

sodium chloride causes the conversion of the double emission (2.8/1 ratio of 510/410) to about a 0.33/1 ratio with an isoemissive point at 480 nm (over the mid-range of salt concentrations) (Figure 1). We believe that the sodium ion leads to emission at ~ 410 nm by virtue of its ability to form an ion pair V with the aminophthalate ion.¹² Photoisomerization does not occur in the excited state VIII, presumably because of the resulting lower net charge on the carboxylate group. Consistent with this view is the observation that potassium ion in aqueous DMSO is less effective than sodium in enhancing the short-wavelength peak, and that calcium, lithium, and the proton (as in the hydrated species VI) are more effective.¹³ Further, in 1 mol % water in acetonitrile (a less polar medium than aqueous DMSO) even potassium is effective in blocking the tautomerism, leading to essentially only the short-wavelength emission.

Chelation by sodium can also be detected in the ground state (eq 2); the absorption maximum at 310 nm for a 10^{-4} M solution in aqueous DMSO (17 mol % water), 4×10^{-3} M in TBH, is broadened at longer wavelengths and shifted to 320 nm as sodium chloride is added (up to $\sim 6 \times 10^{-3}$ M). Further, the shape of the fluorescence emission depends on the excitation wavelength. Irradiation in the short-wavelength region of the absorption spectrum (300 nm or below, where both IV and V absorb strongly) leads to a two-banded emission, whereas irradiation at 350 nm (mainly absorption by V) leads to preponderant emission from VIII (short wavelength) (Figure 2).

More importantly, however, at no excitation wavelength in the presence of sodium ion is the fluorescence emission spectrum identical with the chemiluminescence spectrum of luminol measured under identical conditions (Figure 2). Thus, the photo- and chemically produced excited states under these conditions must differ in detail. In view of the short lifetime of the singlet excited state of aminophthalate in aqueous DMSO (~ 5 nsec),¹⁴ the excited states produced in fluorescence must emit from a sodium ion pair distribution largely fixed by the ground-state ion before light absorption (eq 2). On the other hand, the excited states produced chemically emit from an environment determined at the transition-state stage of the reaction, and apparently a lower fraction of ion pairs with sodium results compared to the photoproduced case. Differences of excited states of this type can serve as probes into the nature of the transition states leading to chemically produced excited states.

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Bivalent and Monovalent Rhodium Porphyrin Complexes

Sir:

Although reports of rhodium(III) porphyrin complexes have appeared,¹⁻³ there are no reports on porphyrin complexes of bivalent rhodium. Yoshida and coworkers⁴ have recently reported on rhodium(I) porphyrin complexes, containing one porphyrin bound to two rhodium atoms and formulated as $H^+[(porphyrin)Rh_2(CO)_4Cl]^-$. Lower valent rhodium porphyrin complexes are of particular interest as possible homogeneous catalysts and also for comparison with cobalt(II) porphyrins which are known to reversibly carry oxygen at low temperatures.^{5,6} We wish to report on the synthesis and characterization of rhodium(I) and rhodium(II) porphyrins and their chemical reactivity.

During attempts to synthesize the tetraphenylporphyrin (TPP) complex $Rh(TPP)Cl$ by the method of Fleischer and Sadasivan,² we found that some preparations contained an esr signal other than that attributable to porphyrin impurities. This signal is due to the presence of a rhodium(II) complex $Rh(TPP)$ which we have now obtained in reasonable yield. The rhodium(III) complex, characterized by analysis and visible, ir, and nmr spectroscopy, is isolated in small yield as $Rh(TPP)Cl \cdot H_2O$ when $[Rh(CO)_2Cl]_2$ is refluxed with TPP in glacial acetic acid under nitrogen; most of the rhodium precipitates as metal. If the carbonyl dimer is added slowly to the TPP in refluxing glacial acetic acid, then the major product is a bivalent rhodium complex. For example, 2 g of $[Rh(CO)_2Cl]_2$ was added to a refluxing solution of 3 g of TPP and 5 g of sodium acetate in 500 ml of acetic acid under nitrogen; about 0.5 g of the $Rh(TPP)$ product was obtained after work-up and chromatography on Fluorosil.

The esr spectrum of the $Rh(TPP)$ complex in chloroform at 77°K is shown in Figure 1 and is typical of previously reported esr spectra for a number of rhodium(II) systems.⁷⁻⁹ The signals occur at $g = 2.089, 2.029, 1.990$; at room temperature, the average of the three anisotropic signals is observed at $g = 2.036$.

The magnetic moment, as determined in the solid state by the Gouy method and in solution by an nmr method,¹⁰ was ca. 1.2 BM, but the value is subject to some uncertainty owing to the large diamagnetic correction. The expected moment for a rhodium(II) compound is ca. 2 BM,¹¹ although metal-metal bonding is typical in rhodium(II) compounds,¹²⁻¹⁴ e.g., Rh_2-

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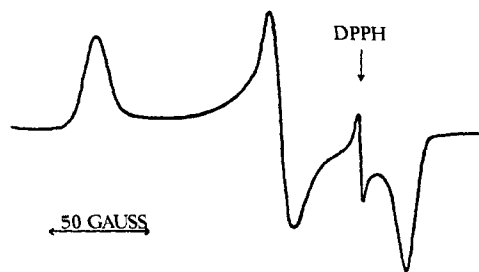


Figure 1. The esr spectrum of $\text{Rh}^{\text{II}}(\text{TPP})$ in chloroform at 77°K .

$(\text{DMG})_4(\text{PPh}_3)_2$ (where DMG is the monoanion of dimethylglyoxime) is diamagnetic;¹³ and low magnetic moments in some phosphine complexes have been attributed¹¹ to metal-metal interactions over 4 \AA . Strong metal-metal interactions along axial positions at first appear unlikely in the tetraphenylporphyrins because of steric restrictions imposed by the phenyl groups,^{15,16} but the possibility that the rhodium is out of the porphyrin plane, allowing a Rh-Rh interaction, cannot be excluded.

The ir of the rhodium(II) complex shows no carbonyl bands. The visible spectrum in chloroform has peaks at 418, 531, 568, and 601 nm. Shifts in the visible spectrum and esr spectrum in coordinating solvents lead us to tentatively assign the species in solution as four coordinate. Analysis of the complex has proved difficult owing to its tendency to retain varying amounts of solvent molecules in the solid state; such behavior is not unusual for metal porphyrins.¹⁷ Molecular weight determination in chloroform indicates a monomeric species.

Stronger evidence for the formulation as a rhodium(II) complex comes from its reaction with hydrogen. In propanol or dimethylformamide (DMF) at 20° , the complex absorbs 0.5 mol of H_2 per Rh to give air-sensitive solutions which yield the diamagnetic rhodium(I) complex, $\text{H}[\text{Rh}(\text{TPP})] \cdot 2\text{H}_2\text{O}$. (Anal. Calcd: C, 70.1; H, 4.4; N, 7.45; O, 4.4; Rh, 13.7. Found: C, 69.14; H, 4.42; N, 7.62; O, 4.70; Rh, 14.18.) The complex contains a titratable proton and has a molar conductance of $16.6 \text{ ohm}^{-1} \text{ cm}^2$ at $5 \times 10^{-4} \text{ M}$ in DMF. Some 1:1 electrolytes of this type have molar conductance values of *ca.* $30 \text{ ohm}^{-1} \text{ cm}^2$ in DMF.¹⁸ The conversion of the rhodium(II) to rhodium(I) and the reverse reaction, readily accomplished by exposure to oxygen, may be followed by changes in conductivity and visible, esr, or nmr spectroscopy; the interconversion by reaction with hydrogen and oxygen has been repeated over several cycles. The change in the visible spectra, showing good isobestic points, is shown in Figure 2. Solutions of the rhodium(I) compound *in vacuo* give no esr signal and give a sharp nmr spectrum consistent with their formulation as a rhodium(I) tetraphenylporphyrin.

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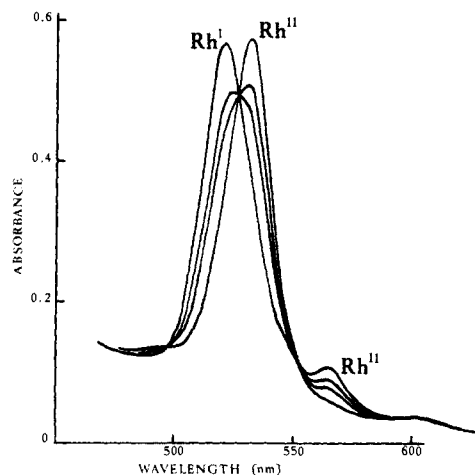
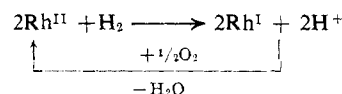


Figure 2. Visible absorption spectra of Rh^{I} and Rh^{II} tetraphenylporphyrin complexes in CHCl_3 (1-cm cell, *ca.* $5 \times 10^{-5} \text{ M}$); intermediate spectra were recorded during oxidation of Rh^{I} using O_2 .

The rhodium(II) compound in DMF catalyzes at ambient conditions the hydrogenation of acetylene, as well as the conversion of hydrogen-oxygen mixtures to water.



No evidence has been obtained for the formation of oxygen complexes by the rhodium(II) tetraphenylporphyrin complex.

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Tris(triphenylphosphine)methyliridium(I). Synthesis, Characterization, and Thermal Decomposition

Sir:

The chemistry of transition metal alkyls continues to be a subject of widespread interest from many points of view. The synthesis,¹⁻⁵ decomposition,^{3,6-8} and inorganic chemistry^{4,7,8} of many transition metal alkyls

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