]^{3-}$ and $[Rh_{17}S_2(CO)_{32}AuL]^{2-}$ (L = PPh_3, PPh_2Me) were made in 0.1 M TBATFB acetonitrile solution, using an Ag/Ag^+ reference and a platinum disk working electrode. The clusters exhibit good solubility in this solvent, and while $[Rh_{17}S_2(CO)_{32}AuL]^{2-}$

are soluble in methylene chloride, the parent cluster is not, so no electrochemical measurements were made in methylene chloride.

Despite the fact that the clusters are all highly negatively charged, they all displayed completely irreversible oxidative electrochemistry. The parent anion, $[Rh_{17}S_2(CO)_{32}]^{3-}$ shows two irreversible, 1-electron oxidation waves, at 0.28 V and 0.42 V, and a much larger oxidation peak at 0.82 V, most likely due to oxidation of fragmentation products (Figure 4). The clusters $[Rh_{17}S_2(CO)_{32}AuL]^{2-}$ exhibit similar behavior, although as expected, they are more difficult to oxidize, by 300-400 mV, due to the lower electron density of these clusters. Table 4 gives the oxidation data for these clusters. It is interesting to note that the AuL adducts exhibit a large reduction current on the reverse san at *ca.* 0V. Figure 5 shows the forward and reverse scans for $[Rh_{17}S_2(CO)_{32}AuPPh_2Me]^{2-}$, with the first two irreversible oxidations on the forward scan, and the large peak at 0.02 V on the reverse scan. The shape and size of this peak indicate that it is due to desorption of material from the electrode surface. However, this peak is not present for the parent cluster. An independent cyclic voltammetric investigation of $AuPPh_3Cl$ under similar conditions shows a similar peak in this region. Therefore, it seems

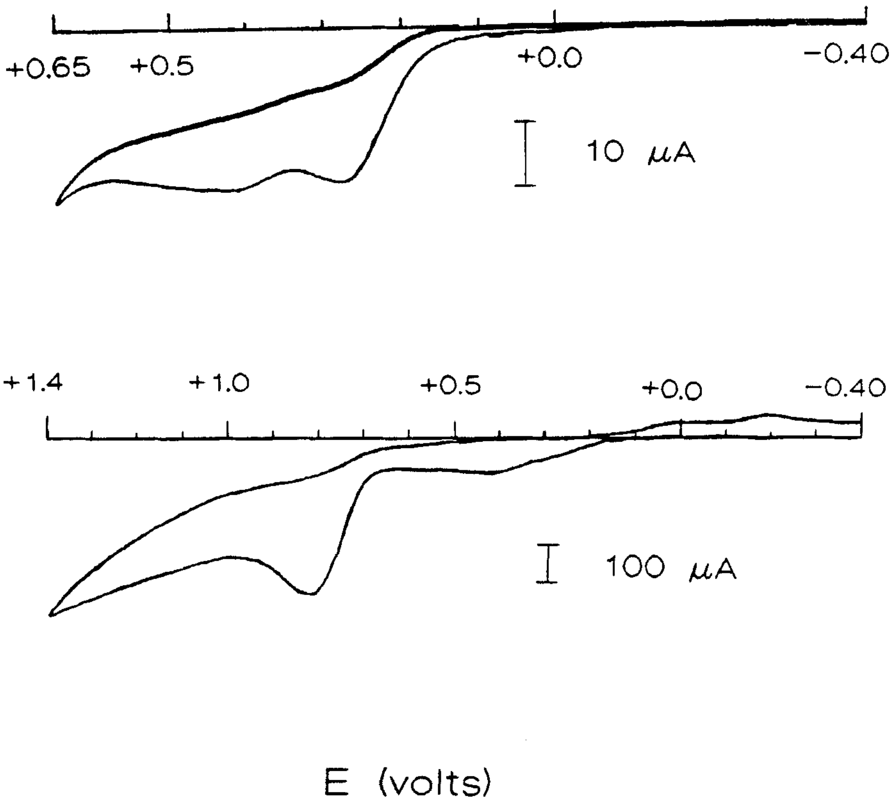

Figure 4 Cyclic voltammogram for $[Rh_{17}S_2(CO)_{32}]^{3-}$ in the anodic direction at a scan rate of 500 mV/sec.

Table 4 Cyclic voltammetric data[a] for the oxidation of the cluster anions.

Cluster	$E_{p,a}$(V)	$E_{p,a}'$(V)	$E_{p,a}''$(V)	$E_{p,c}$(V)
$[Rh_{17}S_2(CO)_{32}]^{3-}$	0.28	0.42	0.82	---
$[Rh_{17}S_2(CO)_{32}(AuPPh_3)]^{2-}$	0.49	0.81	1.18	0.44
$[Rh_{17}S_2(CO)_{32}(AuPPh_2Me)]^{2-}$	0.50	0.82	1.16	0.22

[a] Scan speed 500 mV/s. Potentials are relative to Ag/Ag$^+$ in acetonitrile. Under these conditions, ferrocene exhibited a reversible couple at $E_{1/2} = 0.140$ V (ΔE_p 74 mV).

likely that upon oxidation, the clusters lose the gold phosphine unit, which absorbs to the electrode surface, and subsequently desorbs on the reverse scan, giving rise to the peak noted.

On the other hand the cluster anions exhibit *quasi*-reversible reduction processes. On scanning from −0.4 V to −1.80 V (the solvent limit), $[Rh_{17}S_2(CO)_{32}]^{3-}$ displays two reduction peaks, at −1.11 V and −1.37 V. On the reverse scan there are two oxidation peaks, at −1.04 V and −0.84 V, as shown in Figure 6. If the scan is reversed at −1.25 V (after the first reduction process, but before the second), the first reduction is found to be *quasi*-reversible, with an $E_{1/2}$ of −1.08 V (ΔE_p = 74 mV and $i_{p,a}/i_{p,c}$ = 0.83 at 500mV/s), and the second oxidation peak is not present on this cycle, shown in Figure 6. Therefore the oxidation peak at −0.84 V is due to reoxidation of the product of the second reduction process ($E_{p,c}$ = −1.37 V).

The reversibility of the first reduction process suggests that the cluster can accommodate the addition of one electron without significant change in structure. However, upon the addition of the second electron, the cluster would be expected to undergo significant structural changes, predicted by electron counting rules, which would most likely involve metal-metal bond cleavage. Therefore, the second reduction would be expected to be electrochemically irreversible. This is consistent with the observed cyclic voltammetry.

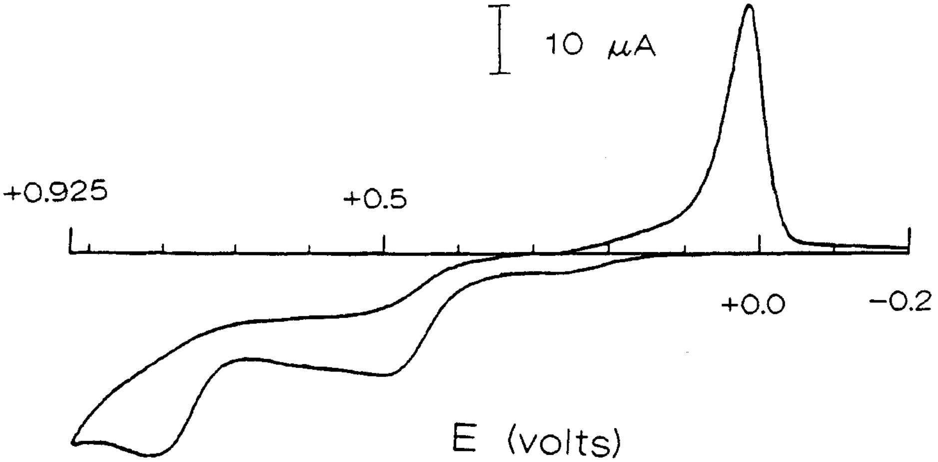

Figure 5 Cyclic voltammogram for $[Rh_{17}S_2(CO)_{32}(AuPPh_3)]^{2-}$ in the anodic direction at a scan rate of 500 mV/sec.

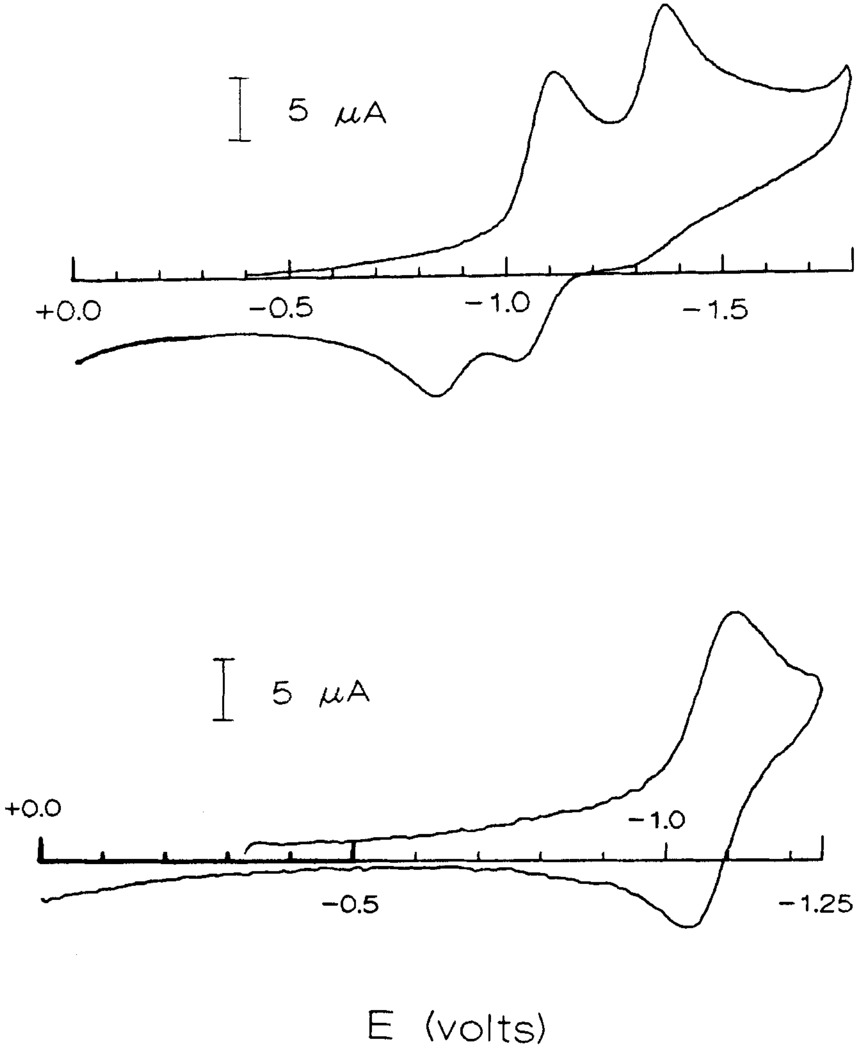

Figure 6 Cyclic voltammogram for $[Rh_{17}S_2(CO)_{32}]^{3-}$ in the cathodic direction at a scan rate of 500 mV/sec.

Table 5 shows the cyclic voltammetric data for the reduction of the clusters studied. As expected, the clusters containing the gold phosphine ligands are reduced at a more positive potential than the parent cluster, again indicative of the fact that the overall electron density on these clusters is lower. Otherwise, the voltammograms are similar, with the first reduction process being *quasi*-reversible to reversible, and the second reduction process irreversible, with reoxidation of the second reduction product occurring at a fairly positive potential. However, in the cyclic voltammogram for each of the clusters containing gold phosphine ligands, an additional oxidation peak is observed on the reverse scan. Figure 7 shows the

Table 5 Cyclic voltammetric data[a] for the reduction of the cluster anions.

Cluster	$E_{1/2}$(V)	ΔE_p(mV)	i_{pa}/i_{pc}	$E_{p,c}'$(V)	$E_{p,a}'$(V)	$E_{p,a}''$(V)
$[Rh_{17}S_2(CO)_{32}]^{3-}$	-1.08	74	0.83	-1.38	-0.84	—
$[Rh_{17}S_2(CO)_{32}(AuPPh_3)]^{2-}$	-0.79	70	0.95	-1.09	-0.49	-0.29
$[Rh_{17}S_2(CO)_{32}(AuPPh_2Me)]^{2-}$	-0.78	68	0.98	-1.07	-0.48	-0.29

[a] Scan speed 500 mV/s. Potentials are relative to Ag/Ag$^+$ in acetonitrile. Under these conditions, ferrocene exhibited a reversible couple at $E_{1/2} = 0.140$ V (ΔE_p 74 mV).

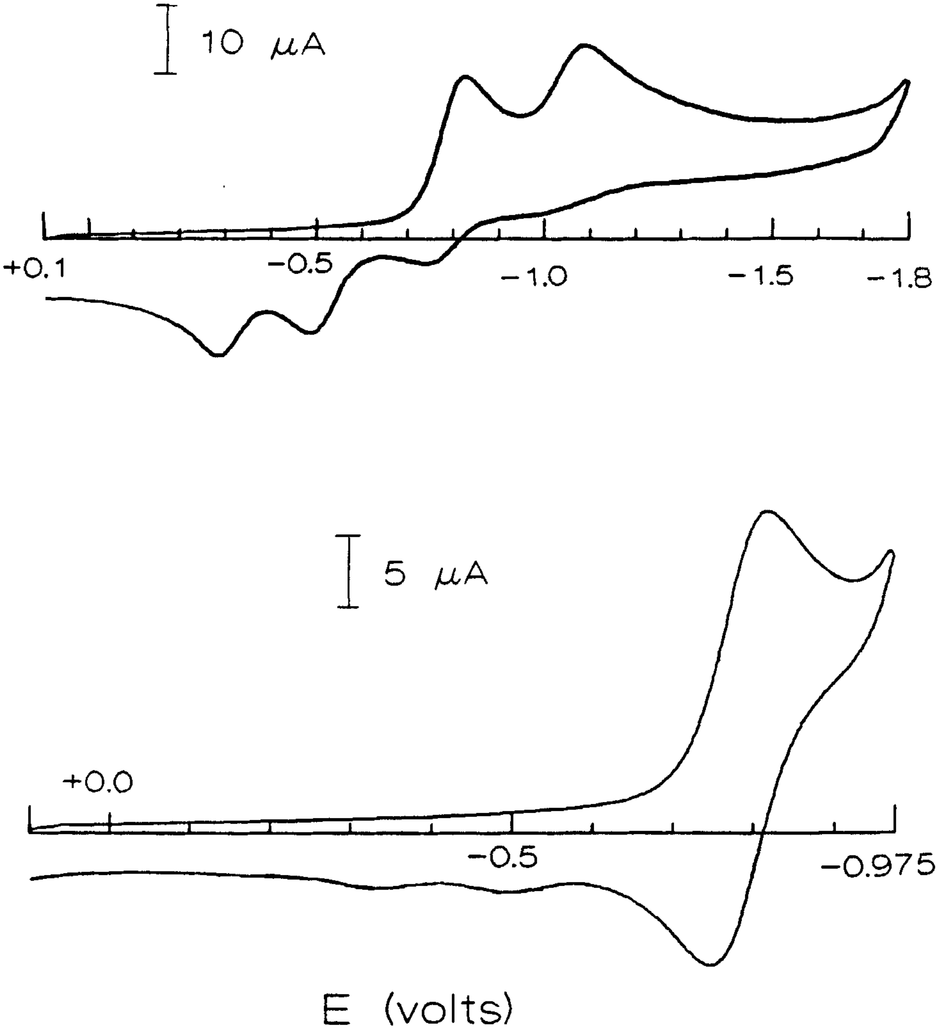

Figure 7 Cyclic voltammogram for $[Rh_{17}S_2(CO)_{32}(AuPPh_3]^{2-}$ in the cathodic direction at a scan rate of 500 mV/sec.

voltammogram for $[Rh_{17}S_2(CO)_{32}AuPPh_3]^{2-}$. If the scan is reversed before the second reduction peak, neither of the two oxidation peaks are observed. This again indicates that these peaks are due to reoxidation of the product from the second reduction.

The nature of the LUMO for the $[Rh_{17}S_2(CO)_{32}]^{3-}$ cluster is not known, however, the addition of the electrophile does not seem to have an appreciable effect upon the reduction process. On the basis of the ^{103}Rh chemical shifts, the interstitial Rh atom has been proposed to have an oxidation state of +1, consistent with the formulation of the cluster unit as a rhodium(1) disulfide encapsulated in a $Rh_{16}(CO)_{32}$ neutral skeleton.[12] This formulation suggests that the first reduction process may involve reduction of the interstitial Rh center.

In summary, all of the clusters studied displayed completely irreversible oxidation electrochemistry, and in fact the clusters appear to undergo fragmentation at potentials of 1.0 V. This is quite different from the electrochemistry noted for some Re_7,[13] Os_{10},[14] Co_6,[15] Ru_6,[15] and Fe_6[16] cluster anions, which all undergo reversible oxidation. However, the Rh_{17} cluster anions studied all undergo reversible reduction electrochemistry, similar to that reported for $[Co_8C(CO)_{18}]^{2-}$,[15] which undergoes two reversible reductions. These results suggest that the clusters studied in this work might exhibit interesting chemistry under reductive conditions, and further studies could be directed at this aspect of the chemistry of these clusters.

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