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## Stable Dodecaphenylporphyrin–Lithium Complexes and their Exchange Reactions

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Stable dodecaphenylporphyrin–lithium complexes are formed at room temperature and the lithium ions of these complexes are replaced easily by other metal ions or organic cations; these lithium complexes can be used as the reagents in the syntheses of various complexes.

Recently, much attention has been devoted to the syntheses of new porphyrins in order to clarify the mechanism of cytochrome P-450 enzyme.<sup>1</sup> We have already synthesized a new class of porphyrins, dodecaphenylporphyrins.<sup>2–4</sup> It has also been reported that the dodeca-substituted porphyrin has several conformations and these conformational variations modulate their redox potentials and light absorption properties.<sup>5</sup> Thus, in order to clarify the properties of dodecaphenylporphyrins, their reactions with metals were studied. Although the usual porphyrin–lithium complex is unstable,<sup>6.7</sup> the dodecaphenylporphyrin–dilithium complex is very stable. In this paper, we report the syntheses and properties of the dodecaphenylporphyrin–dilithium complex.

The dodecaphenylporphyrin–zinc complexes used in this study were synthesized by the reaction of 3,4-diphenylpyrrole,

the corresponding benzaldehyde and zinc acetate in refluxing collidine or acetic acid, and zinc was removed by trifluoroacetic acid–CH<sub>2</sub>Cl<sub>2</sub> system. Three typical dodecaphenylporphyrins **1**, **2** and **3** were used for this study: **1** 5,10,15,20-tetraphenyl-2,3,7,8,12,13,17,18-octaphenylporphyrin, **2** 5,10,15,20-tetra. (*p*-nitrophenyl)-2,3,7,8,12,13,17,18-octaphenylporphyrin and **3** 5,10,15,20-tetra(2',6'-dichlorophenyl)-2,3,7,8,12,13,17,18-octaphenylporphyrin.

The stable dodecaphenylporphyrin-dilithium complex was formed by the reaction of dodecaphenylporphyrin with lithium iodide in methylene chloride. In order to confirm the reactivities with other metals, potassium iodide and sodium iodide were used under the same conditions. However, their complexes of dodecaphenylporphyrin **2** were not formed. The formation reaction of the lithium complex was clarified by



measuring its UV-VIS spectrum. The Soret absorption of dodecaphenylporphyrin 2 in methylene chloride appeared at 474 nm. When lithium iodide was added to this solution, the spectrum changed with time. The intensity of the Soret absorption at 474 nm decreased and the position of Soret absorption shifted to 488 nm and a new peak appeared at 704 nm. The spectra of protonated dication of dodecaphenylporphyrins also showed the peak at about 700 nm. However, the positions and intensities of the Soret absorption and the peak at 704 nm in the spectrum of the lithium complex are different from those of the protonated dication of dodecaphenylporphyrins.8 The formation of dodecaphenylporphyrin 2-dilithium was also confirmed by NMR measurements as shown in Fig. 1. The H NMR spectrum of dodecaphenylporphyrin 2 in  $CD_2Cl_2$  showed two signals from the *p*-nitrophenyl groups at 8 7.60 and 7.75. When lithium iodide was added to this solution, new peaks appeared at  $\delta$  7.95 and 8.20 and four peaks were observed at this time. The intensities of the two peaks at  $\delta$  7.60 and 7.75 decreased while the intensities of new peaks at  $\delta$  7.95 and 8.20 increased with time. Eventually, the peaks of the *p*-nitrophenyl groups ( $\delta$  7.60 and 7.75) and internal hydrogens (NH) of dodecaphenylporphyrin 2 disappeared. Therefore, the new peaks at  $\delta$  7.95 and 8.20 were assigned to the signals from the *p*-nitrophenyl groups of dodecaphenylporphyrin 2-lithium complex.

The lithium complexes of dodecaphenylporphyrins 1 and 3 were also formed easily and the relative initial reaction rates of formation of these lithium complexes were measured. A methanol solution  $(1 \times 10^{-3} \text{ ml})$  of lithium iodide was added to a methylene chloride solution (3 ml) of dodecaphenylporphyrin  $(1 \times 10^{-5} \text{ mol dm}^{-3})$  and the intensity of the Soret absorption of the dodecaphenylporhyrin was measured with time. By using these procedures, the relative ratios of the initial reaction rates were obtained; the ratios of porphyrin 2: porphyrin 1 and porphyrin 3: porphyrin 1 were 0.8 and 0.57, respectively. The slowest reaction rate was found in the reaction of dodecaphenylporphyrin 3 with lithium iodide.

Though the lithium atom is very small and the space of the reaction site of the dodecaphenylporphyrin is large, the reaction rate depends on the steric and electronic effect of the substituents at the *meso* position of dodecaphenylporphyrin. This suggests that a change in the conformation of the porphyrin skeleton occurs with the formation of the lithium complex. After the formation of the dodecaphenylporphyrin **2**-lithium complex, evaporation of the solvent gave needle-type crystals. This solid complex is very air-stable, even when kept for a long time. Elemental analyses (C, H, N) of this crystal indicate that the ratio of dodecaphenylporphyrin **2**: lithium in this complex is 1:2, and mass spectroscopy data support this characterization. The fact that the complex is not moisture sensitive under air is a remarkable result.

As this complex is very stable, it is possible that it could be

J. CHEM. SOC., CHEM. COMMUN., 1992



**Fig. 1** NMR (270 MHz) spectra after the addition of LiI solution to the  $CD_2Cl_2$  solution of dodecaphenylporphyrin **2**. (*a*) After 5 min. (*b*) after 30 min and (*c*) after 60 min. Dodecaphenylporphyrin **2** (7.1 ×  $10^{-6}$  mol) was dissolved in  $CD_2Cl_2$  (1 ml). Lithium iodide (3.55 ×  $10^{-5}$  mol) was added to the mixture of  $CD_2Cl_2$  (0.5 ml) and  $CD_3OD$  (0.1 ml), and this solution was mixed and centrifuged to remove the remaining undissolved lithium iodide. The solution of lithium iodide was added to the solution of dodecaphenylporphyrin **2** and then, NMR measurements were performed.

used as a reagent in the syntheses of other porphyrin derivatives. Thus, exchange reactions by other transition metals were performed. When cobalt acetate was added to a methanol solution of the dodecaphenylporphyrin **2**-dilithium complex, the colour of the solution changed immediately. The Soret band shifted from 498 to 474 nm. In order to confirm the product, the dodecaphenylporphyrin **2**-cobalt complex was prepared using the literature method.<sup>7</sup> The UV-VIS spectrum of the cobalt complex was the same as that from the exchange reaction. Copper, nickel and iron complexes of the dodecaphenylporphyrins can be easily obtained by a similar exchange

reaction. This method can be used to obtain a variety of metal complexes of dodecaphenylporphyrin **2**.<sup>†</sup>

The reactivity of dodecaphenylporphyrin 2–dilithium complex is very high as described above. Accordingly, it must be possible to develop the reaction with other cations. This method was applied to the reaction of dodecaphenylporphyrin 2–dilithium complex (488 nm,  $\varepsilon = 8.11 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) with a quaternary ammonium salt. When cetyltrimethylammonium chloride was added to a CH<sub>2</sub>Cl<sub>2</sub> solution of the dodecaphenylporphyrin 2–dilithium complex, the Soret band shifted from 488 to 505 nm and its intensity increased immediately. After removal of the solvent and purification by recrystallization, elemental analyses were performed. This indicated that the ratio of dodecaphenylporphyrin 2: cetyltrimethylammonium in the new complex (505 nm,  $\varepsilon = 1.03 \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) was 1:2.

As described above, although the dodecaphenylporphyrindilithium complex is very stable under air, its reactivity is high enough for the exchange reaction to occur, and this complex can be used as a reagent in the syntheses of various porphyrin complexes. One of the reasons that dodecaphenylporphyrins have these remarkable properties could be the conformational effect, which is produced by steric hinderance between *meso*and  $\beta$ -phenyl groups.

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<sup>&</sup>lt;sup>†</sup> After the addition of methanol soultion of cobalt acetate  $(1 \times 10^{-3} \text{ mol } \text{dm}^{-3})$ , the reaction of dodecaphenylporphyrin 2-dilithium complex in methylene chloride  $(1 \times 10^{-5} \text{ mol } \text{dm}^{-3})$  with cobalt acetate finished immediately. However, the reaction of dodecaphenylporphyrin 2 with cobalt acetate took 1 h to reach completion under the same conditions. The reactivities of the dodecaphenylporphyrins with metals depend on the substituents at the *meso* position of the dodecaphenylporphyrin.