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$[Rh_{17}(S)_2(CO)_{32}]^{3-}$. 2. ^{13}C NMR Variable-Temperature Study of a Cluster with Localized Carbonyl Fluxionality

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The ^{13}C NMR behavior of the benzyltriethylammonium salt of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ has been studied. The anion could be enriched at 125 °C with no evidence for preferential carbonyl exchange. The limiting, slow-exchange spectrum observed at 40 °C indicates that the solid-state structure is also present in solution. Carbonyl scrambling appears at 60 °C, and coalescence is observed at 120 °C with an estimated free energy of activation of 17.2 ± 0.4 kcal/mol. The unchanged appearance of the resonances at 252.7 and 194.1 ppm and the simultaneous thermal variation of the resonances at 231.3 and 196.8 ppm are interpreted as evidence for the rigid and fluxional characters, respectively, of the two sets of bridging and terminal carbonyl ligands. A full assignment of these resonances is suggested and a mechanism is proposed for the carbonyl scrambling.

Introduction

The high chemical stability of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ and the novelty of the structure[1,2] induced us to investigate its behavior in solution, via ^{13}C variable-temperature NMR spectroscopy. A main purpose of these studies was to gather information about the fluxional properties of the carbonyl ligands that would lead to the completion of previous assignments.[1,2] Moreover, the unusual stability of this cluster and its relative chemical inertness under a variety of reaction conditions[1,2] offered the opportunity for testing of the suggested relationship between fluxionality and reactivity of polynuclear rhodium carbonyl complexes.[3]

We have previously reported the ^{13}C NMR spectrum of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ at 40 °C, with the conclusion that the solid-state structure of the anion is also present in solution.[1,2] We present additional evidence in this report relating to the fluxionality of the carbonyl ligands in the range of −40 to +180 °C together with a probable explanation for the peculiar fluxional behavior of the carbonyl groups of this cluster.

Experimental Section

The salt $[C_6H_5CH_2N(C_2H_5)_3]_3[Rh_{17}(S)_2(CO)_{32}]$, was prepared as previously described.[2] Solutions in acetone-d_6 or sulfolane-d_8 (tetrahydrothiophene 1,1-dioxide) were prepared by dissolving 0.42 g (0.127 mmol) and 0.85 g (0.259 mmol) of the compound in 3 mL of these solvents, respectively, and adding in both cases ca. 20 mg of $Cr(acac)_3$ as a relaxation agent. The former solution was studied in the range of −60 to +40 °C and the latter from 40 up to 180 °C. The enrichment experiments were conducted by stirring the sulfolane-d_8 solution under 1 atm of ^{13}CO, 90% enriched, at 40 °C and 125 °C for 72 and 168 h, respectively.

Spectra were recorded on a Varian XL-100 NMR spectrometer equipped with Fourier transform capabilities using 12-mm sample tubes. A hertz per point value of 0.46 has been used during the whole study. The spectra of the nonenriched sample were obtained by accumulation of 20 000 transients with a 20 μs pulse width and an acquisition time of 1.0 s. Only 2000 transients were collected with the enriched sample, with the same pulse width and acquisition time as those above. Chemical shifts are reported in ppm downfield from tetramethylsilane, used as an external standard.

Results and Discussion

Spectra obtained with a sample treated with enriched ^{13}CO at 40 °C for 72 h showed no significant difference from those of the nonenriched sample. By contrast, a sample warmed to 125 °C for 168 h under the same gaseous phase gave spectra consistent with ^{13}CO enrichment at all the CO sites of the cluster. The absence of $^{13}C-^{13}C$ coupling has been taken as an indication that enrichment has occurred to an extent of 20–30% or less. The similarity between the spectra shown by both the nonenriched[1,2] and the enriched samples (Figure 1) indicates the absence of preferential exchange of the carbonyl ligands under these conditions.

The variation of the spectra with temperature (Figure 1) shows that the low-temperature limiting spectrum is observed at 40 °C, with changes in line width resulting at lower temperatures. Changes in the spectra start appearing at 60

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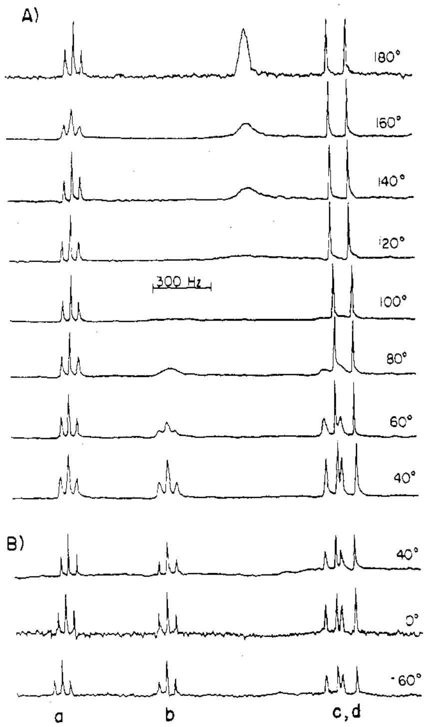

Figure 1. ^{13}C NMR spectra of (A) ^{13}CO-enriched $[C_6H_5CH_2N(C_2H_5)_3]_3[Rh_{17}(S)_2(CO)_{32}]$ in sulfolane-d_8 between 40 and 180 °C and (B) an acetone-d_6 solution of the nonenriched species between −60 and +40 °C. (The resonance bands have been labeled to facilitate cross-referencing with Figures 2 and 3.)

Table I. ^{13}C NMR Results Previously Reported[2] for $[Rh_{17}(S)_2(CO)_{32}]^{3-}$

chem shifts, ppm	252.7	231.8	195.8	194.1
rel intens	1	1	1	1
J(Rh–CO), Hz	40.9	44.5	83.9	97.3
assignment	Rh–C(O)–Rh		Rh–CO	
probable location on Rh layers	basal	internal		

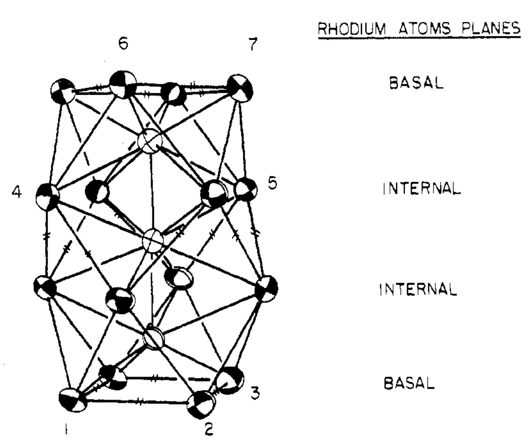

Figure 2. Schematic structural representation of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$: ◒, rhodium atoms coordinated to a terminal carbonyl; -‖-, rhodium–rhodium edge showing a bridge carbonyl. (Some rhodium atoms have been numbered to show their correspondance with Figure 3.)

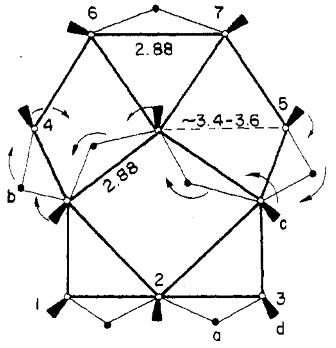

Figure 3. Suggested pathway for carbonyl scrambling in the central section of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$. Only the frontal section of the cluster is shown. (The labeling of the carbonyl ligands and the rhodium atoms is consistent with that in the previous figures.)

°C with a decrease in the peak heights of the bands at 231.3 and 196.8 ppm. Further increases in temperature above 100 °C result in the collapse of these resonances, and at 140 °C the appearance of a coalescence band with a chemical shift of 214.0 ppm is noted. The band continues to sharpen even up to 180 °C. This behavior, together with our ability to regenerate the initial 40 °C spectrum after each one of the higher temperature runs, indicates partial carbonyl ligand scrambling and the reversibility of these changes. It is evident from our previous assignments (Table I)[2] that one set of bridging carbonyls is exchanging with one set of terminal carbonyls, while the other sets of terminal and bridging ligands are rigid within the thermal range examined.

It has been suggested that longer rhodium–carbon distances for bridging carbonyls[5,6] usually result in resonances at lower fields with smaller coupling constants, J(Rh–CO). This correlation provided the basis for the previously reported assignments of the triplet resonances 252.7 and 231.3 ppm, in the spectrum of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$,[1,2] ascribed to bridging carbonyls bonded to two rhodium atoms (rhodium spin number = $^1/_2$) placed on the basal, and internal, rhodium planes,[2] respectively. In contrast, assignment of the terminal carbonyls was precluded by the lack of correlation found for these ligands between Rh–CO distances, ^{13}C ppm, and J(Rh–CO), in the case of rhodium carbonyl clusters. Representative examples are provided by the following: $Rh_6(CO)_{16}$ (Rh–CO, 1.86 Å; ^{13}C, 180.1 ppm; J(Rh–CO) = 70.2 Hz), $[Rh_6(CO)_{15}C]^{2-}$ (Rh–CO, 1.89 Å; ^{13}C, 186.0 ppm; J(Rh–CO) = 77.2 Hz), $[Rh_7(CO)_{16}]^{3-}$ (Rh–CO, 1.82 Å; ^{13}C, 198.2, 205.7, 206.4 ppm; J(Rh–CO) = 81.1, 103.5, 92.8 Hz).[7-11]

The results presented here indicate that the bridging carbonyls, with a resonance centered at 231.3 ppm, are scrambling with the terminal carbonyl ligands whose resonance is located at 196.8 ppm. By contrast, the rigid sets of bridging and terminal carbonyl ligands correspond to the multiplets at 252.7 and 194.1 ppm. We now suggest that the rigid set of ligands is composed of those carbonyls located on the basal rhodium planes while the scrambling ones are found on the rhodium atoms located on the "internal" planes (Figure 2). A rate of exchange of 1920 ± 20 s^{-1} has been estimated for this process at the coalescence temperature. A free energy of activation of 17.2 ± 0.4 kcal/mol has been calculated.[12]

Some mechanistic interpretations of our observations are offered below. A concerted mechanism of carbonyl scrambling similar to that reported for other less complicated clusters[11,13] may be occurring along the central section of the cluster (Figure 3). The similarities between the different kinds of rhodium–rhodium bonding distances on the surface of the cluster, 2.88 Å, and the degree and type of carbonyl coordination to the diverse rhodium atoms[2] indicate that interplane carbonyl mobility is sterically possible (Figure 3). By contrast, carbonyl scrambling in an intraplanar fashion around the internal rhodium planes should be precluded by the length of the rhodium–rhodium interplanar distance on the internal planes, 3.4–3.6 Å.[2]

It is appropriate to observe now that the fluxionality of coordinated carbonyls increases with the negative charge of the cluster or, in other words, with a decrease in the metal atom:negative charge ratio of the cluster[3] and that the nucleophilicity of the delocalized cluster's electron density accumulated on a particular atom has been suggested as a probable cause of carbonyl scrambling.[14] Then, it could be inferred that the deficiency of electron charge in the basal planes could be mainly responsible for the peculiar fluxional behavior of this cluster. Therefore, the rigidity of the basal ligands could be a consequence of the electron-withdrawing effect of the sulfur atoms, while the mobility of the central ligands is indicative of greater electron density on this section of the cluster. Structural parameters of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$, such as the rhodium–sulfur distances and the rhodium–carbon and carbon–oxygen bond lengths for the terminal carbonyls on the basal and internal planes (Figure 2), also tend to support the ideas above (for basal, Rh–CO = 1.85 Å, C–O = 1.14 Å, Rh–S = 2.33 Å; for central, Rh–CO = 1.81 Å, C–O = 1.19 Å, Rh–S = 2.76 Å). The more closed and crowded basal carbonyl geometry present on the basal squares may be an equally important contribution to the observed barriers. Basal interplanar exchange would seem to require higher energy intermediates than the more open zigzag exchange between the internal planes.[15]

An alternate possibility such as the motion of the skeletal rhodium atoms placed on the internal squares, similar to the one proposed for the internal triangle of $[Pt_9(CO)_{18}]^{2-}$,[16] cannot be completely excluded. The fluxionality suggested for the rhodium skeleton of $[Rh_9P(CO)_{21}]^{2-}$ [17] could indicate general scrambling ability of the metal polyhedra of rhodium carbonyl clusters with an encapsulated main-group atom(s). Work is underway to test the occurrence of such behavior.

Registry No. $[C_6H_5CH_2N(C_2H_5)_3]_3[Rh_{17}(S)_2(CO)_{32}]$, 67382-20-1.

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Adducts of Group 5A Trihalides with 1,3-Dimethyl-2(3*H*)-imidazolethione

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A series of complexes with general formula $MX_3(dmit)_n$ were prepared where M = As, Sb, or Bi, X = Cl, Br, or I, and n = 1, 2, or 3. These are in addition to the already reported complexes of $AsCl_3$dmit and $AsBr_3$dmit. This communication reports the synthesis and physical characterization of these complexes and presents solid-state vibrational data collected for $SbCl_3$dmit and $SbBr_3$dmit. The solid-state structure of $SbCl_3$dmit is proposed to be pseudo trigonal bipyramidal with a linear Cl–Sb–Cl group analogous to that reported for the local site symmetry about arsenic in $AsCl_3$dmit. No conclusions were drawn concerning the structure of $SbBr_3$dmit other than it is apparently different from that of $SbCl_3$dmit.

The recently reported structure of $AsCl_3$dmit[2] (dmit = 1,3-dimethyl-2(3*H*)-imidazolethione) indicated that the HSAB[3] nature of the donor atom can lead to structural differences in complexes with the same acceptor. Such an observation is seen in comparing the structures of $AsCl_3$dmit[2] and $AsCl_3NMe_3$.[4] In the case of $AsCl_3NMe_3$, the structure is a pseudo trigonal bipyramid (tbp) with the amine occupying an apical position trans to a chlorine. The structure of $AsCl_3$dmit on the other hand is best described as a dimer consisting of two square-pyramidal $AsCl_4$dmit units sharing a common edge through long bridging chlorine atoms and the sulfur atoms occupying the apices of the two pyramids on opposite sides of the plane formed by the six chlorines. Recently another X-ray structure reported a similar configuration for dibromo(diethyldithiocarbamato)arsenic(III)[5] (see Figure 1). Vibrational data collected for other thiourea type adducts with arsenic trihalides and arylarsenic dihalides were interpreted on the basis of a pseudo-tbp with a linear X–As–X group and the donor in an equatorial position. The crystal structure of $AsCl_3$dmit[6] bore out this prediction but showed that long bridging chlorine bonds connected these tbp units into a loose dimer pair to give the complete bonding picture described above. No evidence of bridging was seen in the solid-state spectra of $AsCl_3$dmit.[2]

This therefore led to the questions of bonding in other complexes of group 5A trihalides and thioureas and the types

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