g of the product was treated with 1.10 g of diphos in 2 ml of acetone and the liquid bulb-to-bulb distilled in vacuo. GLC analysis indicated the presence of two methyl-1,3-cyclohexadiene isomers in approximately a 1:3 ratio. The major isomer was the one found in the THF experiment above.

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(4) (a) The selective hydrogenation of certain dienes per se, is, of course, not novel[5] (for example, see ref 4b and 4c). However, the fact that a possible intermediate in this system is a known, isolable complex, (**1**, the precursor) offers one the opportunity to evaluate its true role in the catalytic process. Such an opportunity has been lacking in other systems. It should also be noted (from a practical point of view) that the majority of other catalysts require high temperatures and/or H_2 pressures while these are successful at 25° and 1 atm of H_2. (b) D. R. Fahey, *J. Org. Chem.*, **38**, 3343 (1973). (c) E. N. Frankel and R. O. Butterfield, *ibid.*, **34**, 3930 (1969).

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(10) Though some of the cationic catalyst systems, particularly $[Rh(NBD)L_3]^+$ (L = PMe_3, $PPhMe_2$), will catalyze the reduction of acetone,[2d] we have so far found no evidence that this relatively slow process could lead to mechanistic complications, at least in systems concerned with the relatively rapid hydrogenation of dienes (see, however, ref 13).

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(12) Interestingly $[Rh(NBD)_2L]^+$ complexes have been isolated by addition of 1 mol of L to $[Rh(NBD)_2]^+$ (ref 2c). Apparently the $[Rh(NBD)_2L]^+$ structure is not as favorable as $[Rh(butadiene)_2L]^+$ since addition of a second L to $[Rh(NBD)_2L]^+$ generates $[Rh(NBD)L_2]^+$ (ref 2c).

(13) Reduction of 2,3-dimethyl-1,3-butadiene with $[Rh(NBD)(PPhMe_2)_3]^+$ in acetone was successful though the rate of diene disappearance was not constant and the mechanism therefore possibly not analogous to that using $[Rh(NBD)(chelate)]^+$ precursors. For example, mechanistic complications related to the reduction of acetone could be significant in this case.[10]

(14) The ratios were estimated by ^1H NMR. The ratio of β:α:olefinic protons should be 3:3:2 for cyclohexene-*3,4*-d_2 and 4:2:2 for cyclohexene-*3,6*-d_2. The found ratio was 3.3:2.7:2.0.

(15) (a) $[Rh(NBD)(PPhMe_2)_2]^+$ was not successful, however, since disproportionation of 1,3-cyclohexadiene to cyclohexane and benzene predominates. This disproportionation is not uncommon and has been found in systems containing related Rh(I) cationic complexes.[15b] (b) M. Green and T. A. Kuc, *J. Chem. Soc., Dalton Trans.*, 832 (1972).

(16) A mixture of 1-methyl-1,4-cyclohexadiene and all three methyl-1,3-cyclohexadiene isomers was prepared by isomerization of the former with potassium *tert*-butoxide in DMF; T. Yamaguchi, T. Ono, K. Nagai, C. C. Sin, and T. Shirai, *Chem. Ind.* (*London*), 759 (1967).

(17) The two intermediate methyl-1,3-cyclohexadiene isomers detected during hydrogenation of 1-methyl-1,4-cyclohexadiene could also be formed stoichiometrically on rhodium as in eq 7 (see experimental section). The isomer not found during hydrogenation was separated from the prepared mixture[16] and identified as 5-methyl-1,3-cyclohexadiene by ^1H NMR. Note that reaction of 1-methyl-1,4-cyclohexadiene with $Fe_3(CO)_{12}$ gave 10% Fe(5-methyl-1,3-cyclohexadiene)$(CO)_3$, 30% Fe(2-methyl-1,3-cyclohexadiene)$(CO)_3$, and 60% Fe(1-methyl-1,3-cyclohexadiene)$(CO)_3$; A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. A*, 332 (1968).

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Electron Spin Resonance of Electrochemically Generated Rhodium(0) Complexes[1a]

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Abstract: Cyclic voltammetry studies of 2,2′-dipyridyl (dip) and 1,10-phenanthroline (phen) complexes of Rh(III) have previously indicated the production of relatively stable Rh(0) having the general formula, $[RhL_2]^0$. A combined coulometry-electron spin resonance study has now been utilized to characterize these unusual paramagnetic Rh(0) complexes. Glassy acetonitrile solution spectra of chemically or electrochemically prepared $[Rh(L)_2]^0$ (77–200 K) produce an axially symmetric $S = \frac{1}{2}$ spectra in the $g = 2$ region for both the phen and dip complexes and no spectra at room temperature. The sign and magnitude of the g factor anisotropy ($g_\perp = 2.01$, $g_\parallel = 1.98$ for $[Rh(dip)_2]^0$ and $g_\perp = 2.01$, $g_\parallel = 1.97$ for $[Rh(phen)_2]^0$) and the absence of resonance at room temperature are consistent with a "distorted square planar" structure for the Rh(0) complexes.

The low oxidation states in first transition series complexes (V(0), Cr(I), Fe(I), Fe(0)) of dipyridyl and its derivatives are frequently characterized by electron spin resonance studies.[2] Within the limitations of ligand field theory, two limiting case descriptions of the highest filled orbital are suggested: (1) a localized metal d type orbital or (2) a delocalized ligand type π orbital. That this ligand field model and the resulting limits are frequently inadequate is best evidenced by the contradictory conclusions obtained for $[Fe(dip)_3]^0$ (dip = 2,2′-dipyridyl) from electrochemical[3] and ESR data,[4] the former indicating a ligand localized radical and the latter a localized d orbital system for this paramagnetic species. For these same π ligands, complexation of a second series ion, with its higher energy d subshell, can produce mixing of d and π orbitals, even in the higher oxidation state complexes such that, for example, the ground and lowest excited states for $[Ru(dip)_3]^{2+}$ contain ligand character[5,6] and therefore cannot be described as localized d-d states. Electrochemical data obtained for this complex are consistent with the delocalized orbital character of the ground state of the $[Ru(dip)_3]^{2+}$,

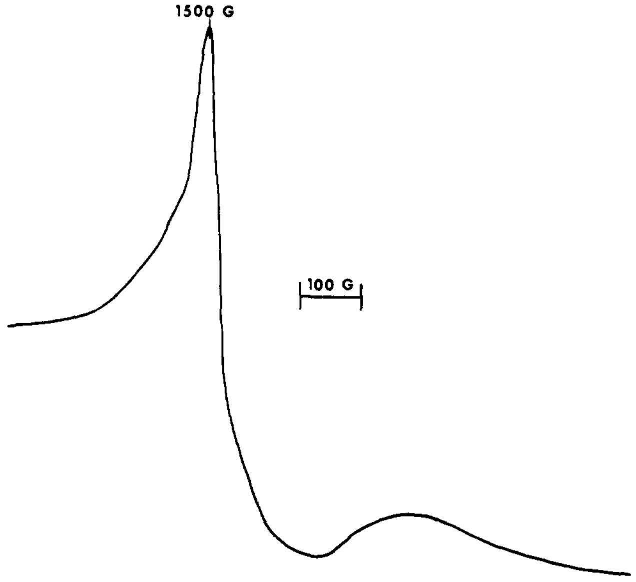

Figure 1. Glassy solution ESR spectrum of Rh(0) species in the $g \approx 4$ region.

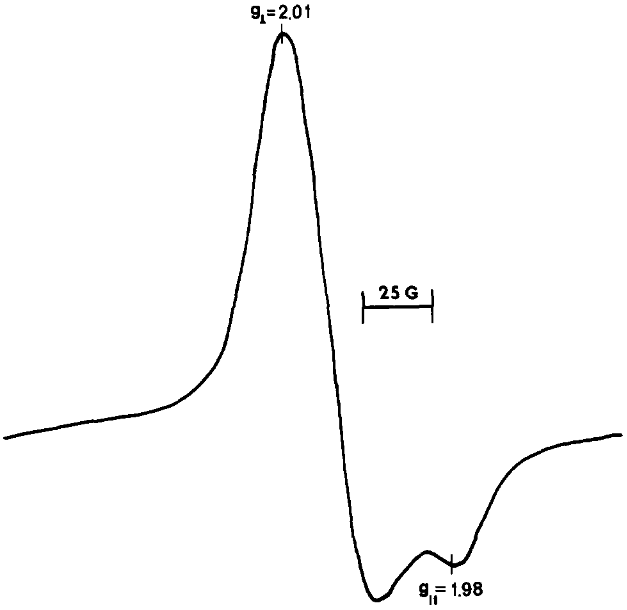

Figure 2. Glassy solution ESR spectrum of Rh(0) in the $g = 2$ region.

Table I. Spin Resonance Parameters for the Monomer and Dimer Rh(0) Complexes

	g	$D^{*\,a}$
dip		
Monomer	$g_\parallel = 1.98 \pm 0.003$ $g_\perp = 2.01 \pm 0.003$	—
Dimer	—	0.08 ± 0.02
phen		
Monomer	$g_\parallel = 1.97 \pm 0.003$ $g_\perp = 2.01 \pm 0.003$	

[a] Ph. Kottis and R. Lefebrre, *J. Chem. Phys.*, **39**, 393 (1963).

$[Ru(dip)_3]^+$, and $[Ru(dip)_3]^0$ complexes.[7,8] Our own interest in the electrochemistry of the isoelectronic $[Rh(dip)_3]^{3+}$ and $[Rh(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) complexes[9,10] have permitted us to obtain unique ESR spectra of the $[Rh(dip)_2]^0$ and $[Rh(phen)_2]^0$ complexes pertinent to the correct description of the ground state for low oxidation state complexes.

Experimental Section

The $[Rh(dip)_3][ClO_4]_3$, $[Rh(phen)_3][ClO_4]_3$, $Rh(dip)_2][ClO_4]$, and $[Rh(phen)_2][ClO_4]$ complexes were synthesized using literature methods.[11,12] The electrolysis and voltammetry were accomplished in a three-compartment cell using a Princeton Applied Research (PAR) Model 173 potentiostat with ir compensation and a triangle wave generator. Current-time measurements were done with a Heath strip chart recorder and the curves integrated with a planimeter. All measurements were done in purified acetonitrile[9] solvent under prepurified nitrogen atmosphere in a glove bag with the electrolysis solution purged with dried nitrogen (treated with O_2 removing catalyst) for 60 min prior to electrolysis.

Electron spin resonance measurements were done with a JEOLCO X-band ESR spectrometer. Samples taken from the electrolysis cell under nitrogen were transferred to evacuated ($\sim 10^{-2}$ mm) sample tubes and spectra recorded immediately.

Results

Electrolysis of $[Rh(dip)_3]^{3+}$ solution at −1.2 V produced $[Rh(dip)_2]^+$, a dark purple solution; cyclic voltammetry was used to qualitatively indicate the reduction of the starting material to Rh(I). Electrolysis of a 5×10^{-3} M solution of $[Rh(dip)_3]^{3+}$ indicated consumption of 1.8 electrons. Continued electrolysis at −1.5 V of Rh(I) solutions produces a black solid, apparently $[Rh(dip)_2]^0$.[9] Coulometry of the Rh(I) solution indicates consumption of 0.9 electron. For reduction of the chemically produced[12] $[Rh(dip)_2]^+$ solution, current-time curves and cyclic voltammetry were used to determine that the reduction was 99% complete prior to determination of ESR spectra. The stepwise reduction of $[Rh(phen)_2]^0$ was complicated by the strong adsorption[10] accompanying the reduction but the sum of the n values (2.75) and the ESR data were consistent with that of the analogous dip complex.

Electron spin resonance spectra at room temperature of the nitrogen purged sample gave no spectra for the tris starting materials, Rh(I) solutions, or the Rh(0) solutions. At 77 K, solutions containing the tris Rh(III) species or the bis Rh(I) species gave no ESR signal. Those solutions of $[Rh(dip)_2]^+$ (produced chemically or electrochemically) electrolyzed at −1.5 V give two anisotropic signals (Table I) at low temperature (77–200 K), one in the $g \approx 4$ region (Figure 1) and a second more intense signal in the $g = 2$ (Figure 2) region. The intensity ratio for the two lines is dependent upon preparation method with the $g = 4$ signal disappearing for Rh(0) solutions of greater initial concentration of Rh(I) while the $g = 2$ signal is significantly enhanced for these more concentrated solutions. This intensity variation as a function of initial Rh(I) concentration indicates that two distinct species are present in solution for the dip complex. Solutions containing either $[Rh(phen)_2]^0$ or $[Rh(dip)_2]^0$ give almost identical 77 K spectra in the $g = 2$ region.

Conclusions

The anisotropic line shape of the $g = 2$ signal for both complexes is characteristic of an axially distorted $S = \frac{1}{2}$ complex[13] with $g_\perp > g_\parallel$. The rationale of the $g \sim 4$ line as due to a species having substantial g anisotropy is unlikely in the absence of additional related structure in the high field region. The position and shape of the line are suggestive of "forbidden" $\Delta m = 2$ transitions associated with an $S = 1$ species. An $S = 1$ dipole-dipole dimer produced from interaction of monomeric $S = \frac{1}{2}$ species has been identified for a number of square planar Cu(II) complexes.[14-16]

The sign of the g factor anisotropy ($g_\perp > g_\parallel$) and the absence of the ESR signal at room temperature are not typical of a d^9 complex.[17] For example, copper(II) complexes having the unpaired electron in the $d_{x^2-y^2}$ orbital result in $g_\parallel > g_\perp$.

Moreover, even for those Cu(II) complexes having $g_\perp > g_\parallel$ (unpaired electron in a d_{z^2} orbital), the resonance can be seen at room temperature.[18]

Additionally, the small g factor anisotropy observed at 77° is not consistent with rotational broadening at room temperature. The small g-factor anisotropy (small spin-orbit interaction) indicates that the unpaired electron resides in a nondegenerate state, hence a rapid spin lattice relaxation seems unlikely since such a mechanism requires a spin-orbit perturbation.

The possibility remains that the Rh(0) species at room temperature in this concentration range is dimerized and the resultant $S = 1$ signal broadened by the spin-spin interaction. The magnitude of D^* (Table I) estimated assuming $g = 2.00$ is sufficient to rationalize such broadening. Cyclic voltammetry[9,10] did not indicate the presence of a dimer, for either the phen or dip complex. However, the adsorption and precipitation of the phen complexes made detection of such a dimer species difficult. Indeed, a dipole-dipole type dimer species with a reduction potential similar to that of the monomer here would likely not be distinguished even in the voltammetry of the dip complexes where adsorption is not significant.

The magnitude of the g anisotropy for the monomeric $[\mathrm{Rh(dip)_2}]^0$ ($g_\perp = 2.01, g_\parallel = 1.98$) and $[\mathrm{Rh(phen)_2}]^0$ ($g_\perp = 2.01, g_\parallel = 1.97$) is much less than that of a typical d^9 Cu(II) system.[17,18] Consequently the Rh(0) species cannot be considered a d^9 crystal field complex. Consideration of the complex as a ligand localized complex containing dip^{-1} or phen^{-1} is obviously not appropriate since the dip^{-1} species has an isotropic g factor.[19] Therefore, the Rh(0) complexes are best considered as delocalized orbital complexes, i.e., metal containing heterocycles.

Such an electronic structure accounts for the relative stability of the $[\mathrm{Rh(dip)_2}]^+$ and $[\mathrm{Rh(dip)_2}]^0$ and the phen analogues and is consistent with the "distorted planar" trans type structure determined by x-ray diffraction for the $[\mathrm{Pd(dip)_2}]^{2+}$ complex,[20,21] isoelectronic with the $[\mathrm{Rh(dip)_2}]^+$ and $[\mathrm{Rh(phen)_2}]^+$ species.

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(1) (a) Research jointly sponsored by the National Council of Science and Technology of Romania and the National Science Foundation, USA. (b) North Carolina State University. (c) Visiting Scientist from the Quantum Chemistry Department, Institute of Physical Chemistry, Bucharest 9, Romania. (*d*) Institute of Physical Chemistry.
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Reduction of Pentaamminecobalt(III) Complexes of Aromatic Nitriles by Chromium(II)

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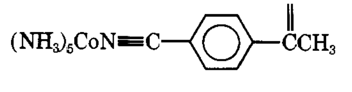
Abstract: The reductions of the pentaamminecobalt(III) complexes of 3-formylbenzonitrile, 4-formylbenzonitrile, furanacrylonitrile, cinnamonitrile, and acetoxybenzonitrile by chromium(II) have been studied. The reductions all follow the rate law $-(\mathrm{d}\ln(\mathrm{Co^{3+}})/\mathrm{d}t) = k[\mathrm{Cr^{2+}}]$. The 3-formyl complex has a specific rate constant of 77 ± 8 $M^{-1}\,s^{-1}$ at 25° and $\mu = 0.5$ M. The 4-formyl derivative is reduced at a rate of $2.5 \pm 0.2 \times 10^5$ $M^{-1}\,s^{-1}$ at 25° and $\mu = 0.5$ M. In the latter system the reductant attacks the remote formyl carbonyl oxygen producing the intermediate A_3 which has been detected spectrally. The $(\mathrm{NH_3})_5\mathrm{Co}^{3+}$ complex of 4-formylbenzonitrile is 30% hydrated in aqueous solution, and the dehydration reaction has also been studied. The furanacrylonitrile, cinnamonitrile, and acetoxybenzonitrile complexes are reduced by an outer-sphere process with rate constants 0.020 ± 0.002, 0.022 ± 0.004, and 0.021 ± 0.003 $M^{-1}\,s^{-1}$ at 25° and $\mu = 0.5$ M, respectively. The results are discussed in terms of the reducibility of the ligands and the stabilities of the precursor complexes. Comparison to analogous carboxylato complexes is also made.

The reductions of $(\mathrm{NH_3})_5\mathrm{CoN{\equiv}CR}^{3+}$ complexes by chromium(II) have been shown to occur by remote attack of the reductant when suitable binding groups are available on the R group. For example, the reduction of



$$(\mathrm{NH_3})_5\mathrm{CoN{\equiv}C{-}C_6H_4{-}C({=}O)CH_3}^{3+}$$

proceeds by attack of chromium(II) at the remote acetyl oxygen.[1] The study of nitrile complexes is considerably simplified with respect to the analogous carboxylato complexes since there is no adjacent position available to bind chromium(II) or protons. In the latter case it is thought that protonation of the adjacent carboxylato oxygen reduces the energy of the empty π antibonding orbitals thus allowing a more facile reduction process.[2]