Electron Addition to Dirhodium Complexes: An Electron Spin Resonance Study

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Exposure of dilute solutions of $Rh_2(O_2CMe)_4$ and $Rh_2(O_2CCF_3)_4$ in various solvents to ^{60}Co γ-rays resulted in electron capture, the resulting unstable species being detected and characterized by e.s.r. spectroscopy. $Rh_2(O_2CMe)_4$ gave an axially symmetric anion with the electron located primarily in a combination of d_{z^2} orbitals. The initial species showed an e.s.r. spectrum which was solvent independent, but the products formed on annealing varied with the solvent. It is suggested that ligand loss precedes dissociation into monorhodium species. $Rh_2(O_2CCF_3)_4$ gave a non-axial species upon irradiation at 77 K, showing that ligand loss is more facile, as expected for the weak $CF_3CO_2^-$ ligand.

The complex $Rh_2(O_2CR)_4$ has received an increasing amount of attention in the last few years. A partial crystal-structure determination of 'rhodium acetate' [1] (Figure 1) showed it to be dimeric, consisting of two rhodium(II) ions bridged by four acetate groups. One water molecule occupies each of the axial sites. The diamagnetism of the formally d^7 complex was attributed to Rh–Rh bonding. Early studies, such as that by Johnson *et al.*,[2] focused attention on the reaction of the complex with ligands to form axially-bound adducts. More recently, the molecular and electronic structure of the dimeric molecule has been examined in detail. In 1971, Cotton *et al.*[3] published a complete crystal structure of $Rh_2(O_2CMe)_4{\cdot}2H_2O$ and found a Rh–Rh bond distance of 2.386 Å. A molecular orbital scheme produced by Dubicki and Martin [4] indicated that the bond order was one. More sophisticated calculations by Christoph and Koh [5] and Norman *et al.*[6] have supported that view and it now seems to be widely accepted.[7]

Wilson and Taube [8] found that the Rh_2^{4+} unit is remarkably stable and characterized it by means of its electronic spectrum. They also noted that the Rh_2^{4+} unit could be chemically oxidized to Rh_2^{5+}. Ziolkowski and co-workers [9] have pursued these studies, finding that $[Rh_2(O_2CMe)_4(H_2O)_2]ClO_4$ could be readily prepared and was stable in the solid state. They also determined the crystal structure, finding a Rh–Rh bond length of 2.316 Å. Recently, Kawamura *et al.*[10] prepared $[Rh_2(O_2CR)_4(PR'_3)_2]^+$, where R = Me, Et, or CF_3 and PR'_3 = PPh_3 or $P(OPh)_3$. These cations were prepared either electrochemically or by radiolysis in a halocarbon matrix, a method first suggested for use in the preparation of cations for e.s.r. studies by Shida *et al.*[11] From the e.s.r. spectra they deduced that the s.o.m.o. (semi-occupied molecular orbital) has σ symmetry with respect to the P–Rh–Rh–P axis. In addition, the hyperfine coupling to phosphorus nuclei indicated marked delocalization onto the axial ligands. The g shifts were consistent with this view, $g_{\parallel}$ being close to free spin and $g_{\perp}$ fairly large and positive. Theoretical (SCF-Xα-SW) calculations on $Rh_2(O_2CMe)_4{\cdot}2H_2O$, possessing rather weakly bound water molecules in the axial positions, showed that the h.o.m.o. (highest occupied molecular orbital) was the Rh–Rh δ* bond.[6] Removal of an electron from such an orbital would give a s.o.m.o. of the wrong symmetry to account for the observed e.s.r. spectra. However, Bursten and Cotton [12] showed that the addition of a strong base, such as PH_3, to the axial positions, causes the Rh–Rh σ* orbital to rise in energy relative to the other occupied orbitals, so that it then becomes the h.o.m.o. or, in the case of the radical cations, the s.o.m.o. This orbital possesses the right symmetry to explain the e.s.r. results.[10] Kawamura *et al.*[10] noted, however, that they were unable to prepare the corresponding anions, and related that to electrochemical studies on the dirhodium tetracarboxylates.[13] These studies showed that the cations were formed easily and reversibly, using electrochemical methods, but that the singly reduced species was formed irreversibly and was unstable.

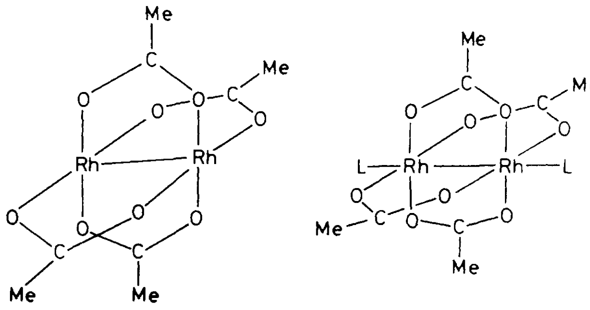

$Rh_2(O_2CMe)_4$ $Rh_2(O_2CMe)_4{\cdot}2L$
(L = H_2O, PPh_3, MeOH, pyridine, *etc.*)

Figure 1. Structure of 'rhodium acetate'

The use of ionizing radiation is a very powerful method for the preparation of either electron-gain or electron-loss species.[14] This may be accomplished by judicious choice of solvents. Thus, a solvent whose radical cation is effectively trapped in the rigid medium, but which does not react efficiently with mobile electrons can be used to give electron-capture species. The use of solvents such as methanol (CD_3OD) or 2-methyltetrahydrofuran to give radical anions is long established.[14] For instance, the radical anions of $[Mn_2(CO)_{10}]$,[15,16] $[Mn_2(CO)_8(PR_3)_2]$ (R = Bu^n or OEt),[15] and $[Re_2(CO)_{10}]$ [16] have been prepared by γ-radiolysis of dilute solutions of the parent molecules in such solvents. This is the procedure we have used to prepare the radical anion of $Rh_2(O_2CMe)_4$, which is the subject of this report.

Experimental

$Rh_2(O_2CMe)_4{\cdot}2MeOH$ was prepared by a published procedure.[17] The analogous fluoroacetate complex was prepared by exchange with $CF_3CO(OH)$, as described by Johnson *et al.*[2] Solutions were prepared in methanol, CD_3OD, 2-methyltetrahydrofuran (mthf), or other solvents and were frozen in liquid nitrogen as small glassy beads. They were irradiated at 77 K in a Vickrad ^{60}CO γ-ray source with doses of up to 5 Mrad.

Electron spin resonance spectra were obtained in a Varian E-109 spectrometer calibrated with a Hewlett-Packard

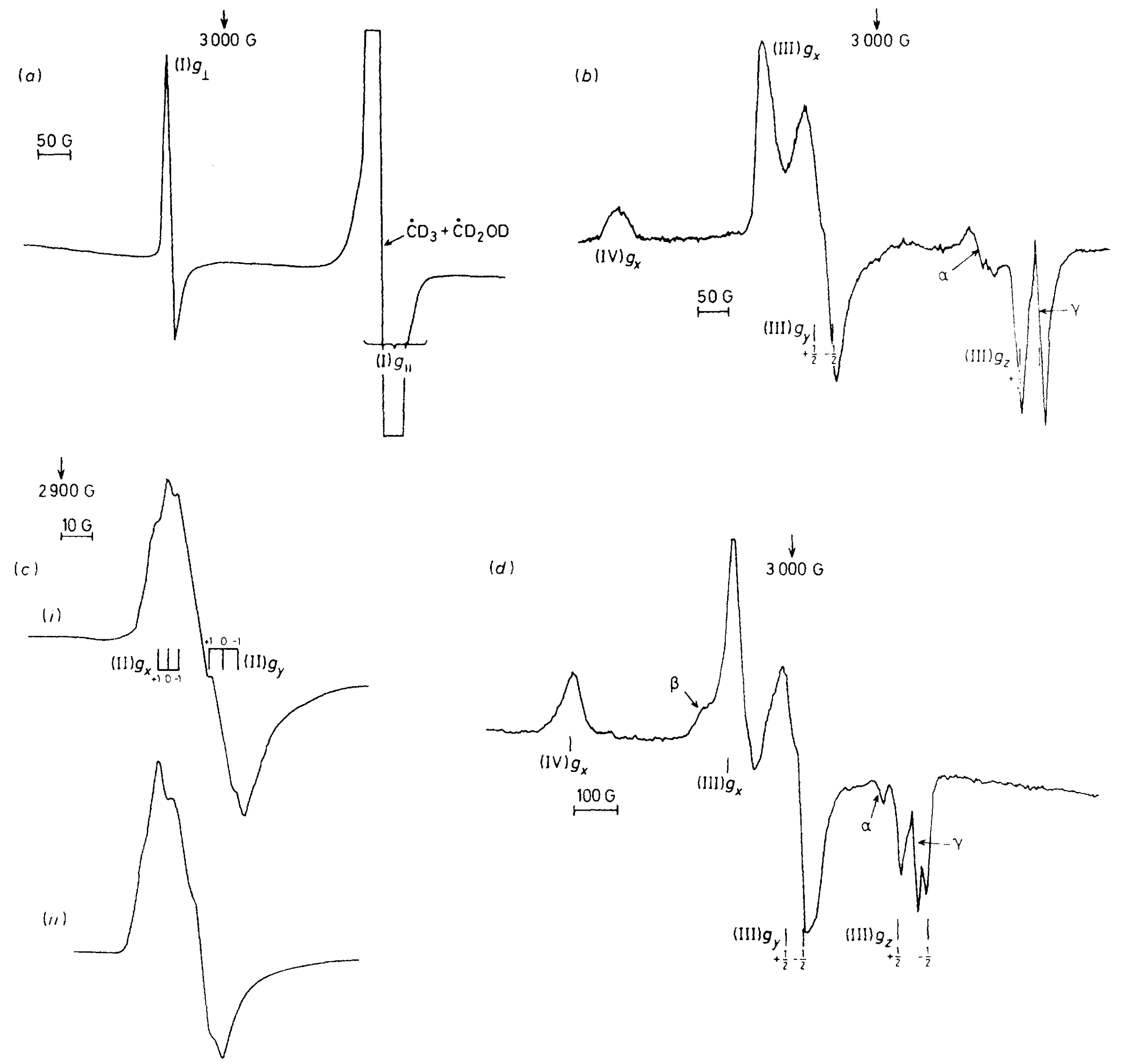


Figure 2. First-derivative *X*-band e.s.r. spectra for $Rh_2(O_2CMe)_4$ in various solvents after exposure to ^{60}Co γ-rays at 77 K and in some cases annealing to various temperatures and re-cooling to 77 K for measurement. (*a*) In CD_3OD-D_2O at 77 K, showing the $g_\perp$ feature assigned to the parent anion, $[Rh_2(O_2CMe)_4]^{\cdot-}$: the $g_\parallel$ feature is hidden beneath the intense solvent radical lines at $g = 2.00$. (*b*) As (*a*), after annealing to *ca.* 130 K, showing features assigned to species (III) [there is a small sharp impurity line γ at the free-spin superimposed on the $-\frac{1}{2}$ (*z*) feature for species (III)]. It is probable that the line marked α, at $g = 2.065$ is g_y for species (IV), and that g_z is in the 2.00 region. (*c*) (*i*) In pure CD_3OD after slight annealing, showing the resolved g_x and g_y features assigned to species (II). These features are reproducible. (*ii*) Simulation of the g_x and g_y features using the data in the Table. (*d*) In mthf, after annealing to near the glass point to remove solvent radicals, showing features assigned to species (III). The sharp line at free-spin (γ) is the same impurity signal. This is retained when the other features are lost. Features α and β may be associated with species (IV) whose g_x line is shown at 2.59. Feature α is close to that shown in (*b*) at 2.065

5246L frequency counter and a Bruker B-H 12 E field probe, standardized with diphenylpicrylhydrazyl (dpph). After measurement at 77 K, samples were annealed until significant changes were obtained in their spectra and then re-cooled to 77 K for further measurements.

Results

Dirhodium tetra-acetate and dirhodium tetrakis(trifluoroacetate), when dissolved in CD_3OD or mthf and γ irradiated, gave e.s.r. spectra which were readily attributable to electron-capture species [Figure 2(*a*)]. The initial species observed when $Rh_2(O_2CMe)_4$ solutions were irradiated had a strong perpendicular feature at $g_\perp = 2.24$. This was solvent independent for the solvents CD_3OD, mthf, glycerine, and ethylene glycol. The associated parallel feature, expected at *ca.* $g = 2.00$, was never observed, being covered by intense solvent features in that region. However, for CD_3OD solutions we can say that $g_\parallel$ must lie in the range 1.99—2.01, which is the range obscured by solvent features. The parallel feature must lie in the high-field side of the perpendicular feature. We have examined the spectrum up to *ca.* 12 000 G, corresponding to a $g_\parallel$ value of *ca.* +0.5. Any value less than this would be unprecedented. Also, in view of the high intensity of the perpendicular feature, we can argue firmly that there must be ample intensity for the parallel feature, so we would have

Table. E.s.r. parameters for rhodium complexes

		g Values			*A* Values/G [a]		
Species	Solvent	*x*	*y*	*z* [b]	*x*	*y*	*z*
(I)	CD_3OD-D_2O CD_3OD mthf	2.24	2.24	2.00	*c*		
(II)	CD_3OD	2.248	2.240	2.00 [b]	*ca.* 3.5	*ca.* 3.5	*b*
(III)	CD_3OD-D_2O	2.32	2.25	2.006	*b*	15	20
	mthf	2.27	2.14	2.005	*b*	15	20
(IV)	CD_3OD-D_2O	2.57	*d*	*d*	*c*	*d*	*d*
	mthf	2.59	*d*	*d*			

[a] G = 10^{-4} T. [b] Feature must be located beneath intense solvent signal, therefore error is *ca.* ±0.01. [c] Not resolved, therefore $\leqslant 3$ G. [d] *y* and *z* features never clearly defined; for species (IV), it is probable that $g_y \approx 2.065$ and $g_z \sim 2.00$ [see Figure 2(*b*)].

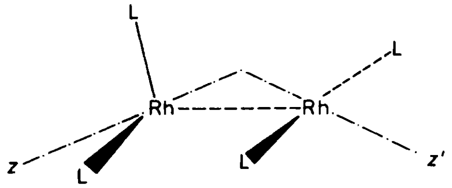


Figure 3. Postulated partially dissociated A-frame structure for the electron-capture centre. The number of bound ligands is uncertain

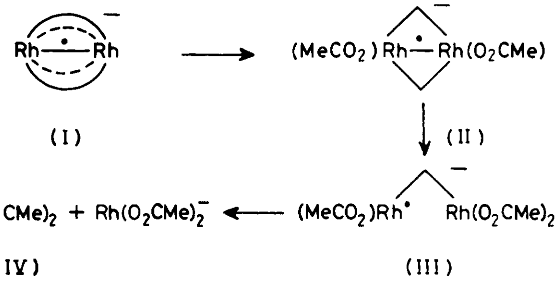
detected it had it been outside the free-spin region. All attempts to anneal away the solvent features so that the rhodium parallel line could be observed were frustrated by the instability of the anion. The features associated with the anion disappeared before the intense solvent lines. As these features were lost, others grew in their place in a sequence that was solvent dependent.

The e.s.r. parameters for these features are given in the Table, and some typical spectra are shown in Figure 2. Rhodium (^{103}Rh has $I = \frac{1}{2}$, 100% abundant) has an extremely small nuclear moment and in all but a few cases, noted in the Table, we were unfortunately unable to detect its hyperfine coupling. This hampers our ability to make definitive statements regarding the structures of the species giving rise to the features observed.

Discussion

The Acetate Complex.—As stated above, the spectrum observed in solutions of $Rh_2(O_2CMe)_4$ γ irradiated at 77 K in anion-forming solvents is assigned to an axially symmetric radical anion, $[Rh_2(O_2CMe)_4]^{\cdot -}$, being characteristic of an axial radical with the unpaired electron in a s.o.m.o. of d_{z^2} character. This assignment agrees with the Xα calculations of Norman and Kolair[6] which show that the l.u.m.o. (lowest unoccupied molecular orbital) of the parent molecule is the $^8b_{1u}$ orbital, coming from the d_{z^2} orbitals and making up the Rh–Rh σ* and Rh–solvent σ* bonds. We were unable to observe any Rh splitting on the perpendicular feature for the first formed species (I). Unfortunately, the parallel feature which would be expected to show a larger Rh interaction was hidden by solvent lines, so we cannot calculate any 'experimental' spin densities for rhodium. However, on slight annealing of solutions in pure CD_3OD, the perpendicular feature became better defined, showing slight splitting into *x* and *y* features, each comprising a poorly defined triplet [Figure 2(*c*)]. Simulation suggests the triplet nature of these lines which cannot be reproduced using doublets. This spectrum was quite reproducible. This confirms the presence of two equivalent rhodium nuclei in species (II) and hence also in species (I) to which it is very closely related. We conclude that (I) is the parent anion $[Rh_2(O_2CMe)_4]^{\cdot -}$, the s.o.m.o. being d_{z^2} in form and equally distributed on the two rhodium atoms.

Annealing the samples in various solvents gave rise to an interesting series of changes (shown below). In all cases, loss of the initial species was quite irreversible, in keeping with Bear's electrochemical studies.[13]



The major species formed from species (I) or (II) in CD_3OD and mthf on annealing is species (III), whose *y* and *z* features appear as doublets rather than triplets [Table and Figure 2(*b*) and (*d*)]. Thus this species has the unpaired electron largely confined to one rhodium atom and the axial symmetry has been lost. Although dissociation of the Rh–Rh bond is possible, we consider this to be most unlikely in these low temperature, rigid solvents, and suggest that loss of a ligand from one rhodium has occurred, thereby switching the s.o.m.o. from the σ* orbital to one that is largely on one side of the molecule. This suggestion is supported by our results for the trifluoroacetate complex which gave such asymmetric species at much lower temperatures. This accords with the weak coordinating power of the $CF_3CO_2^-$ ligands.

A feature (g_x) in the 2.57—2.59 region was also detected [species (IV)], but although this gained intensity on annealing it never constituted a major part of the spectrum and it was difficult to be sure of the other two *g* values. [Probably $g_y \sim 2.065$ and $g_z \sim 2.00$, as indicated in Figure 2(*b*).] This species is probably also formed by ligand loss, but we cannot guess its structure from the present evidence.

A possible A-frame structure for species (III)[18] which accords with chemical expectation is shown in Figure 3. Since the g values for (III) are slightly different in CD_3OD and mthf, it may be that weak solvent interaction is important in these intermediates.

The magnitude of the hyperfine splitting is quite normal for rhodium complexes, but our inability to resolve the x feature means again that we cannot calculate spin densities from the coupling constants.

The Trifluoroacetate Complex.—The trifluoroacetate anion is a much weaker ligand than the acetate anion, and hence is expected to be lost from the anion more readily. When solutions of $Rh_2(O_2CCF_3)_4$ in CD_3OD or mthf were irradiated at 77 K, the initial spectrum comprised a pair of features at $g_x = 2.54$ and $g_y = 2.33$. We assume a third g feature (g_z) hidden under the central radical lines [species (V)]. Warming above 77 K resulted in loss of these features and the appearance of a second pair of features at $g_x = 2.38$ and $g_y = 2.25$ [species (VI)]. Both (V) and (VI) have spectra typical of radicals with a fully anisotropic g tensor. Evidentally, in this case, ligand loss occurs even at 77 K, and we were unable to trap the parent anion. It is interesting that in this case a species with large Δg values is converted into one having smaller g shifts. There is unfortunately insufficient information for us to say much about the structures of these electron-capture species except to say that ligand loss by the parent anion does indeed occur more readily than for the acetate.

Finally, we mention that $RhCl_3 \cdot 3H_2O$, in CD_3OD-D_2O, showed similar, although not identical, behaviour. The initial species observed at 77 K, after irradiation, has a fully anisotropic g tensor, with $g_x = 2.58$ and $g_y = 2.41$. Annealing yields a rather broad $g_\perp$ at just about the average of the foregoing values, $g_\perp = 2.48$ and $g_\parallel = 2.00$.

Conclusions

We have prepared $[Rh_2(O_2CMe)_4]^{\cdot -}$ by γ irradiation of solutions of the parent molecule at 77 K. Evidence for this includes axial symmetry, insensitivity to solvent, incipient resolution into hyperfine triplets for species (II) [derived from (I) in CD_3OD solvent], and, especially, expectation based on experience with many similar systems. This species is extremely unstable, being converted into at least two other species by unimolecular breakdown on annealing above 77 K. Comparison of the acetate and trifluoroacetate complexes suggests that this is due to ligand loss rather than breaking the Rh–Rh bond.

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