Electron Paramagnetic Resonance Study of the Adduct of a Nitroxide and Rhodium Trifluoroacetate Dimer

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Abstract: The ESR spectrum of the Lewis acid-base adduct of the rhodium trifluoroacetate dimer and 2,2,6,6-tetramethylpiperidine-*N*-oxyl is reported. The spectrum of the complexed nitroxide shows a sizable *g*-value shift, compared to the uncomplexed base, as well as a rhodium hyperfine coupling, to one rhodium, of 1.7 ± 0.2 G. About −0.4 G of the rhodium hyperfine is assigned to the nuclear spin-orbital interaction and the rest to Fermi contact coupling via spin polarization. The *g*-value shift and Rh hyperfine coupling are interpreted in terms of a perturbation molecular orbital analysis for the adduct.

Nitroxide spin labels have come into common usage to probe the solution structure of large molecules. These radicals are especially attractive for ESR studies because they are detectable at very low concentrations (less than 10^{-5} M) and because their narrow ESR line widths (about 1 G) make it possible to measure small changes in g and a_N values. With the exception of the work of Eames and Hoffman,[2] the few studies on the effect on the ESR from a nearby heavy atom have not been thorough.[3-7] Such interaction changes the g value, changes the ^{14}N hyperfine coupling constant, and, under favorable conditions, gives additional hyperfine due to the heavy atom. It would be valuable not only to characterize such a system to pave the way for possible applications, but also to interpret it as quantitatively as possible and to use these results, where direct nitroxide-heavy atom bonding occurs, to learn about the nature of the Lewis acid-base interaction. We have performed such a study using the diamagnetic acid rhodium(II) trifluoroacetate and 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TMPNO) as the nitroxide base. Although a wide variety of transition metals have been reported to form several types of metal-nitroxide complexes, this is the first report of a nitroxide complex involving rhodium.

This system is of further interest because the spin label enables us to obtain some appreciation of how coordination to one of the metals influences the nature of the metal-metal interaction. Since the I value of rhodium is ½, the observation of rhodium hyperfine provides a probe of the metal contributions to the resulting molecular orbitals.

Experimental Section

TMPNO[8] and rhodium acetate[9] were prepared by literature methods. Conversion to the trifluoroacetate was effected by exchange with trifluoroacetic acid as has been reported for the preparation of molybdenum trifluoroacetate.[10] The exchange was carried out twice to ensure complete exchange.

ESR spectra of identical samples were measured with Varian E-9 (X-band) and E-15 (Q-band) spectrometers. Spectra were recorded at either ambient temperature or 80 °C on degassed toluene solutions 1.0×10^{-3} M in TMPNO and saturated (ca. 10^{-3} M) in rhodium trifluoroacetate.

Isotropic ESR computer line shape simulations[11] were performed assuming a Lorenzian line shape.

Results and Discussion

Rhodium(II) carboxylate dimers are isostructural with the familiar copper(II) acetate dimer, with one oxygen from each of the four carboxylate groups bound to one rhodium and the other oxygens completing the four O-C-O bridges to the second rhodium.[12] Although there has been some dispute about the correct molecular orbital diagram from such dimers, it appears that the orbital ordering qualitatively depicted in Figure 1 is correct.[13] When the appropriate number of electrons are added, it is seen that there is formally a rhodium-rhodium single bond. Rhodium butyrate has been shown to form 1:1 and 2:1 adducts with various bases without dimer cleavage, forming bonds which are presumably collinear with the metal-metal bond.[14] No evidence of adduct formation is found between TMPNO and rhodium butyrate; however, when the stronger acid rhodium trifluoroacetate is used, the isotropic ESR spectra at X- and Q-band frequencies shown in Figure 2 are observed.

The X-band spectrum (Figure 2a) shows the typical three line pattern for the uncomplexed TMPNO centered at $g = 2.005$. In addition, two new features are seen downfield of the uncomplexed radical, a doublet and a shoulder. These are assigned to two of the three lines for the complexed radical, the third line presumably hidden under the central line of the free nitroxide. The X-band spectrum clearly shows a large shift in g value for the rhodium complexed radical as well as a sizable rhodium hyperfine; however, the spectra overlap too much for accurate measurements of a_N and g for the bound nitroxide. Running the spectra at Q-band gives well-separated spectra proving that two species are present with different g values. The Q-band spectrum (Figure 2b) contains three sets of 1:1:1 triplets. The most intense set at higher field is assigned to free TMPNO. The second-most intense triplet at lower field is assigned to the nitroxide in the TMPNO-rhodium trifluoroacetate adduct. In addition, the Q-band spectrum contains an additional weak triplet in the same region as the bound nitroxide, but with broader lines. This triplet is tentatively assigned to some precipitated nitroxide-rhodium adduct since it has essentially the same g and a_N values as the bound nitroxide but has broader lines. An alternative assignment would be to a bisnitroxide adduct. This last triplet is not noticeable at X-band due to decreased sensitivity.

The lines are broader at Q-band making the rhodium hyperfine less apparent. This line broadening is easily explained on the basis of g-factor and hyperfine anisotropy. According to Kivelson,[15] the line width of individual lines can be expressed as $W(m) = K + A + Bm + Cm^2$ where A and B are functions of the magnetic field strength, the anisotropies in g and a_N, and the rotational correlation time and m is the nuclear magnetic quantum number. At the higher magnetic fields for Q-band, A is larger, thus increasing the line widths. In order to increase the resolution at Q-band the rotational correlation time must be decreased. This can be accomplished by raising the temperature. Figures 2c (~20 °C) and 2d (~80 °C) show the effect of raising the temperature. At the higher temperature, the line width is about 0.2 G smaller, permitting better resolution of the rhodium hyperfine.

For the free nitroxide, g is found to be 2.0052 (1) and a_N is 15.5 (1) in good agreement with literature data in this solvent.[8] From the Q-band spectrum, a_N (bound) is 16.7(1) G, giving

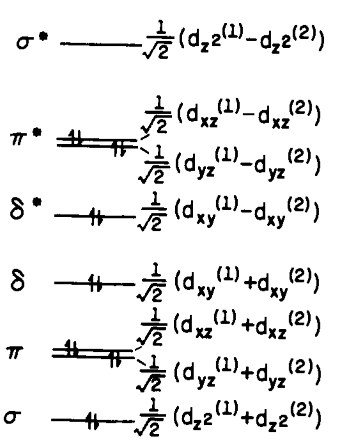

Figure 1. Qualitative MO diagram for rhodium trifluoroacetate. The ordering is based on the assumptions that the 4d manifold (except $d_{x^2-y^2}$) is separate from other filled and empty orbitals and that relative energies are determined by symmetry-allowed mixing of orbitals on the two metals proportional to extent of overlap.

an increase in a_N of 1.2 G, g(bound) is 2.0150. The shift in g upon complexation was calculated from the formula:[16] $\Delta g = g(\text{bound}) - g(\text{free}) = -(\Delta H/H)g(\text{free})$, using the free nitroxide as an internal reference. ΔH is the difference in magnetic field between the centers of the bound and free signals and H is the magnetic field at the center of the reference spectrum. Δg is found to be 0.009 84 (1) which is the largest g shift yet reported for a bound nitroxide.

The increased ^{14}N hyperfine upon complexation is comparable to that previously observed for nitroxide adducts.[17,18] It has been explained as follows:[8] electron density in orbitals which are π-bonding with respect to the N-O bond is expected to flow toward the oxygen upon adduct formation; hence, electron density in π* orbitals, where the unpaired electron resides, increases near the nitrogen. This increase has been related quantitatively to the adduct bond strength[18] for hydrogen bonding acids. An extrapolation to this new type of acid would correspond to a weak (~4 kcal mol^{-1}) enthalpy of adduct formation for the 1.2 G increase.

Weak hydrogen bonding causes g to decrease linearly with an increase in a_N for the closely related di-*tert*-butyl nitroxide.[17,19] The g and a_N values for TMPNO exhibit similar behavior. The g shift in the rhodium-nitroxide molecule due to complexation can be estimated from the above correlation to be −0.0004.

The observed g shift is due to both spin-orbit coupling with the rhodium and to electron redistribution within the nitroxide. Using $\Delta g_{\text{obsd}} = 0.009\,84$ and $\Delta g_{\text{NO}} = -0.0004$ gives the g shift due to spin-orbit coupling with the rhodium of 0.0102.

The small but reproducible splitting on the resolved line in the X-band spectrum and the inflection in all three lines for the Q-band spectrum of the bound nitroxide is assigned to the rhodium (^{103}Rh, 100% natural abundance, $I = \frac{1}{2}$) directly bound to the nitroxide. An alternative assignment to ^{1}H hyperfine from trace impurities of a hydrogen-bonding acid such as water is ruled out for two reasons: Such hyperfine has not been previously observed[18] and it is incompatible with the large observed g shift. The line width and hyperfine constant are almost equal in magnitude. Computer simulation shows that the line shape is quite sensitive to the value of the hyperfine constant in this region. Computer line shape simulation and the observed peak-to-peak line width for both the X- and Q-bands yields an a_{Rh} equal to 1.7 ± 0.2 G. The rhodium hyperfine coupling does not differ noticeably at higher temperatures. The same analysis shows that the Q-band lines are broader than the X-band lines by about 0.7 G (2.0 vs. 1.3 G) at room temperature. The computer simulation of the Q-band spectrum showed that the signal assigned to the precipitated adduct cannot cause the inflection assigned to the rhodium hyperfine, but instead seems to be causing decreased resolution, making the rhodium splitting less apparent.

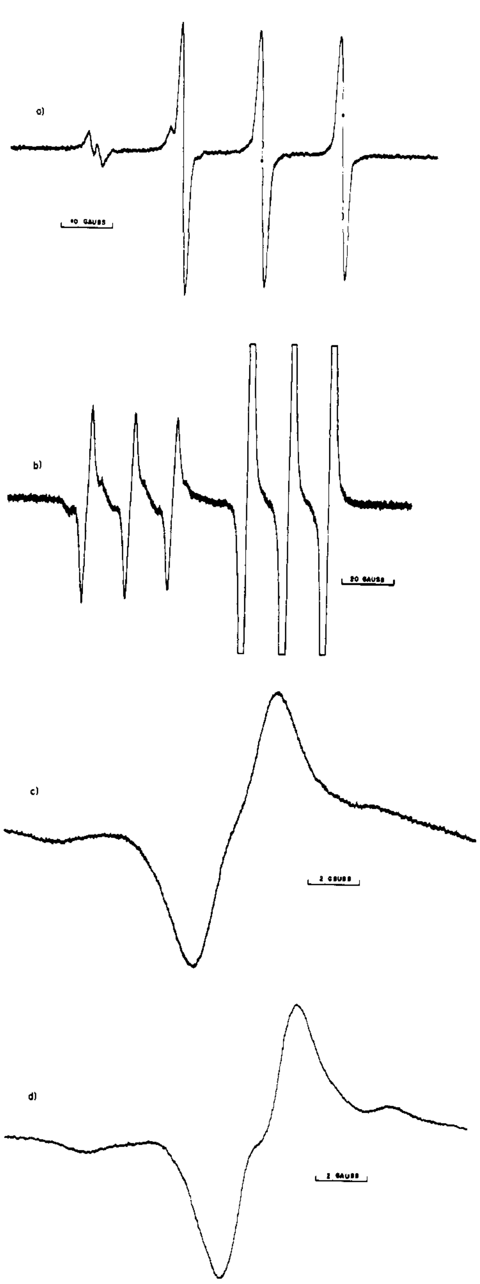

Figure 2. (a) X-Band and (b) Q-band ESR spectra of toluene solution saturated in rhodium trifluoroacetate and ca. 10^{-3} M in TMPNO. (c) Expansion of the lowest-field Q-band line of the bound nitroxide showing the hyperfine splitting assigned to Rh ($I = \frac{1}{2}$). Spectra a, b, and c are at room temperature. (d) Same as c, except at elevated temperature (~80 °C). In all spectra, the magnetic field increases to the right.

^{103}Rh hyperfine is due not only to the familiar Fermi contact term, which measures the unpaired s-electron density at the rhodium nucleus, but also to the interaction of this nucleus with the orbital angular momentum of any unpaired spin that resides in a rhodium 4d orbital. This nuclear spin-orbit contribution is proportional to the spin-orbit coupling constant, so it is generally neglected in organic radicals and becomes increasingly important in heavier transition metal complexes. A quantitative estimate of this term is made possible by assuming that the increased g value of the 1:1 adduct is due solely to the presence of the rhodium atom which gives the hyperfine.

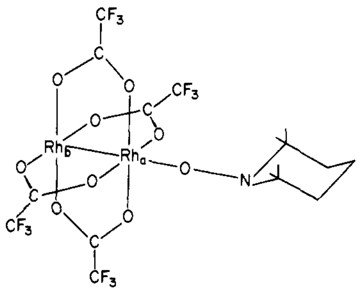

Figure 3. Structure assumed for the adduct of TMPNO with rhodium trifluoroacetate.

Then[20]

$$A_{\mathrm{L \cdot I}} = g_N \beta_N \langle r^{-3} \rangle (g - g_0)$$

where $A_{\mathrm{L \cdot I}}$ is in gauss, g_N is the nuclear g value, β_N is the nuclear magneton, $\langle r^{-3} \rangle$ is the average value of r^{-3} for a 4d orbital of Rh(II), and g_0 is the free electron g value, or, in this example, the g value of the free nitroxide radical. Hence, $g - g_0$ represents the net orbital angular momentum gained by the electron by virtue of its proximity to the rhodium. Using the tabulated value of $\langle r^{-3} \rangle$ of 6.8 au determined by calculation,[21] a value of −0.4 G is obtained for $A_{\mathrm{L \cdot I}}$. Thus, a substantial amount of the hyperfine can be explained without recourse to s-electron density. Although no crystal structure studies have been done on nitroxide radical adducts, it seems plausible that the metal, oxygen, and nitrogen atoms form a plane that is perpendicular to the orbital containing the unpaired electron on the nitroxide. In this case, the orbital containing the odd electron will have no s character and the main Fermi contact contribution to the rhodium hyperfine must be due to spin polarization resulting in β spin at the rhodium nucleus. This would have the opposite sign as the nuclear spin-orbital term, $A_{\mathrm{L \cdot I}}$. Since the absolute value of the measured hyperfine is 1.7 G and the nuclear spin-orbit contribution has been estimated as −0.4 G, the Fermi contact contribution is about 2.1 G. (A full electron in a Rh(I) 5s orbital would give a splitting of −849 G.[21] The negative sign arises because the rhodium nuclear moment is negative.) The sign of the observed hyperfine is thus predicted to be positive as a consequence of the spin polarization of the adduct bond.

The next interesting feature of the spectrum is the appearance of rhodium hyperfine from only one of the rhodiums even though the σ^* orbital is equally composed of both rhodium atoms in the trifluoroacetate. A hyperfine splitting from a second nonequivalent rhodium about one-third the size of that observed would not be detected. Setting such a limit indicates considerably different contributions from the two rhodium atoms in the acceptor molecular orbital of the very weak adduct formed with the nitroxide. This result can be understood with the aid of the molecular orbital diagram for the 1:1 adduct shown in Figure 4.

Consider first the σ interaction, which is largely described by the molecular orbital labeled Ψ_3. The observation of Rh hyperfine from the single directly bonded rhodium nucleus, a, requires that the metal contribution to the MO labeled Ψ_3 be greater for Rh(a) than for Rh(b). This metal contribution could be $4d_{z^2}$ and 5s atomic orbitals. If both rhodium atoms made equal contribution to Ψ_3 triplet rhodium hyperfine would have been observed when this MO underwent spin polarization. The observed result indicates larger contribution from Rh(a) leading to a doublet with the contribution from Rh(b) being too small to be observed. The nonequivalance of the rhodiums in MO Ψ_3 results from a greater overlap of Rh(a) than that of Rh(b) with the nitroxide lone pair. Accordingly, in MO Ψ_1 the contribution from Rh(b) will be larger than that from Rh(a). The extent to which Rh(b) does contribute to MO Ψ_3 will determine the extent to which the acceptor orbital can delocalize the electron density donated from the nitroxide lone pair over both metals, and increase the polarizability of the acid center. However, even the weak interaction of Rh(a) with the nitroxide has drastically reduced the Rh(b) character to the acceptor orbital. The change in metal composition of the essentially metal-metal σ bonding orbital also provides a polarizability mechanism. This experiment provides no information regarding this orbital composition.

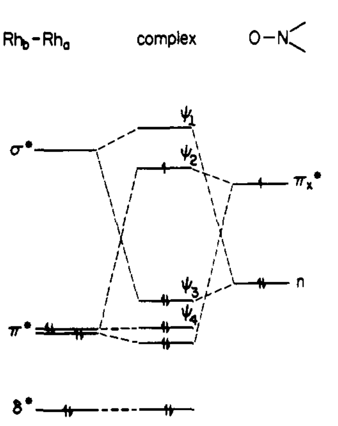

Figure 4. Qualitative MO diagram of one-to-one adduct of rhodium trifluoroacetate with TMPNO. MO's Ψ_1 through Ψ_4 make the major contributions in the analysis.

A similar effect results from a consideration of the interaction of the π^* orbital on the ligand with those on the metal. Ψ_2, the orbital containing the unpaired electron, is still mainly N-O π^*, but has the right symmetry to mix in a small amount of $4d_{xz}$. The overlap of the oxygen p_x with the rhodium (a) d_{xz} orbital leads to nonequivalent rhodium contributions to MO Ψ_2. This places the odd electron directly into a metal d ordital which is reported[21] to give rise to a negative coupling constant. This rhodium character gives the unpaired electron some orbital angular momentum, which is responsible for the shift in the g value (vide infra) and the nuclear spin-orbital contribution to the rhodium hyperfine (vide supra).

The shift in the g value may also be rationalized in terms of the MO diagram in Figure 4. The MO's of the adduct may be written as linear combinations of the metal and nitroxide orbitals. For instance,

$$\Psi_2 = \beta \pi^*_{xz\mathrm{M}} - (1 - \beta^2)^{1/2} \pi^*_{x\mathrm{L}}$$

would be the orbital containing the odd electron. Here subscripts M and L refer to metal and ligand, respectively. The expression for the shift in the g value given by a perturbation treatment[21] is:

$$g = g_0 + \frac{\beta^2}{3} \sum_i \left(\pm \frac{C_i{}^2 n \lambda}{\Delta E_{i2}} \right)$$

where ΔE_{i2} is the energy separation between Ψ_2 and Ψ_i and C_i is the coefficient of the metal orbital in Ψ_i. The + sign is for contributions from filled orbitals and the − sign is for contributions from empty orbitals. Note that g can be different from g_0 only if β^2 is not zero. A rough estimate of β^2 can be obtained by approximating the terms within the summation. Since experimentally, g is greater than g_0, the contributions from filled orbitals must dominate. Making some approximations for $C_i{}^2$ and ΔE_{i2} gives a value for β^2 of about 0.05.

This provides support for the qualitative bonding scheme provided in Figure 4. There is a σ donation from a nitroxide oxygen lone pair into the Rh d_{z^2} orbital and there is also back-donation from the Rh d_{xz} orbital into the π^* nitroxide orbital containing the unpaired spin.

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Stereochemistry of the Hydroformylation of Olefinic Hydrocarbons with Cobalt and Rhodium Catalysts

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Abstract: (*E*)- and (*Z*)-3-methyl-2-pentene, the three isomeric methylcyclohexenes, as well as 1,2-dimethylcyclohexene and 2-methyl-1-methylidenecyclohexane have been hydroformylated in the presence of rhodium or cobalt catalysts in order to investigate the stereochemistry of the reaction. Conclusive evidence is provided that both catalytic systems promote cis addition of hydrogen and formyl group to the olefins. Some aspects of the isomerization phenomena accompanying the hydroformylation have been clarified, and two different mechanisms responsible for the formation of isomeric aldehydes have been proved.

Although the hydroformylation of olefins has been extensively investigated, experimental evidence concerning the stereochemistry of the addition of hydrogen and a formyl group to the double bond is still scarce.[1] Prevailing cis addition has been ascertained in the cobalt-catalyzed hydroformylation of 3β,20β-diacetoxy-Δ^5-pregnene[2] and of 3,4,6-tri-*O*-acetyl-D-glucal.[3] Contrasting evidence exists in the literature in the case of the stoichiometric synthesis of aldehydes from olefinic substrates and hydrido- or deuteridotetracarbonylcobalt.[1] The stereochemistry of the hydroformylation catalyzed by other metals has not been previously investigated. We became interested in the steric aspects of the hydroformylation and particularly in the degree of stereospecificity of the reaction in connection with our research on the asymmetric hydroformylation catalyzed by cobalt and rhodium complexes containing chiral ligands;[4] in a preliminary communication we have shown that in the case of hydridocarbonyltris(triphenylphosphine)rhodium as the catalyst, the reaction proceeds with cis stereochemistry.[5] Similar results have been achieved by other authors using rhodium supported on alumina as the catalyst.[6] The analogous investigation carried out with cobalt catalyst is complicated by the hydrogen shift reactions occurring in the substrate during the hydroformylation[7] and this is probably the main reason for the lack of quantitative data in this field.

In the present paper the hydroformylation of (*E*)- and (*Z*)-3-methyl-2-pentene, as well as of the three isomeric methylcyclohexenes, of 1,2-dimethylcyclohexene, and of 2-methyl-1-methylidenecyclohexane is described. Conclusive evidence is provided that both rhodium and cobalt catalysts promote a stereospecific cis addition of carbon monoxide and hydrogen to the double bond. From the results obtained a deeper insight has been achieved for the isomerization phenomena accompanying the hydroformylation. Furthermore the existence of at least two different mechanisms responsible for the formation of isomeric aldehydes, other than those predicted from the direct hydroformylation of the double bond, has been proved.

Results and Discussion

(A) Hydroformylation of (*E*)- and (*Z*)-3-Methyl-2-pentene with Hydridocarbonyltris(triphenylphosphine)rhodium or Dicobalt Octacarbonyl as Catalyst Precursors. The absolute predominance of the threo or of the erythro isomer, obtained in the hydroformylation of (*E*)- or (*Z*)-3-methyl-2-pentene (Table I), indicates, beyond any doubt, the overwhelming cis stereochemistry of the rhodium-catalyzed hydroformylation.

The relatively small amounts of erythro or threo epimer obtained from (*E*) and (*Z*) substrate, respectively, might be accounted for by either a trans hydroformylation of the original olefin or a cis hydroformylation of the cis–trans isomerized substrate. Beside the already published results,[5] the following points should be mentioned: (a) The degree of deuteration of the substrate skeleton, as shown by the analysis of the methyl esters obtained from the primary reaction products, is the following: methyl *threo*-2,3-dimethylpentanoate was monodeuterated ($d_1 > 90\%$), methyl *erythro*-2,3-dimethylpentanoate, methyl 3-ethylpentanoate, and methyl 4-methylhexanoate were dideuterated ($d_2 >$ 90, 80, and 85%, respectively). (b) No deuterium scrambling seems to occur during the reaction. Within the limits of NMR analysis, deuterium occupies only position 3 in methyl *threo*-2,3-dimethylpentanoate and only positions 3 and 4 in methyl 3-ethylpentanoate and methyl