© 2001 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 74, 739—746 (2001)

Synthesis of New Diaryl-Substituted Triple-Decker and Tetraaryl-substituted Double-Decker Lanthanum(III) Porphyrins and Their Porphyrin Ring Rotational Speed as Compared with that of Double-Decker Cerium(IV) Porphyrins

Masato Ikeda, Masayuki Takeuchi, Seiji Shinkai,* Fumito Tani,† and Yoshinori Naruta†

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581

†Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Fukuoka 812-8581

(Received September 28, 2000)

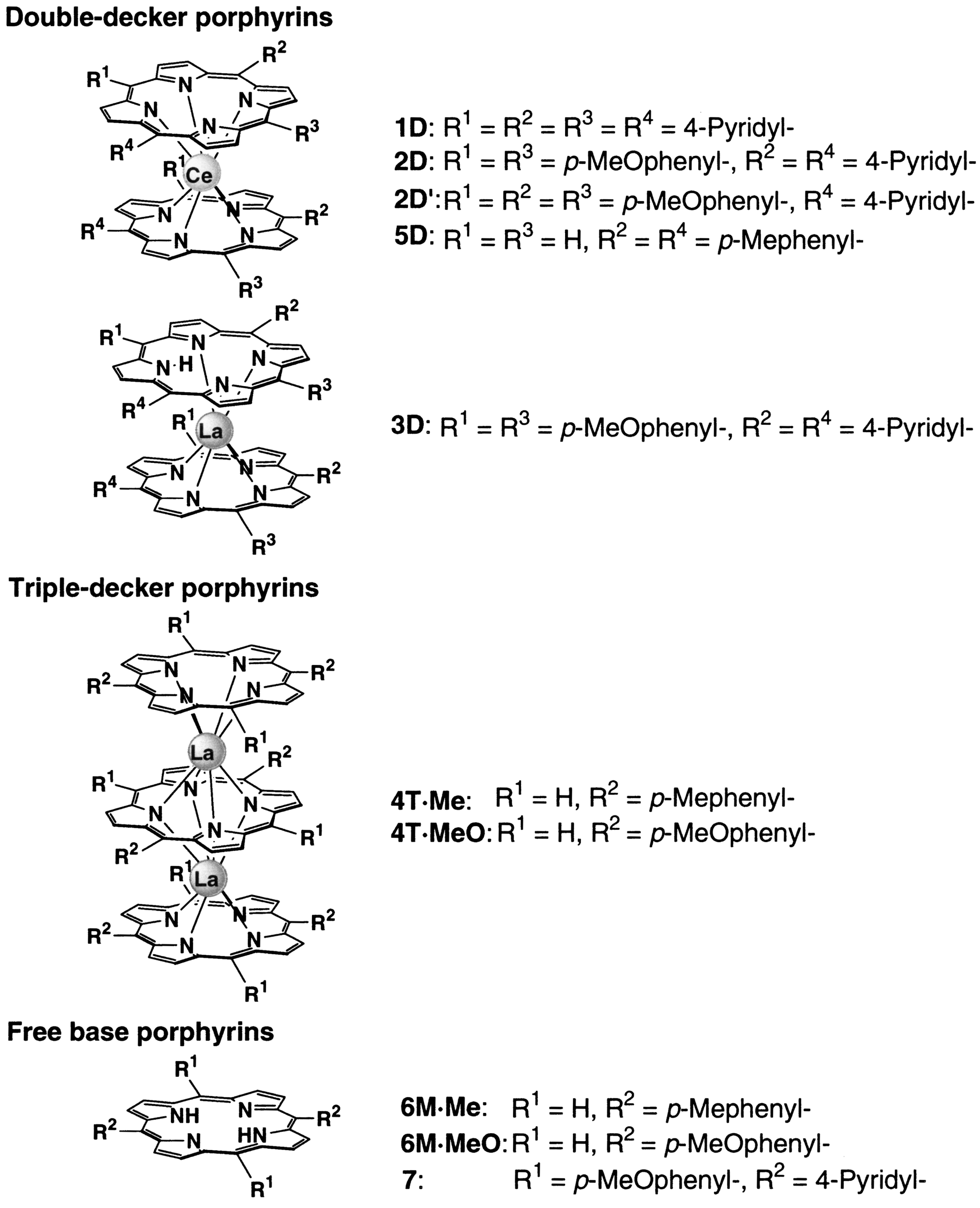
Tetraaryl-substituted cerium(IV) double-decker porphyrin (**2D**), tetraaryl-substituted lanthanum(III) double-decker porphyrin (**3D**), and diaryl-substituted lanthanum(III) triple-decker porphyrins (**4T•Me** and **4T•MeO**) were newly synthesized and their porphyrin ring rotation rates were systematically estimated by means of a VT NMR spectroscopic method. In **2D** the coalescence temperature (T_c) for the porphyrin ring rotation was higher than 110 °C, whereas in **3D** it appeared at ca. 0 °C. In diaryl-substituted cerium(IV) double-decker porphyrin (**5D**) it appeared at 13 °C whereas in **4T•Me** and **4T•MeO** they were lower than −80 °C. These results consistently support the view that the porphyrin ring rotation rates in lanthanum(III)-based porphyrins are much faster than those in cerium(IV)-based porphyrins. The difference is reasonably explained by the difference in the ion size between these two metal ions. Since these sandwich-type porphyrins can act as novel scaffolds for designing positive allosteric recognition systems, La(III) complexes which feature the faster porphyrin ring rotation should be useful to develop more efficient positive allosteric systems.

Positive and negative allosteric effects are seen throughout nature where biological events must be efficiently regulated in response to chemical or physical signals from the outside world. The biomimetic design of such allosteric systems is of great significance in order to efficiently regulate the complexation ability or the catalytic activity of artificial receptors according to an allosteric manner.[1–10] Furthermore, this methodology is very useful to amplify and convert weak chemical or physical signals into other signals which are convenient for us to read out and record. It is known, however, that among them design of a homotropic positive allosterism, in which the same guest metals or molecules are bound autoacceleratively to the host is extremely important but extremely difficult.[9] We previously found that a porphyrin-based bis(porphyrinato)cerium(IV) double-decker **1D** shows a unique homotropic positive allosterism.[11] In this system, the binding event of the first dicarboxylic acid guest to a pair of pyridyl groups can suppress the rotation of the two porphyrin planes without inducing a plane inclination;[12] the subsequent binding of the three dicarboxylic acid guests to the remaining three pairs of pyridyl groups can then occur cooperatively.[11] This novel recognition system is now being extended to memory storage systems,[12,13] metal scavenging systems,[14,15] sugar binding systems,[16] etc. However, the rotational rate of these porphyrin planes, which plays a crucial role in the allosterism, frequently lies between the NMR time-scale and the human time-scale[13,17] and the quantitative estimation has been very difficult.

To obtain an insight into a quantitative correlation between the porphyrin ring rotational rate and *meso*-substituents or sandwiched metals, we newly synthesized tetraaryl-substituted cerium(IV) double-decker porphyrin **2D**, tetraaryl-substituted lanthanum(III) double-decker porphyrin **3D**, and diaryl-substituted lanthanum(III) triple-decker porphyrins **4T•Me** and **4T•MeO** and compared their porphyrin ring rotational rates with those of a known compound, diaryl-substituted cerium(IV) double-decker porphyrin **5D** (Chart 1).[18] We have found that the rotational rate is deeply associated not only with *meso*-aryl substituents and sandwiched metals but also with a protonation-deprotonation equilibrium in **3D**.

Results and Discussion

It is known that Ce(IV) forms double-decker porphyrins bearing *meso*-aryl substituents such as **2D**, **2D′**, and **5D**.[19] La(III) can also form a similar double-decker structure with porphyrins bearing four meso-aryl substituents, but four nitrogens in one porphyrin coordinate to La(III), whereas in another porpyrin three nitrogen coordinates to La(III) but another nitrogen remains uncoordinated as NH. One can thus compare the influence of central metals between Ce(IV) and La(III) on the porphyrin ring rotational rate, taking this uncoordinated NH group into consideration. On the other hand, La(III) tends to form the 2:3 La(III)/porphyrin triple-decker with *meso*-unsubstituted porphyrins (e.g., octaethylporphyrin).[20] These complicated situations make it difficult to directly estimate the influence of *meso*-substituents on the porphyrin rotational rate between Ce(IV) and La(III) complexes. It thus occurred to us that if one can synthesize a Ce(IV) double-decker and La(III) triple-decker from the same porphyrin, one may obtain an in-



1D: $R^1 = R^2 = R^3 = R^4$ = 4-Pyridyl-
2D: $R^1 = R^3$ = *p*-MeOphenyl-, $R^2 = R^4$ = 4-Pyridyl-
2D': $R^1 = R^2 = R^3$ = *p*-MeOphenyl-, R^4 = 4-Pyridyl-
5D: $R^1 = R^3$ = H, $R^2 = R^4$ = *p*-Mephenyl-

3D: $R^1 = R^3$ = *p*-MeOphenyl-, $R^2 = R^4$ = 4-Pyridyl-

4T·Me: R^1 = H, R^2 = *p*-Mephenyl-
4T·MeO: R^1 = H, R^2 = *p*-MeOphenyl-

6M·Me: R^1 = H, R^2 = *p*-Mephenyl-
6M·MeO: R^1 = H, R^2 = *p*-MeOphenyl-
7: R^1 = *p*-MeOphenyl-, R^2 = 4-Pyridyl-

Chart 1.

sight into the basic difference between Ce(IV) and La(III) and that between double-decker and triple-decker structures. With this object in mind, we newly synthesized La(III)-based triple-deckers **4T•Me** and **4T•MeO** in addition to Ce(IV)-based double-decker **5D**[18] from the same (for **4T•Me**) or similar (for **4T•MeO**) diaryl-substituted porphyrins and compared their dynamic spectral properties with those of more sterically-crowded tetraaryl-substituted double-deckers **2D** and **3D**. We have found on the basis of VT NMR measurements that the porphyrin rotational rate is very different between La(III) complexes and Ce(IV) complexes.

Synthesis of 4T•Me and 4T•MeO. The time course of the reaction between $[La(acac)_3]\bullet nH_2O$ and 5,10-bis(*p*-methoxyphenyl)porphyrin (**6M•MeO**) was monitored by GPC and MALDI TOF MS. The typical GPC chromatogram (after 1 h) is shown in Fig. 1. The measurements of MALDI TOF MS established that they are assignable to **6M•MeO** (retention time 40.2 min: *m*/*z* 522.60), La(III) double-decker (retention time 37.2 min: *m*/*z* 1179.29), and La(III) triple-decker **4T•MeO** (retention time 35.8 min: *m*/*z* 1838.38). The peak areas for each peak are plotted against the reaction time in Fig. 2. It is seen from Fig. 2 that even through a considerable amount of **4T•MeO** is already yielded, a significant amount of unreacted **6M•MeO** still remains. In contrast, the concentration of La(III) double-decker is always low. The results imply that the formation of La(III) double-decker from **6M•MeO** is slow, but once La(III) double-decker is yielded, the subsequent reaction to **4T•MeO** readily takes place. The similar time-dependence was also observed for the reaction of $[La(acac)_3]\bullet nH_2O$ with **6M•Me** to yield **4T•Me**. Presumably, the NH group remaining in La(III) double-decker interacts with La(III) and the activated NH group facilitates the reaction with second La(III). This energetic reaction course makes it difficult to isolate La(III) double-decker porphyrins formed from less sterically-

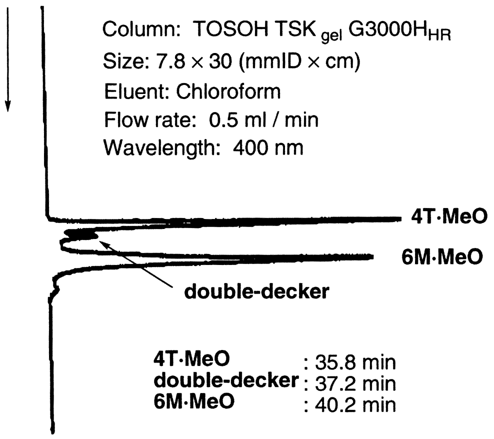


Fig. 1. GPC chromatogram after 1 h for the reaction mixture of $[La(acac)_3]•nH_2O$ and **6M•MeO**: for details of the reaction conditions see Experimental.

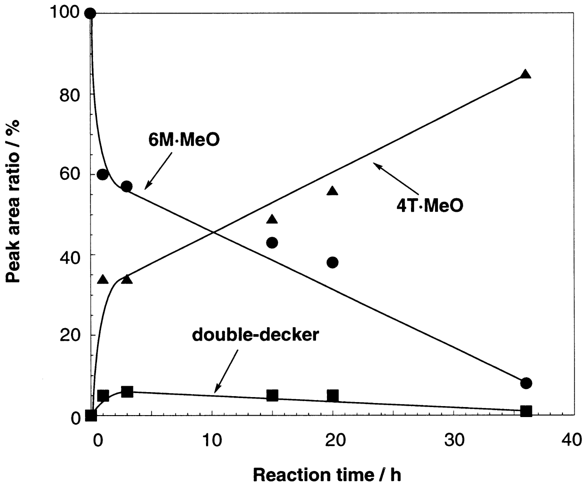


Fig. 2. Time cource of the reaction between $[La(acac)_3]•nH_2O$ and **6M•MeO**.

crowded porphyrins. In tetraaryl-substituted porphyrins, however, the energetically-favorable reaction with second La(III) is suppressed by unfavorable steric crowding among aryl groups. This balance governs the relative stability between double-decker porphyrins and triple-decker porphyrins in the La(III) complexes.

Rotational Rates of Ce(IV) Double-Decker Porphyrin 5D vs. La(III) Triple-Decker Porphyrins 4T•Me and 4T•MeO. The absorption spectrum of **4T•MeO** is compared with that of **6M•MeO** in Fig. 3. The most distinct differences between these two spectra are a shift of the Soret band to shorter wavelength (410 nm for **6M•MeO** and 396 nm for **4T•MeO**) and a broadening effect of the Q bands observed for **4T•MeO**. Similar phenomena were also observed for other La(III) double- and triple-deckers and were attributed to a face-to-face-type interaction of porphyrin π-systems.[20,21] However, the blue shift of the Soret band for **4T•MeO** is smaller than that for **5D** (384 nm) consisting of the same porphyrin skeletons.[18] The difference could suggest that the porphyrin-porphyrin distance in **4T•MeO** is somewhat longer than that in **5D**.

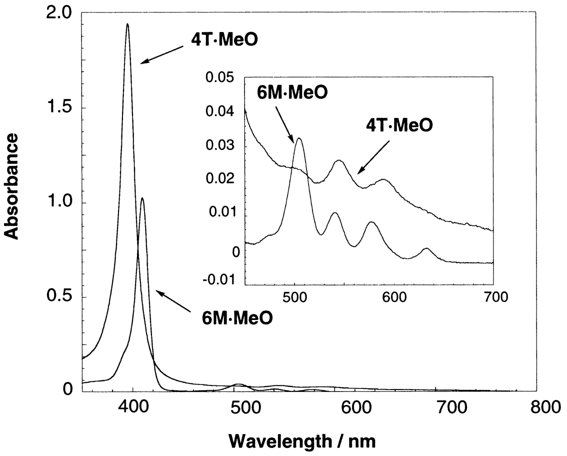


Fig. 3. Absorption spectra of **4T•MeO** (3.3×10^{-5} mol dm^{-3}) and **6M•MeO** (3.3×10^{-5} mol dm^{-3}) in dichloromethane at 25 °C.

For VT ^1H NMR spectra of double- and triple-decker porphyrins, one may expect two coalescence temperatures (T_c) arising from two different molecular motions, that is, the rotation of *meso*-aryl groups and that of porphyrin planes. The VT ^1H NMR spectra for **4T•MeO** are shown in Fig. 4. The signals were assigned with assistance of 2D-COSY and NOESY spectroscopies. The *p*-MeO groups (and also *p*-Me groups in **4T•Me**) were introduced in order to simplify the peak splitting pattern in phenyl proton region. Owing to this molecular design, three pairs of different *o*- and *m*-phenyl proton peaks appear separately at −40 °C: in the order of the chemical shift (from high to low magnetic field) they are assigned to *exo o*- and *m*-phenyl protons in the outer porphyrins (peaks a and b, respectively), *endo o*- and *m*-phenyl protons in the outer porphyrins (peaks c and h, respectively), and *o*- and *m*-phenyl protons in the inner porphyrin (peaks k and j, respectively). The consistent trend that the *o*-phenyl proton peaks appear at higher magnetic field than the *m*-phenyl proton peaks is explained in terms of the larger shielding effect of the porphyrin π-systems on the *o*-phenyl protons. The fact that peaks a and b appear at a particularly high magnetic field is associated with the out-warped planes of the outer porphyrins:[19–21] in this characteristic porphyrin structure, the *o*- and *m*-phenyl protons reside on the porphyrin-based shielding region.

With the increase in the measurement temperature, peaks a and h and peaks b and c gradually coalesce and apparently disappear at 60 °C. Such a finding shows that the T_c for the rotation of the *p*-methoxyphenyl substituents in the outer porphyrins exists at 60 °C. According to the Gutowsky and Holm equation,[22] this T_c corresponds to the interconversion rate (k_c) of 830 s^{-1}. The *p*-methoxyphenyl substituents in the inner porphyrin should have a rotational rate different from that in the outer porphyrins. However, it cannot be estimated from the VT ^1H NMR spectra because of their symmetrical structure. Similar results were also obtained by the VT ^1H NMR spectra (400 MHz) of **4T•Me** (the spectra are not shown herein): the *o*- and *m*-phenyl proton peaks in the outer porphyrins coalesce at 60 °C, which corresponds to $k_c = 840\ s^{-1}$.

The rotation of the porphyrin planes can be monitored by a

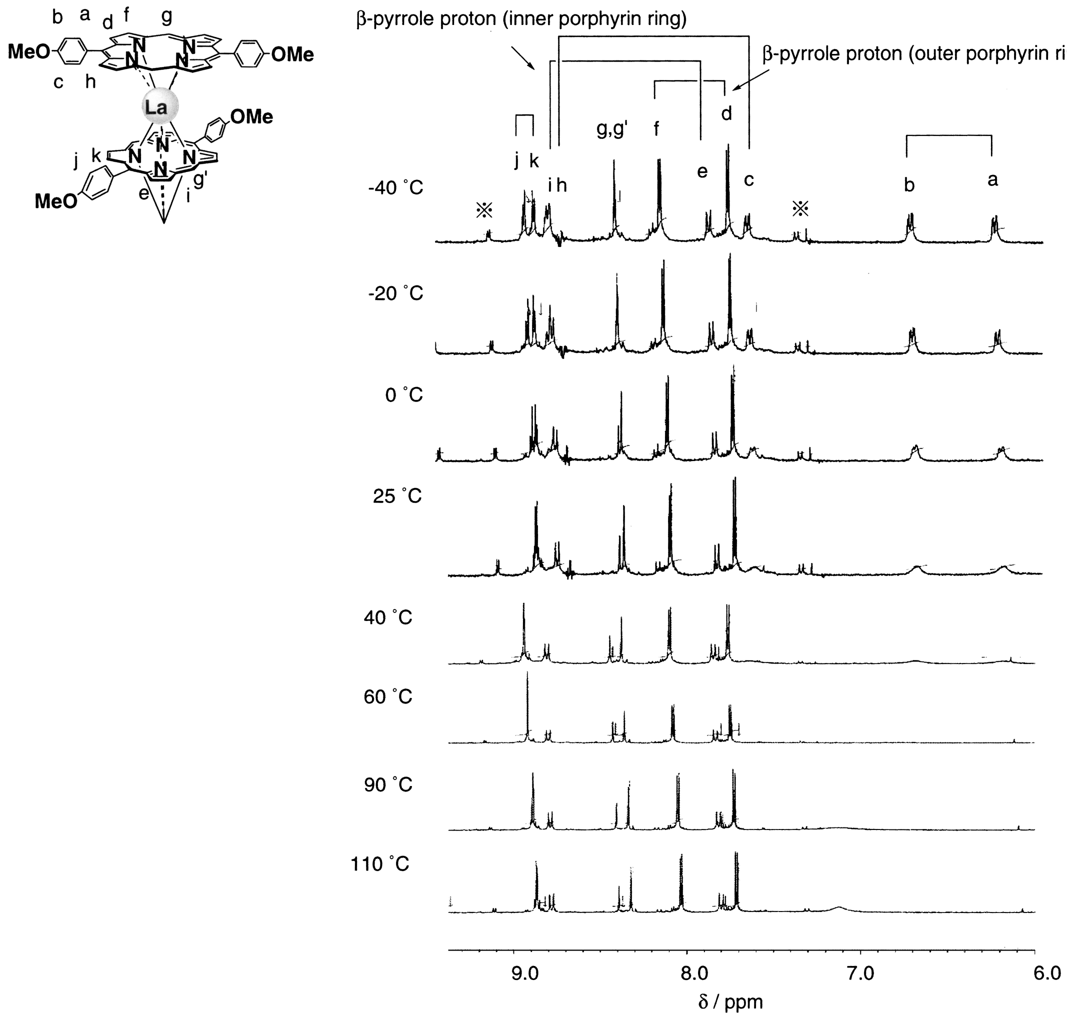


Fig. 4. VT ^{1}H NMR 400 MHz spectra of **4T•MeO** (1.5 mmol dm^{-3}) in CD_2Cl_2 (−40–25 °C) or $CDCl_2CDCl_2$ (40–110 °C) (The lines connect the spin-coupled signals).

change in the *β*-pyrrole proton peaks.[17,18] As seen in Fig. 4, however, the splitting patterns for the *β*-pyrrole protons in both outer porphyrins and inner porphyrin are very simple, averaged ones, which are scarcely changed at −40–110 °C. The results support the view that the rotational rate of the porphyrins is faster than the ^{1}H NMR (400 MHz) time-scale. Expecting the peak splitting of the *β*-pyrrole proton peaks, we repeated the measurements using a 600 MHz ^{1}H NMR apparatus at −80–20 °C but could not find any significant difference in the spectral pattern (the spectra are not shown herein). Similarly, no peak splitting of the *β*-pyrrole protons was recognized for **4T•Me** at −80–110 °C. One can regard, therefore, that the *T*c values are still lower than −80 °C (Table 1). It is known that in tetraaryl-substituted Ce(IV) double-decker porphyrins the por-

Table 1. Rotation of Meso-Aryl Groups and Porphyrin Rings

		T_c (NMR, k_c)	
Porphyrins	Solvents[a)]	Rotation of meso-aryl groups[b)]	Rotation of porphyrin rings
2D	A	60 °C (600 MHz, 1170 s^{-1})	> 110 °C (600 MHz)
2D′[c)]	A	60 °C (400 MHz, 760 s^{-1})	> 150 °C (400 MHz)
3D	B	peaks not identified	ca. 0 °C (600 MHz)
3D$^-$	C	ca. 25 °C (600 MHz, 840 s^{-1})	25 °C (600 MHz, 110 s^{-1})
5D[d)]	D	data not shown	13 °C (270 MHz, 80 s^{-1})
4T•Me	A	60 °C (400 MHz, 840 s^{-1})	< −80 °C (600 MHz)
4T•MeO	A	60 °C (400 MHz, 830 s^{-1})	< −80 °C (600 MHz)

a) A: CD_2Cl_2 (−80–25 °C), $(CDCl_2)_2$ (25–110 °C), DMSO-d_6 (90–150 °C), B: $CDCl_3$, C: $CDCl_3$–Pyridine-d_5 (1 :1 v/v)), D: Toluene-d_6. b) From the coalescence of *o*-proton in aryl groups(pyridine groups for **2D**, **2D′**, and **3D**). c) Data from Ref. 21. d) Data from Ref. 22.

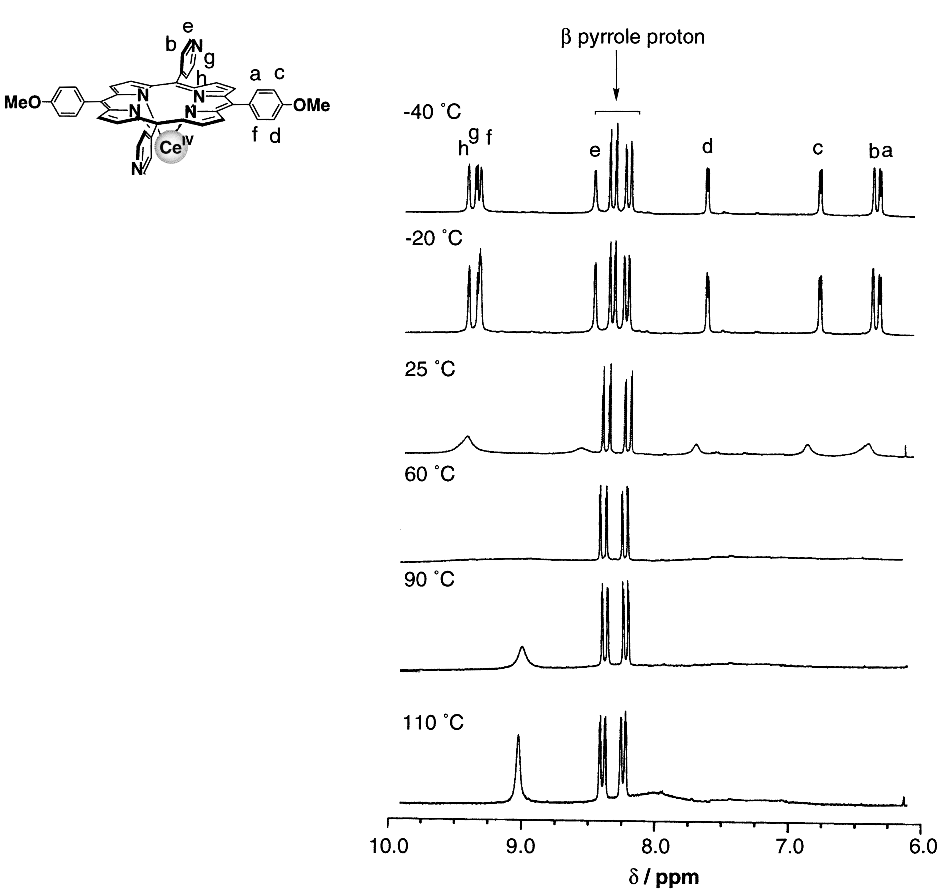


Fig. 5. VT ^{1}H NMR (600 MHz) spectra of **2D** (1.0 mmol dm^{-3}) in CD_2Cl_2 (−40–25 °C) or $CDCl_2CDCl_2$ (40–110 °C).

phyrin do rotate but the rate is much slower than the ^{1}H NMR time-scale.[12,13,17,18] One may thus expect that in sterically less-crowded diaryl-substituted Ce(IV) double-decker porphyrins the rotational rate becomes closer to the ^{1}H NMR time-scale. In fact, Aida et al.[18] proposed the T_c = 13 °C (270 MHz, k_c = 80 s^{-1}) for the porphyrin ring rotation of **5D** (Table 1). Since triple-decker porphyrins should be sterically more crowded than double-decker porphyrins, the facile porphyrin ring rotation in **4T•Me** and **4T•MeO** can be ascribed to the nature of sandwiched La(III) ions. Such results suggest that the porphyrin-porphyrin distance in La(III) triple-decker porphyrins is longer than that in Ce(IV) double-decker porphyrins.[23] This trend is consistent with the finding that the shift of the Soret band is smaller in La(III) triple-decker porphyrins than in Ce(IV) double-decker porphyrins (*vide supra*).

Rotational Rates of Ce(IV) Double-Decker Porphyrin 2D vs. La(III) Double-Decker Porphyrin 3D. We previously examined the VT ^{1}H NMR spectra of tetraaryl(one 4-pyridyl and three *p*-methoxyphenyl)-substituted Ce(IV) double-decker porphyrin **2D′**.[17] Although the T_c for the aryl substituents were recognized at 60 °C (400 MHz, k_c = 760 s^{-1}), the *β*-pyrrole proton peaks were finely split and unaffected up to 150 °C.[21] The results indicate that the rate of the porphyrin ring rotation is much slower than the ^{1}H NMR time-scale. The VT ^{1}H NMR spectra of **2D** bearing two 4-pyridyl and two *p*-methoxyphenyl substituents are shown in Fig. 5. The T_c for the rotation of the *meso*-aryl substituents was recognized at 60 °C (600 MHz ^{1}H NMR), but the coalescence of the *β*-pyrrole proton peaks was not observed up to 110 °C (600 MHz ^{1}H NMR). One can reconfirm from such results that the porphyrin rings in **2D** and **2D′** rotate at rates much slower than the ^{1}H NMR time-scale.[11,12,17,18]

Here, we compare the rotational rate of porphyrin rings between **2D** and **3D** in order to obtain an insight into the difference between Ce(IV) and La(III). To do this experiment quantitatively one has to estimate the dissociation state of **3D**. As shown in Fig. 6, the absorption maximum of the Soret band of

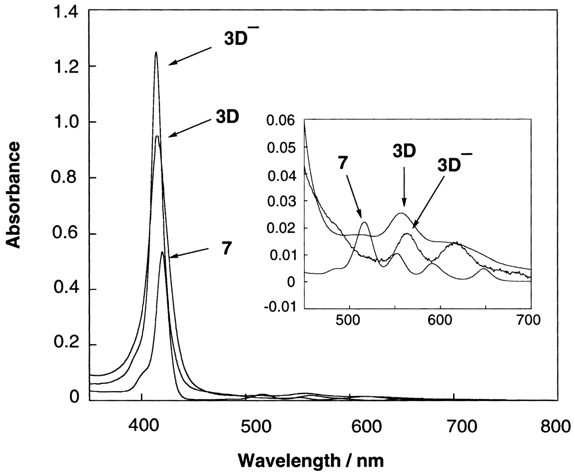


Fig. 6. Absorption spectra of **3D** and **7** (1.0×10^{-5} mol dm^{-3}) at 25 °C.

3D (in chloroform) shifts to shorter wavelength (417 nm) from that of 5,15-bis(*p*-methoxyphenyl)-10,20-di(4-pyridyl) porphyrin **7** (421 nm). Addition of pyridine induced a further shift of the absorption maximum to 415 nm and an increase in the extinction coefficient. These changes are attributed to dissociation of the NH group in **3D** to the N^- group in **3D**$^-$. In Fig. 7 the absorbance at 415 nm is plotted against the concentration of added pyridine. It is seen from Fig. 7 that the spectral change is saturated above 40 vol% pyridine. Furthermore, **3D**$^-$ has two Q bands at 563 nm and 614 nm whereas **3D** only displays a peak at 563 nm. Similar behavior is observed for protonated forms of bis(porphyrinato)lanthanum(III).[21] Therefore the Q band observed above 600 nm is typical for the anion in the porphyrin rings. We thus collected the spectral data for **3D**$^-$ in a mixed solvent of chloroform:pyridine = 1:1 (v/v).

The VT ^{1}H NMR spectra of **3D** and **3D**$^-$ are shown in Fig. 8. One can readily notice that the spectra for **3D**$^-$ are much simpler, reflecting the more symmetrical structure of **3D**$^-$ relative to that of **3D**. It is also seen from Fig. 8 that in **3D**$^-$ there are only two inequivalent *β*-pyrrole protons as in a structurally-equivalent Ce(IV) double-decker porphyrin **2D**, whereas in **3D** there are four inequivalent protons. Obviously, this inequivalence in **3D** is due to the NH group being present only in one porphyrin ring. One may conclude, therefore, that although prototropy can take place among four nitrogens in two porphyrins, the exchange rate is slower than the ^{1}H NMR timescale. The concerned *β*-pyrrole proton peaks for **3D**$^-$ are broadened with the temperature drop and decoalesce at 25 °C (Fig. 8B). The T_c for the *β*-pyrrole proton peaks in **3D** could not be estimated precisely because of the complexity of the ^{1}H NMR spectra. Figure 8A shows, however, that above 5 °C four inequivalent *β*-pyrrole proton peaks can separately be recognized. This means that the T_c exists below 5 °C (at ca. 0 °C). The difference supports the view that the porphyrin rings in monoprotonated **3D** rotate much faster than symmetrical, deprotonated **3D**$^-$. Although the rotation of the *meso*-aryl substituents cannot be evaluated precisely because of the complexity and the serious overlap with other peaks, the T_c is approximately estimated to be ca. 25 °C from the spectral shape change.

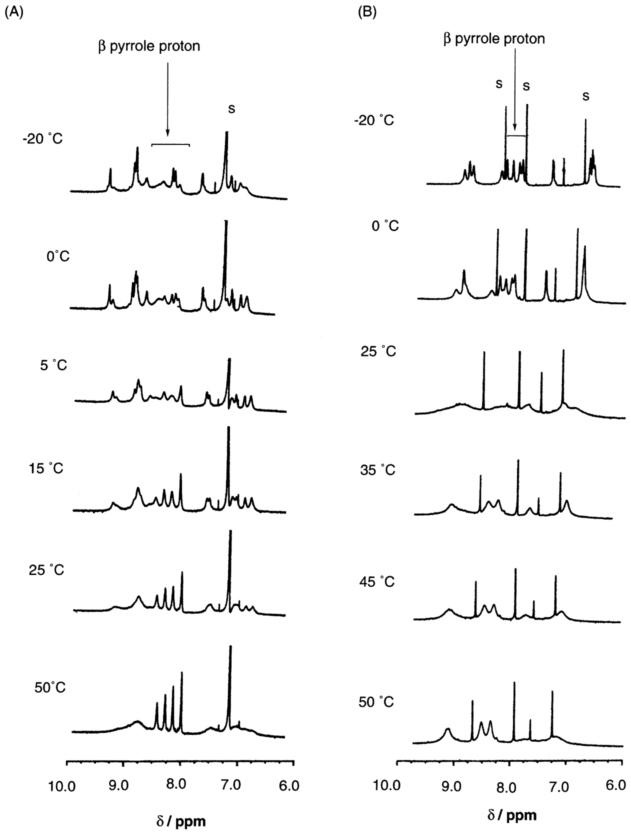


Fig. 8. VT ^{1}H NMR (600 MHz) spectra of (*A*) **3D** (1.0 mmol dm^{-3}) in $CDCl_3$ and (B) **3D**$^-$ (1.0 mmol dm^{-3}) in $CDCl_3$:pyridine-d_5 = 1:1 (v/v) (s; solvent).

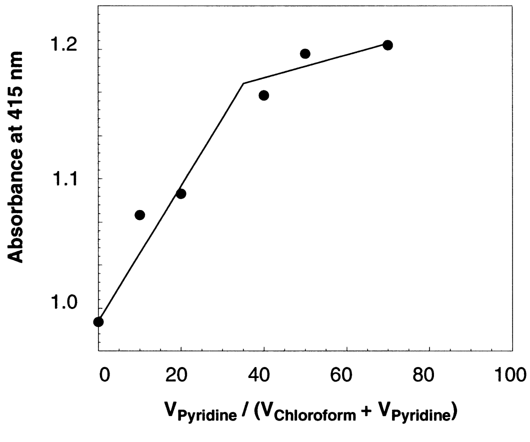


Fig. 7. Plot of A_{415} of **3D** vs. pyridine vol%.

The porphyrin ring rotational mode of **3D**$^-$ may be compared with that of a structurally-equivalent **2D** as a basis for the discussion on the difference between Ce(IV) and La(III). We previously investigated **2D′**, from which we obtained T_c = 60 °C for the *meso*-aryl substituents rotation and T_c > 150 °C for the porphyrin rings rotation. We obtained the similar coalescence temperatures for **2D** (see Table 1). The T_c values for the *meso*-aryl substituents rotation and the porphyrin rings rotation in **3D**$^-$ are ca. 25 °C and 25 °C, respectively: the difference establishes, here again, that the porphyrin rings in La(III) double-deckers can rotate faster than those in Ce(IV) double-deckers.

Conclusions

The foregoing results consistently indicate that regardless of either double-deckers or triple-deckers, the porphyrin rings rotation of La(III) complexes is much faster than that of Ce(IV) complexes, whereas the *meso*-aryl substituents rotation is not much different between Ce(IV) and La(III) complexes. The difference in the porphyrin rings rotation is reasonably explained by the difference in the ionic radii between Ce(IV) (97 pm) and La(III) (118 pm) for the coordination number of 8. The novel finding suggests that as a scaffold for designing positive allosteric systems, La(III) complexes should be superior to Ce(IV) complexes because the energy gap between the first guest binding (which suppresses the porphyrin rings rotation) and the subsequent guest bindings (to preorganized binding sites) should be larger in La(III) complexes than in Ce(IV) complexes. The design of new positive allosteric systems using La(III) double- and triple-decker porphyrins is currently continued in this laboratory.

Experimental

General. All starting materials and solvents were purchased from Tokyo Kasei Organic Chemicals or Wako Organic Chemicals and were used as supplied. ^{1}H NMR spectra were recorded either on a Jasco JEOL GSX-400 (400 MHz) or a Brucker DRX 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane as an internal standard. Mass spectral data were obtained using a JEOL JMS HX110A high-resolution magnetic sector FAB mass spectrometer. UV/vis spectra were recorded with a Shimadzu UV-2500 PC spectrophotometer. HPLC analysis was performed on a Shimadzu HPLC LC-9A with a TOSOH TSK$_{gel}$ G3000H$_{HR}$ (7.8 × 30 (mmID × cm)) column.

Synthesis. Syntheses and identifications of **2D**,[11] **2D′**,[17] **6M•Me**, **6M•MeO**,[24] and **7**[11] have been reported previously. Lanthanum(III) porphyrin complexes were synthesised from corresponding free base porphyrins according to the method of Buchler and co-workers.[20] Although we have tried to confirm the purity of **3D**, **4T•Me**, and **4T•MeO** by the elemental analysis several times, there are some disagreements between the experimental and theoretical values. This problem was also observed in previous reports.[19,20] The purity of compounds used here were confirmed by TLC, HPLC, HRMS-FAB, and NMR as well as by the elemental analysis.

Bis[5,15-bis(4-methoxyphenyl)-10,20-bis(4-pyridyl)porphyrinato]lanthanum(III) (3D). To a stirred solution of 5,15-bis(4-methoxyphenyl)-10,20-bis(4-pyridyl)porphyrin (**7**) (100 mg, 0.148 mmol) in 1,2,4-trichlorobenzene (15 ml) was added [La(acac)$_3$]•nH$_2$O (193 mg, ca. 3 eqiv). The mixture was heated at reflux temperature for 48 h under nitrogen atmosphere. After cooling to room temperature the solvent was removed in vacuo. The residue was purified by column chromatography [silica, chloroform–methanol = 10:1 (v/v)] and size exclusion chromatography [Bio-beads SX-1, chloroform] to yield 3D as a purple solid (20 mg, 13%). ^{1}H NMR (−40 °C, CDCl$_3$-pyridine-d_5 = 1:1 (v/v), 600 MHz) δ 4.06 (s, 12H), 7.01 (d, 4H), 7.04 (d, 4H), 7.09 (d, 4H), 7.75 (d, 4H), 8.28 (d, 4H), 8.34 (d, 4H), 8.40 (d, 4H), 8.40 (d, 4H), 8.50 (d, 4H), 8.60 (d, 4H), 9.17 (d, 4H), 9.23 (d, 4H), 9.31 (d, 4H); FAB HRMS (magic bullet) m/z 1489.4075 ([M + H]$^+$ requires 1489.4081); Calcd for $C_{88}H_{61}LaN_{12}O_4\bullet 2H_2O$: C, 68.48; H, 4.38; N, 10.89%. Found: C, 68.52; H, 4.60; N, 9.87%; R_f (TLC (silica, CHCl$_3$)) 0.15.

Tris[5,15-bis(4-methoxyphenyl)porphyrinato]dilanthanum(III) (4T•MeO). To a stirred solution of 5,15-bis(4-methoxyphenyl)porphyrin (**6M•MeO**) (50 mg, 0.096 mmol) in 1,2,4-trichlorobenzene (10 mL) was added [La(acac)$_3$]•nH$_2$O (93 mg, ca. 3 equiv). The mixture was heated at reflux temperature for 28 h under nitrogen atmosphere. After cooling to room temperature the solvent was removed in vacuo. The residue was purified by column chromatography [silica, benzene–dichloromethane = 1:2 (v/v)] and size exclusion chromatography [Bio-beads SX-1, benzene] to yield **4T•MeO** as a brown solid (31 mg, 55%). ^{1}H NMR (−40 °C, CD$_2$Cl$_2$, 600 MHz) δ 4.11 (s, 12H), 4.50 (s, 6H), 6.29 (d, 4H), 6.77 (d, 4H), 7.71 (d, 4H), 7.82 (d, 8H), 7.93 (d, 4H), 8.21 (d, 8H), 8.47 (s×2, 6H), 8.85 (m, 8H), 8.93 (d, 4H), 9.00 (d, 4H); FAB HRMS m/z (magic bullet) 1839.3525 ([M + H]$^+$ requires 1839.3903); Calcd for $C_{102}H_{72}La_2N_{12}O_6\bullet C_6H_6$: C, 67.74; H, 4.10; N, 8.77%. Found: C, 66.08; H, 4.37; N, 8.10%; R_f (TLC (silica, CHCl$_3$)) 0.19.

Tris[5,15-bis(4-methylphenyl)porphyrinato]dilanthanum(III) (4T•Me). This compound was synthesized in a similar manner to **4T•MeO.** Yield (25 mg, 42%). ^{1}H NMR (−40 °C, CD$_2$Cl$_2$, 600 MHz) δ 2.71 (s, 12H), 3.12 (s, 6H), 6.23 (d, 4H), 7.04 (d, 4H), 7.81 (d, 8H), 7.98 (d, 4H), 8.21 (m, 12H), 8.49 (s, 4H), 8.50 (s, 2H), 8.84 (m, 8H), 8.94 (d, 4H), 9.01 (d, 4H); FAB HRMS (magic bullet) m/z 1743.3585 ([M + H]$^+$ requires 1743.4208); Calcd for $C_{102}H_{72}La_2N_{12}\bullet 0.5CHCl_3$: C, 69.97; H, 4.64; N, 8.55%; Found: C, 69.85; H, 5.24; N, 7.94%; R_f (TLC (silica, CHCl$_3$)) 0.17.

This work was supported by a Grant-in-Aid for COE Research "Design and Control of Advanced Molecular Assembly Systems" from the Ministry of Education, Science and Culture (#08CE2005). We thank Ms. E. Okasaki of Kyushu University for HRMS measurements.

References

1 T. G. Traylor, M. J. Mitchell, J. P. Ciconene, and S. Nelson, *J. Am. Chem. Soc.*, **104**, 4986 (1982).

2 a) J. Rebek, Jr, *Acc. Chem. Res.*, **17**, 258 (1984); b) J. Rebek, Jr, T. Costello, L. Marshall, R. Wattley, R. C. Gadwood, and K. Onan, *J. Am. Chem. Soc.*, **107**, 7481 (1985).

3 a) I. Tabushi, S. Kugimiya, M. G. Kinnaird, and T. Sasaki, *J. Am. Chem. Soc.*, **107**, 4129 (1985); b) I. Tabushi and S. Kugimiya, *J. Am. Chem. Soc.,* **108**, 6926 (1986).

4 P. D. Beer and A. S. Rothin, *J. Chem. Soc., Chem. Commun.*, **1988**, 52.

5 R. C. Petter, J. S. Salek, C. T. Sikorski, G. Kumaravel, and F.-T. Lin, *J. Am. Chem. Soc.*, **112**, 3860 (1980).

6 H.-J. Schneider and D. Ref, *Angew. Chem., Int. Ed. Engl.*, **29**, 1159 (1990).

7 R. P. Sijbesma and R. J. Nolte, *J. Am. Chem. Soc.*, **113**, 6695 (1991).

8 Y. Kobuke and Y. Satoh, *J. Am. Chem. Soc.*, **114**, 789 (1992).

9 K. Kobayashi, Y. Asakawa, Y. Kato, and Y. Aoyama, *J. Am. Chem. Soc.*, **114**, 10307 (1992).

10 M. Takeuchi, T. Imada, and S. Shinkai, *J. Am. Chem. Soc.*, **118**, 10658 (1996).

11 a) M. Takeuchi, T. Imada, and S. Shinkai, *Angew. Chem., Int. Ed. Engl.,* **37**, 2096 (1998); b) M. Ikeda, M. Takeuchi, A. Sugasaki, A. Robertson, T. Imada, and S. Shinkai, *Supramol. Chem.*, in press.

12 A. Sugasaki, M. Ikeda, M. Takeuchi, A. Robertson, and S. Shinkai, *J. Chem. Soc., Perkin Trans. 1*, **1999**, 3259.

13 A similar idea for memory storage was reported by Aida et al. using a chiral sadle porphyrin: a) Y. Furusho, T. Kimura, Y. Mizuno, and T. Aida, *J. Am. Chem. Soc.,* **119**, 5267 (1997); b) Y. Mizuno, T. Aida, and K. Yamaguchi, *J. Am. Chem. Soc.*, **122**, 5278 (2000).

14 M. Ikeda, T. Tanida, M. Takeuchi, and S. Shinkai, *Org. Lett.*, **2**, 1803 (2000).

15 A similar idea using ditritylacetylenes was recently reported: T. E. Glass, *J. Am. Chem. Soc.*, **122**, 4522 (2000).

16 a) A. Sugasaki, M. Ikeda, M. Takeuchi, K. Koumoto, and S. Shinkai, *Tetrahedron*, **56**, 4717 (2000); b) A. Sugasaki, M. Ikeda, M. Takeuchi, and S. Shinkai, *Angew. Chem. Int. Ed. Engl.,* **39**,

3839 (2000).

17 M. Takeuchi, T. Imada, M. Ikeda, and S. Shinkai, *Tetrahedron Lett.,* **39**, 7897 (1998).

18 a) K. Tashiro, K. Konishi, and T. Aida, *Angew. Chem., Int. Ed. Engl.*, **36**, 856 (1997); b) K. Tashiro, T. Fujiwara, K. Konishi, and T. Aida, *Chem. Commun*., **1998**, 1121; c) K. Tashiro, K. Konishi, and T. Aida, *J. Am. Chem. Soc.,* **122**, 7921 (2000).

19 For the syntheses of bis(porphyrinato)metal double-deckers see a) J. W. Buchler and M. Nawra, *Inorg. Chem*., **33**, 2830 (1994); b) J. W. Buchler, V. Eiermann, H. Hanssum, G. Heinz, H. Rüterjans, and M. Schwarzkopf, *Chem. Ber*., **127**, 589 (1994); c) J. W. Buchler, A. De Cian, J. Fischer, P. Hammerschmitt, J. Löffler, B. Scharbert, and R. Weiss, *Chem. Ber*., **122**, 2219 (1989); d) J. W. Buchler and G. Heinz, *Chem. Ber.,* **129**, 1073 (1996); e) J. W. Buchler and G. Heinz, *Chem. Ber.,* **129**, 201 (1996) and references cited therein; f) J. Jiang, K. Machida, E. Yamamoto, and G. Adachi, *Chem. Lett.,* **1991**, 2035; g) J. Jiang, K. Machida, and G. Adachi, *Bull. Chem. Soc. Jpn.,* **65**, 1990 (1992); h) J. Jiang, K. Machida, and G. Adachi, *J. Alloys. Comp.,* **32**, 950 (1993), and references cited therein.

20 For the syntheses of tris(porphyrinato)metal triple-deckers see a) J. W. Buchler and B. Scharbent, *J. Am. Chem. Soc*., **110**, 4272 (1988); b) W. Buchler, M. K.-Botulinski, J. Löttler, and B. Scharbert, *New. J. Chem*., **16**, 545 (1992).

21 J. W. Buchler and D. K. P. Ng, In "The Porphyrin Handbook," ed by K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego (2000), Vol. 3, Chap. 20.

22 H. G. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

23 The crystallographic works related to porphyrin–phthalocyanine metal complexes have been reported previously. The metal-nitrogen distances in La(III) complexes are longer than that in Ce(IV) complex: a) M. Lanchlar, A. D. Cian, J. Fischer, and R. Weiss, *New. J. Chem.*, **12**, 729 (1988); b) D. Chabach, M. Tahiri, A. D. Cian, J. Fischer, R. Weiss, and M. E. M. Bibout, *J. Am. Chem. Soc*., **117**, 8548 (1995).

24 J. S. Manka and D. L. Lawrence, *Tetrahedron Lett*., **30**, 6989 (1989).