Hydridorhodium(III) Porphyrin and Porphyrin Rhodium(II) Dimer

Sir:

The chemical behavior of low valent rhodium porphyrins has been reported by two groups.[1,2] When tetraphenylporphine ($TPPH_2$) is used as a square planar ligand, divalent RhTPP has been characterized as a monomeric complex on the basis of magnetic moment and ESR signals, although rhodium(II) complexes tend to form a metal-metal bond.[3-5] A monovalent rhodium complex of $TPPH_2$ was obtainable by reduction of Rh(II)-TPP with H_2 gas and formulated as $H^+[TPPRh^I]^-{\cdot}2H_2O$. We have found that chemical properties of the low valent rhodium complex of the ETIO type porphyrin such as octaethylporphyrin ($OEPH_2$) substituted with alkyl groups at β-positions of pyrroles are notably different from those of the rhodium complex of *meso*-tetraphenylporphine.[2] We wish to report on the results for the rhodium octaethylporphyrin complexes; the first synthesis of the hydridorhodium porphyrin, $OEPRh^{III}$-H, and the dimeric complex formulated as $[OEPRh^{II}]_2$ with Rh-Rh bonding.

The introduction of H_2 gas into a methanol solution of $OEPRh^{III}$-Cl (**1**) resulted in the formation of deep orange precipitates that showed an intense and sharp absorption at 2220 cm^{-1} assignable to the Rh-H stretching vibration in the IR spectrum. When the basic alcoholic solution of $[OEPRh^I]^-$ anion generated by the reduction of **1** with $NaBH_4$ was acidified with acetic acid, the same complex was obtainable in good yield (80%). Upon acidification by using CH_3CO_2D in the latter procedure, a new band due to the Rh-D stretching vibration appears at 1595 cm^{-1}.

$$\begin{tikzcd}
\mathrm{OEP{\cdot}Rh^{III}{\cdot}Cl} \arrow[rr, "H_2"] \arrow[dr, "NaBH_4"'] & & \mathrm{OEP{\cdot}Rh^{III}{\cdot}H} \\
& \mathrm{[OEP{\cdot}Rh^{I}]^-} \arrow[ur, "H^+"'] &
\end{tikzcd}$$

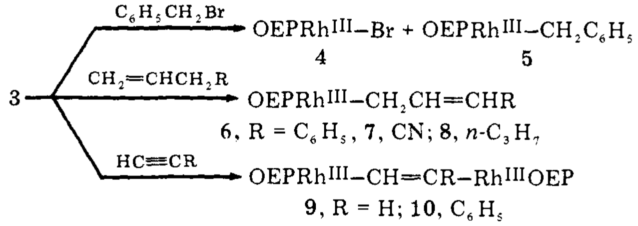
Microanalysis agrees with five-coordinated hydridorhodium(III)-OEP (**2**), mp 280 °C dec. Anal. Calcd for $C_{36}H_{45}N_4Rh$: C, 67.91; H, 7.12; N, 8.80. Found: C, 67.95; H, 7.26; N, 8.74. Complex **2** is sparingly soluble in methanol. When dissolved in benzene, the color of the solution turned from orange to brown. Monitoring spectral change of **2** in benzene indicates that the intensities of the Soret at 397 nm and visible bands at 512 and 543 nm due to **2** simultaneously decrease and the Soret band splits into two bands at 352 and 388 nm with the four isosbestic points at 368, 425, 497, and 553 nm. Recrystallization of the air-sensitive brown solution of toluene under argon afforded violet crystals, **3**, mp > 310 °C. Anal. Calcd for $C_{72}H_{88}N_8Rh_2{\cdot}C_7H_8$: C, 69.59; H, 7.09; N, 8.22. Found: C, 69.88; H, 7.19; N, 8.23. The NMR spectrum of **3** in benzene-d_6 shows the sharp absorptions at τ 0.77 (singlet, meso protons, 8 H), 5.59 (double quartet, methylene protons, 16 H, J_{gem} = 14 Hz), 6.08 (double quartet, methylene protons, 16 H), and 8.32 (triplet, methyl protons, 48 H). The signals due to toluene have also been observed to indicate the inclusion of this molecule in **3**. The IR spectrum of the benzene solution of **3** under degassed condition shows no Rh-H stretching absorption. These findings give evidence to verify the formation of the binuclear complex $[OEPRh^{II}]_2$ from **2**. Concomitant liberation of hydrogen gas was confirmed by GLC analysis of the gas from the reaction vessel (eq 1). H_2 gas was detected when complex **2** was heated at 60-70 °C in toluene for a week in a degassed sealed tube. The electronic spectrum of **3** shows a marked contrast with those of other divalent metalloporphyrins.[6]

$$2OEPRh^{III}\text{-}H \xrightarrow[\text{benzene}]{} [OEPRh^{II}]_2 + H_2 \qquad (1)$$

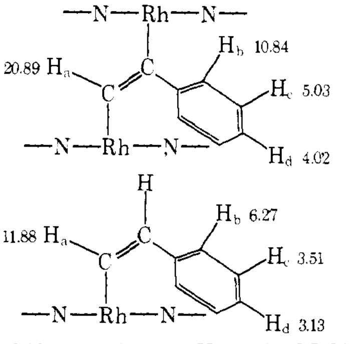
In spite of d^7 rhodium ion, spin pairing of d electrons from two divalent rhodium ions through the metal-metal bonding rationalizes the diamagnetic sharp signals in the NMR spectrum of **3**. Magnetic susceptibility of **3** at 25 °C is determined to be $\chi = -0.65 \times 10^{-6}$ indicating its diamagnetic character. This NMR spectrum resembles that of $[OEPRu^{II}]_2$ in two respects: the methylene protons are diastereotopic and the positions of the chemical shifts are quite similar to those of the dimeric Ru(II) complex.[7] Since the electronic spectrum of **2** is identical with that of alkylrhodium(III)-OEP, the oxidation state of rhodium is considered to be the trivalent.[8] The electron donating groups at the peripheral positions of OEP may increase the electron density of hydrogen atom. Therefore, the Rh-H bond of **2** seems to be more covalent than that of the complex $H^+[TPPRh^I]^-$ reported by James and Stynes.[2]

Hydridocobal(III) oxime and hydridorhod(III) oxime have been prepared and found to form alkylmetal(III) complexes by the reactions with alkyl halides and multiple bonds.[9,10] The formation of dimeric metal(II) complexes from these hydrido complexes has never been reported. The reaction behavior of **3** toward alkyl halides, olefins, and acetylenes has been examined and the results are summarized in Scheme I.

Scheme I. The reactions of $[OEPRh^{II}]_2$ (**3**)



When 100 times the molar amount of organic substrate was added to the 30-mL benzene solution of 100 mg of **3** under argon atmosphere, the reaction was completed within several minutes. Through the same mechanism established for the Co(II) complexes,[11,12] the abstraction of a bromo radical from benzyl bromide and the capture of benzyl radical resulted in the formation of $OEPRh^{III}Br$ (**4**) and $OEPRh^{III}$-$CH_2C_6H_5$ (**5**) in 39 and 26% yield, respectively. Complex **3** reacted rapidly with allylic compounds such as allylbenzene allylcyanide and 1-hexene to give organorhodium complexes **6**, **7**, and **8** in 50-60% yields. The formation of organorhodium(III)-OEP complexes can be explained in terms of the addition of Rh(II) ion to the terminal carbon of the olefin and the elimination of the hydrogen radical from the allylic position with simultaneous migration of the double bond.[13] Treatment of **3** with acetylene and phenylacetylene afforded the bridged complexes **9** and **10**, respectively, in moderate yields.



The chemical shifts (τ value) of H_{a-d} in $CDCl_3$ by using Me_4Si as an internal reference.

The proton chemical shifts of the vinyl (H_a) and phenyl (H_b, H_c, and H_d) protons in the NMR spectrum of **10** appear at much higher magnetic field than those of the β-*cis*-styrylrhodium(III)-OEP complex[8] due to the strong ring current effect from the two porphyrin rings. Complexes **4-10** have been characterized by NMR, IR, and microanalysis. The reaction behavior of **3** toward alkyl halides and acetylenes is quite akin to those of some Co(II) complexes.[11,12,14-16] While the reactions of olefins with divalent cobalt complexes had not given unambiguous results, the generation of a metal–carbon bond has been effected in the case of divalent rhodium porphyrin as noted above. Further studies on the properties of OEPRh(III)–H and $[\mathrm{OEPRh^{II}}]_2$ are in progress.

References and Notes

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(13) In the case of the reaction of **3** with allylbenzene, two organic products with a higher boiling point than allylbenzene were detected from the distillate of the reaction mixture by means of gas chromatography. In addition, hydrogen gas could not be found in the reaction vessel.
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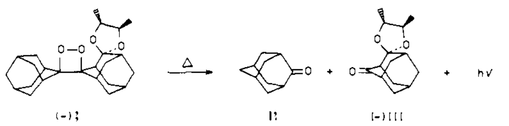
The Detection of Optical Activity in Chemiluminescence

Sir:

We have reported,[1] that the optically active dioxetane (−)-I shows chemiluminescence as a result of the reaction shown:

Scheme **I.** Thermal Decomposition of the Optically Active 1,2-Dioxetane (−)-I



In this equation *hν* represents emission from the ketones II and (−)-III. Since one of the emitting species is chiral, one expects the luminescence of this system to be circularly polarized. We have now succeeded in measuring this circular polarization of luminescence (CPL).

The light induced CPL[2] and chemically induced CPL are obviously closely related, the latter differing—inter alia—in the manner in which the excited state is obtained. When optically active dioxetane (−)-I[1] (4 mg in 1 mL of dodecane) was injected into a specially constructed cell[3a] maintained at a temperature close to 197 °C, light was emitted for about 10 min.

In a series of measurements reproducible data were obtained; some of these are depicted in Figures 1 and 2. Figure 1 shows the chemiluminescence as a function of wavelength.[3b] It appears that the spectrum is characteristic of ketone fluorescence.[2f] Apparently under these experimental conditions phosphorescent processes are effectively quenched. In Figure 2 two curves are shown. Curve A measures the total intensity of the chemiluminescence as a function of time. After injection of the solution at $t = 0$ the intensity grows until thermal equilibrium is reached; afterwards curve A represents the decay curve of the chemiluminescence at temperature T. As expected for the unimolecular decomposition of 1,2-dioxetanes this curve obeys first-order kinetics. The second curve (B) represents the circular anisotropy ΔI of the chemiluminescence as a function of time,[3c] measured in an apparatus described earlier.[4] The nonzero value of ΔI in the chemiluminescence is prima facie evidence for chirality in the emitting species and represents to our knowledge the first measurement of this kind. A useful parameter to describe optical activity in emission is the dissymmetry factor which equals the ratio of $\Delta I = I_L - I_R$ to the average intensity $I = \frac{1}{2}(I_L + I_R)$, i.e., $g_{\mathrm{chemlum}} = \Delta I/I$. From several experiments we find $g_{\mathrm{chemlum}} = +(3 \pm 1) \times 10^{-3}$. Lacking the experimental g_{lum} value for the light-induced CPL of pure (−)-III,[5] an estimated value for the chemically induced CPL may be derived as follows. Previous work[2f] indicates that in a series of ketones g_{lum} is roughly a factor 5 smaller than g_{abs}, the dissymmetry factor in the $n \rightarrow \pi^*$ absorption band.[6] We now make two assumptions: the factor 1/5 also applies to the $g_{\mathrm{lum}}/g_{\mathrm{abs}}$ ratio of ketone (−)-III; and the ratio of excited states of the emitting species II/(−)-III is about 1/1. Based on these assumptions g_{chemlum} is expected to be $\frac{1}{10}g_{\mathrm{abs}} = +4 \times 10^{-3}$. This is in qualitative agreement with the observed value $+(3 \pm 1) \times 10^{-3}$.

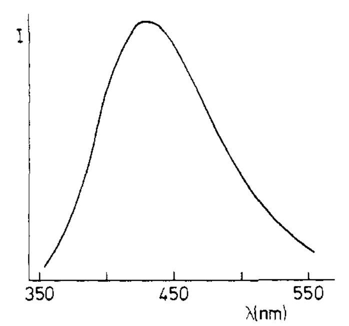


Figure 1. Luminescence spectrum from the thermal decomposition of (−)-I.

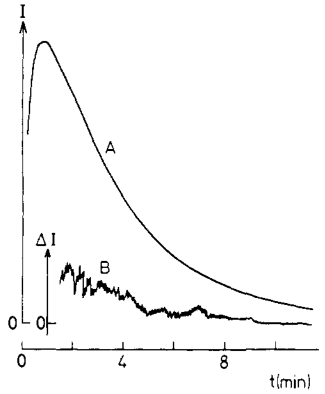


Figure 2. A, Decay curve of chemiluminescence of (−)-I. Intensity in arbitrary units. B, Circular anisotropy, ΔI, of the chemiluminescence as a function of time, ΔI in arbitrary units. Both curves measured over entire band width.

This successful measurement represents only a first step in the investigation of circular polarization of chemiluminescence of this and related systems. It is evident that an area of excited state geometry[2g] and mechanism is now open to study using this new tool. Novel may also be the implication of our observation on model system I to similar phenomena in nature. No mention of the possibility that bioluminescence might be cir-