

Unusual Tautomerism involving Proton Migration between Metal and Pyrrolic Nitrogen in a Hydridorhodium Phthalocyanine Complex

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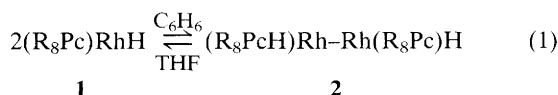
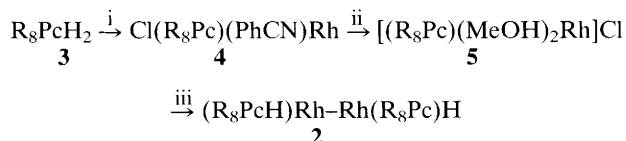
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Hydrido(1,4,8,11,15,18,22,25-octapentylphthalocyanato)rhodium, an unprecedented hydrido metallophthalocyanine, exhibits an unusual tautomerism involving proton migration from rhodium to pyrrolic nitrogen.

In contrast to metalloporphyrins, of which many hydrido complexes have been described,^{1,2} no hydrido complex of any metallophthalocyanine has been reported, even though various alkyl and aryl complexes of metallophthalocyanines³ have been known for some time. We report here the synthesis of hydrido(1,4,8,11,15,18,22,25-octapentylphthalocyanato)rhodium, (R₈Pc)RhH **1**, its unusual tautomerism involving reversible proton migration between the Rh and a pyrrolic nitrogen,⁴ and the reversible formation, from the two tautomers, a 'mixed' dimer, presumably the Rh–Rh bonded hydrido complex (R₈PcH)Rh–Rh(R₈Pc)H **2**.

The synthesis in Scheme 1 gives, instead of the intended product **1**, blue crystals which are best formulated as **2**.[†] Complex **2** may be regarded as a dinuclear complex formed by the heterolytic splitting of H₂ by the Rh–Rh bonded dimer [(R₈Pc)Rh]₂ **6**[‡] with the H[–] ion bonded to a Rh and the H⁺ ion bonded to a pyrrolic nitrogen of the other (R₈Pc)Rh moiety. In [2H₈]THF (THF = tetrahydrofuran), **2** is converted to **1**, exhibiting the expected ¹H NMR spectrum for the

five-coordinate (R₈Pc)RhH with a high-field doublet (δ –34.01, *J*_{RhH} 30.3 Hz).[§] However, in benzene solutions, **2** gives a more complicated ¹H NMR spectrum, the alkyl and aryl region (δ 0–8.5) of which is shown in Fig. 1(A). In addition, there are two broad resonances at δ 10.5 (1H) and –39.1 (1H), which are assigned to the NH and RhH resonances, respectively. These assignments are supported by the ¹H and ²H NMR spectra of deuteriated **2** prepared by substituting D₂ for H₂ in step iii of Scheme 1. The IR spectrum of **2** also indicates the presence of an N–H bond (KBr pellet, ν_{NH} 3373 and ν_{ND} 2478 cm^{–1}), which is maintained in benzene solutions (ν_{NH} 3385 cm^{–1}). Although neither the KBr pellet nor the benzene solution of **2** gives a peak that can be assigned to the Rh–H vibration,⁵ we believe that the blue needle crystals of **2** obtained in Scheme 1 have the proposed dimeric structure, deduced from the IR and the NMR spectra of **2** in benzene. An alternative structure for **2** with the H⁺ ion bonded to a bridge nitrogen instead is incompatible with the ¹H NMR spectra in Fig. 1, which show the presence of four kinds of benzene rings in **2**. The interconversion between **1** and **2** is achieved by changing the solvent, as depicted in eqn. (1).



Scheme 1 Reagents and conditions: i, [Cl(CO)₂Rh]₂, PhCN, 145 °C, 6 h; ii, CHCl₃–MeOH, 25 °C; iii, H₂, n-C₅H₁₁OH, 110 °C

[†] Analytical data for **2**: Found (sample 1): C, 72.9; H, 8.3; N, 9.4; Rh, 6.9. Found (sample 2): C, 73.3; H, 8.2; N, 9.3; Rh, 9.0; Cl, <0.2. Calc.: C, 73.4; H, 8.3; N, 9.5; Rh, 8.7%. Compound **3** was prepared by the method of M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown and A. J. Thomson, *J. Chem. Soc., Chem. Commun.*, 1987, 1086. Compounds **4** and **5** have been characterized by their elemental analyses and by their ¹H NMR spectra.

[‡] Prepared by air oxidation of **2**, and characterized by its elemental analysis and ¹H NMR spectrum.

The variable temperature ¹H NMR spectra of **2** in C₆D₆ are shown in Fig. 1. At 20 °C, there are four resonances in the aromatic region: δ 8.032 (2H), δ 7.743 (4H), δ 7.500 (1H) and δ 7.100 (1H, buried under the C₆H₆ resonance). The δ 7.743 resonance is assigned to the aryl Hs of the (R₈Pc)RhH moiety while the remaining three resonances in the aromatic region are assigned to the (R₈PcH)Rh moiety, which has three types

[§] Additional ¹H NMR data: δ 7.838 (8H, s), 4.567 (16H, m), 2.224 (16H, q), 1.631 (16H, q), 1.410 (16H, sext) and 0.869 (24 H, t). Coordination of a THF molecule as the sixth ligand seems likely. No IR peak for Rh–H vibration is observed in this solution.

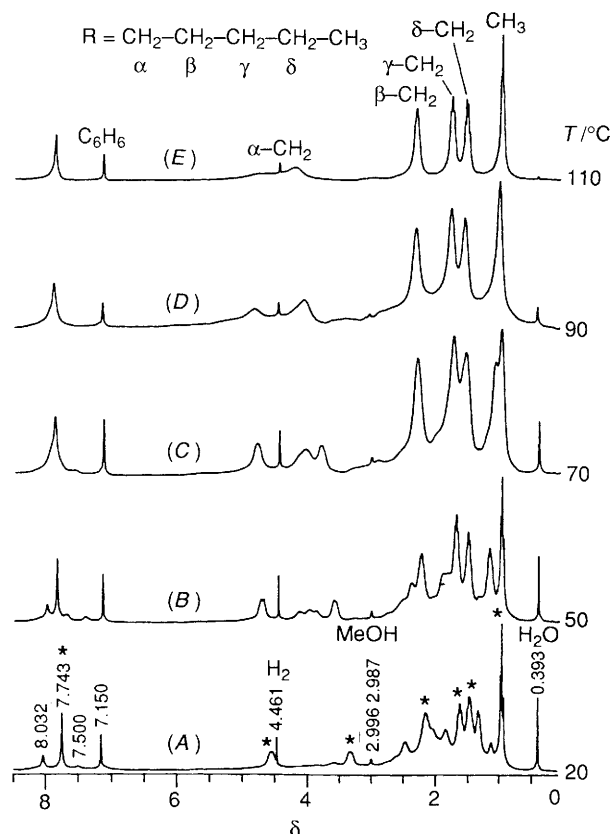


Fig. 1 Selected variable temperature ^1H NMR spectra (300 MHz) of $(\text{R}_8\text{PcH})\text{Rh}-\text{Rh}(\text{R}_8\text{Pc})\text{H}$ **2** in C_6D_6 ($\text{R} = \text{n-pentyl}$, 650 mmHg H_2 added)

of benzene rings with a ratio of 2:1:1. In the alkyl region, there is a set of resonances (marked by asterisks), which account for about half of the alkyl hydrogens and are assigned to the $(\text{R}_8\text{Pc})\text{RhH}$ moiety. The large separation of the resonances of the two diastereotopic H atoms of the $\alpha\text{-CH}_2$ (δ 3.3 and 4.6) is consistent with deshielding of the alkyl protons by two $(\text{R}_8\text{Pc})\text{Rh}$ macrocycles since in all the mononuclear $(\text{R}_8\text{Pc})\text{Rh}$ complexes \parallel that we have synthesized, the separation between the resonances for the two H atoms of $\alpha\text{-CH}_2$ is no greater than 0.2 ppm, while that for the dinuclear **6** is 1.02 ppm. As the temperature is increased, the three aromatic resonances, as well as the alkyl resonances, for $(\text{R}_8\text{PcH})\text{Rh}$ start to coalesce. We attribute these coalescences to migration of the NH proton among the four pyrrolic N atoms. \parallel Consistent with this interpretation, the resonances for $(\text{R}_8\text{Pc})\text{RhH}$ moiety undergo very little change up to 70 °C. At 110 °C, all the alkyl H atoms except the $\alpha\text{-CH}_2$ ones have coalesced to show only one type of pentyl group. We attribute this to the averaging of the alkyl groups in the two $(\text{R}_8\text{Pc})\text{Rh}$ macrocycles by the site exchange between NH and RhH. An alternative structure for **2**, namely, $\text{H}(\text{R}_8\text{PcH})\text{Rh}-\text{Rh}(\text{R}_8\text{Pc})$, in which the H^- and the H^+ ions are on the same $(\text{R}_8\text{Pc})\text{Rh}$ moiety, is ruled out because the NH and RhH site exchange would not have equilibrated the alkyl groups of the two $(\text{R}_8\text{Pc})\text{Rh}$ moieties. The variable temperature ^2H NMR

\parallel In addition to **4** and **5**, the following compounds have been synthesized and will be reported elsewhere: $(\text{R}_8\text{Pc})\text{RhMe}$ and $\text{Cl}(\text{R}_8\text{Pc})(\text{PBu}_3)\text{Rh}$.

\parallel The two resonances at δ 0.39 and 2.99 are assigned to H_2O and MeOH, respectively. Neither of these compounds participated in the exchange process since the linewidth of the δ 0.39 resonance did not change with temperature. Spectrum (A) was regenerated after the solution was cooled to 20 °C. The diminished intensities for H_2O and MeOH resonances at higher temperatures are attributed to their distillation from the solution.

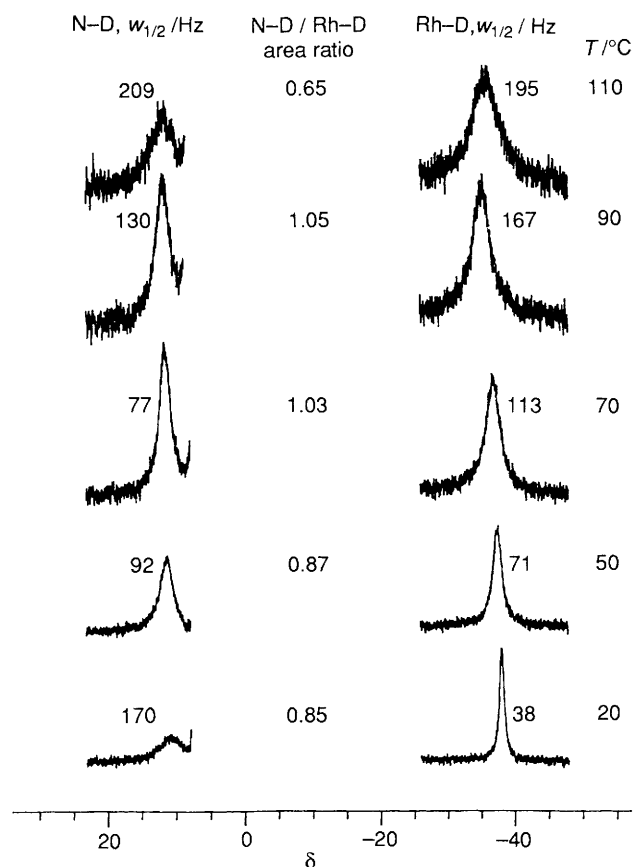


Fig. 2 Selected variable temperature ^2H NMR spectra (46.1 MHz) of $(\text{R}_8\text{PcD})\text{Rh}-\text{Rh}(\text{R}_8\text{Pc})\text{D}$ [$^2\text{H}_2$]-**2** in C_6H_6 ($\text{R} = \text{n-pentyl}$, 650 mmHg D_2 added)

spectra of deuteriated **2** in C_6H_6 (Fig. 2) show that the ND and RhD resonances maintain, within experimental error, a ratio of 1:1 throughout the same temperature range, indicating **1** as a very minor species, if present at all in benzene, under these conditions. The RhD resonance shows continuous broadening, while that of ND first narrows and then broadens as the temperature is increased from 20 to 110 °C. Therefore, there exists a fast exchange process for the NH proton, in addition to its exchange with RhH. We attribute this additional process to rotation about the Rh-Rh bond, \parallel which would equilibrate the conformational isomers, *i.e.*, the eclipsed and the staggered configurations of **2**.

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- Reversible alkyl migration between metal and pyrrolic nitrogens is well known in porphyrin chemistry, but the corresponding proton migration has not been reported. See K. L. Kunze and P. R. Ortiz de Montellano, *J. Am. Chem. Soc.*, 1983, **105**, 1380, and references therein.
- Hydrido complexes that do not show M-H stretching vibrations are well known. See J. J. Levison and S. D. Robinson, *J. Chem. Soc. (A)*, 1970, 96 and references therein.