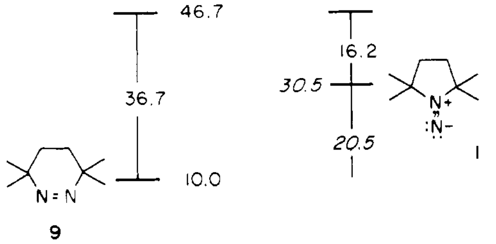
membered to a five-membered cyclic 1,1-diazene causes (a) a shift to higher energy for the n-π^* transition and a shift to higher wavenumber (cm^{-1}) for the N=N stretching frequency, not unlike that of the isoelectronic counterparts, cyclohexanone → cyclopentanone[19] and (b) similar E_a values for thermal fragmentation. Assuming similar mechanisms are operating in the decomposition of **1** and **2**, we would conclude that the difference in strain energies of these five- and six-membered cyclic 1,1-dialkyldiazenes is small, unlike five- and six-membered cyclic 1,2-diazenes.[20]

Finally, the heat of formation ($\Delta H_f = 10.0 \pm 0.6$ kcal/mol) and the enthalpy of activation ($\Delta H^{\ddagger} = 36.7 \pm 0.5$ kcal/mol) for decomposition of 3,3,6,6-tetramethyltetrahydropyridazine (**9**) are known.[20] The sum of these two values affords a value of the heat of formation of the corresponding transition state, $\Delta H_f^{\ddagger} = 46.7$ kcal/mol. If similar intermediates of similar energy intervene in the decomposition of **1** and **9**, subtraction of the enthalpy of activation for the decomposition of **1** ($\Delta H^{\ddagger} = 16.2$ kcal/mol, in hexane) affords the first approximate value for the ΔH_f of a 1,1-dialkyldiazene; i.e., $\Delta H_f(\mathbf{1}) = 30.5$ kcal/mol. This value would indicate the 1,1-diazene **1** has a higher heat of formation than the cis 1,2 isomer **9** by 20 kcal/mol.[21]



Acknowledgments. The authors are grateful to the National Science Foundation (CHE75-06776) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References and Notes

[1] (a) Hinsberg, W. D., III; Dervan, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 1608. (b) *Ibid.* **1979**, *101*, 6142.

[2] For reviews of 1,1-diazene behavior see: (a) Lemal, D. M. In "Nitrenes", Lwowski, W., Ed.; Interscience: New York, 1970; Chapter 10. (b) Ioffe, B. V.; Kuznetsov, M. H. *Russ. Chem. Rev.* (*Engl. Transl.*) **1972**, *41*, 131.

[3] Baldwin, J. E.; Brown, J. E.; Hofle, G. *J. Am. Chem. Soc.* **1971**, 93, 788.

[4] Successive treatment of 2,2,5,5-tetramethylpyrrolidine[5] with $NaNO_2$ and lithium aluminum hydride[17] afforded 1-amino-2,2,5,5-tetramethylpyrrolidine (**3**).

[5] For synthesis of 2,2,5,5-tetramethylpyrrolidine see Lunt, E. (May Baker Ltd., Dagenham, Engl.) *Proc. Int. Symp. Nitro Compounds, 1963* **1964**, 291–315.

[6] Hydrocarbons **4-7** are observed in a ratio of 32:31.3:2.3:1, respectively.[7] Tetrazene **8** was isolated and characterized.

[7] Hydrocarbon products were analyzed by analytical VPC (DBT, 60 °C) and compared with authentic samples.

[8] Chromatography on deactivated basic aluminum at −81 °C using dimethyl ether-propane as solvent removed the *tert*-butyl alcohol and unreacted 1-amino-2,2,5,5-tetramethylpyrrolidine resulting in 1,1-diazene with ≤5% tetrazene impurity. Because the 1,1-diazene is sensitive to trace acid, it is important to add triethylamine to the chromatographed solution.

[9] The red solution is introduced via Teflon tubing connected to sample injection ports into a specially designed copper-jacketed quartz cell attached to a cryogenic system[10] maintained at −78 °C.

[10] Air Products Laboratory cryogenic system, Model LC-1-100 liquid nitrogen Dewar assembly, Model WMX-1A optical shroud with injector parts.

[11] Analogous to the solvent effects on the n-π^* transition of the carbonyl group.[12]

[12] Calvert, J. G., Pitts, J. N. "Photochemistry"; Wiley: New York, 1966; p 257.

[13] The N=N stretching vibration of a symmetrical trans azo compound is forbidden in the infrared but absorbs in the 1576-cm^{-1} (6.35 μ) region of the Raman spectrum.[14]

[14] Silverstein, R. M.; Bassler, G. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1967; p 99.

[15] Reference 14, p 66.

[16] Successive treatment of 2,2,5,5-tetramethylpyrrolidine with $Na^{15}NO_2$ (Prochemicals Limited, N.J.), lithium aluminum hydride,[17] and *tert*-BuOCl-Et_3N afforded the ^{15}N-labeled 1,1-diazene 1.

[17] Roberts, J. R.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 3228.

[18] From the NMR experiment (EM-390), we measured the concentration of 1 against an internal standert (CH_2Cl_2). From this we calculate the extinction coefficient for the n-π^* transition of 1, $\epsilon \sim 20 \pm 3$.

[19] 2,2,6,6-Tetramethylcyclohexanone: λ_{max} (Et_2O) 305 nm, IR 1690 cm^{-1} (C=O stretch). 2,2,5,5-Tetramethylcyclopentanone: λ_{max} (Et_2O) 296 nm, IR 1730 cm^{-1} (C=O stretch).

[20] Engel, P. S. *J. Am. Chem. Soc.* **1976**, *98*, 1972. Engel, P. S.; Hayes, R. A.; Keifer, L.; Szilagyi, S.; Timberlake, J. W. *Ibid.* **1978**, *100*, 1876, and references cited there.

[21] The 1,2-diazene **9** is not found in the products in the thermal decomposition of the 1,1 isomer 1.

[22] Alfred P. Sloan Research Fellow, 1977–1979; Camille and Henry Dreyfus Teacher-Scholar, 1978–1983.

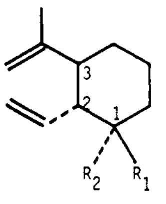
Peter G. Schultz, Peter B. Dervan*[22]
Contribution No. 6065
Crellin Laboratory of Chemistry
California Institute of Technology
Pasadena, California 91125

Received August 13, 1979

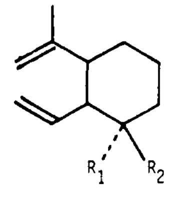
Stereochemical Course of the Cope-Claisen Rearrangement of the Stereoisomeric 2-Vinyl-3-isopropenylcyclohexylvinyl Ethers. A System Having $\Delta G^{\ddagger}_{\text{Claisen}} \gg \Delta G^{\ddagger}_{\text{Cope}}$

Sir:

We have previously demonstrated that the Cope-Claisen rearrangement provides a useful method for driving unfavorable Cope rearrangement equilibria by means of an irreversible Claisen rearrangement.[1] With an interest in constructing chiral germacrane compounds from chiral carvone derivatives, we have investigated the fate of the four diastereomeric vinyl ethers **1a** (TT), **1b** (CT), **2a** (TC), and **2b** (CC)[2] when subjected to thermolysis.

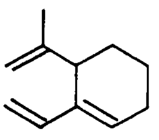


1

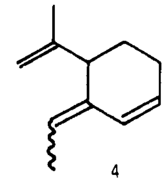


2

a, $R_1 = OCH{=}CH_2$, $R_2 = H$
b, $R_1 = H$, $R_2 = OCH{=}CH_2$



3



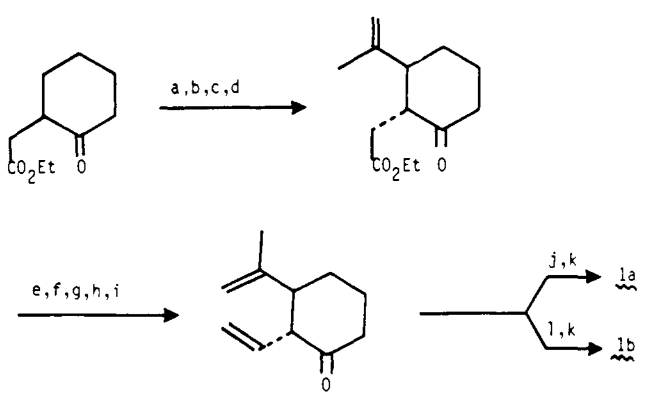
4

Vinyl ethers[3] **1a** (TT) and **1b** (CT) were prepared as outlined in Scheme I, while the preparation of isomer **2a** (TC) has been previously described.[1]

Thermolysis at 312 °C (evacuated sealed tube) of isomers **1** bearing trans-vinylic groups (Table I, entries 1 and 2) provided a nearly identical distribution of products consisting of (*Z*,*Z*)-8-methyl-2,7-cyclodecadiene-1-acetaldehyde (**10**),[1] a mixture of four major olefins, and an inseparable mixture of two aldehydes, which were shown by 270-MHz NMR not to be any of the geometric endocyclic isomers of **10.** The mass spectra (GC-MS) of the four olefins displayed parent ions (M^+ 148) in agreement with the loss of acetaldehyde from the parent compounds. The 270-MHz NMR spectrum of two of these olefins permitted them to be assigned structures **3** and **4.** In contrast to the isomers **1a** (TT) and **1b** (CT), the product ratio of **10**:(**5** + olefins) is significantly higher as is the absolute

0002-7863/80/1502-0880$01.00/0

Scheme I[a]



[a] (a) SO_2Cl_2; (b) DBU, (c) $(i\text{-}C_3H_5)_2CuLi$, Et_2O, Me_2S, 0 °C; (d) NaOEt, EtOH, 25 °C; (e) $(CH_2OH)_2$, p-TsOH, C_6H_6; (f) $LiAlH_4$, Et_2O; (g) o-$NO_2C_6H_4SeCN$/n-Bu_3P/THF; (h) H_2O_2, 0 → 25 °C; (i) HOAc/H_2O, 45-55 °C; (j) Li/NH_3, EtOH, NH_3, −78 °C; (k) $EtOCH{=}CH_2$, $Hg(OAc)_2$; (l) LiH(sec-Bu)$_3$B.

yield in the thermolysis of the isomer **2a** (TC, entry 3).

Thermolysis of either **1a** (TT) or **1b** (CT) at 255 °C (entries 4 and 5) produced an equilibrium mixture (55:45) of **1a–1b**, respectively, without conversion into products.[5] Under identical conditions (entry 6), the isomer **2a** (TC) provided the Cope-Claisen aldehyde **10** and recovered **2a** as the major products. The minor constituents of the reaction mixture consisted of the aldehydes **5** and isomer **2b** (CC)[3] whose mass spectrum[4] was virtually identical with that of isomers **1a** (TT), **1b** (CT), and **2a** (TC).

These data reveal a dynamic Cope interconversion of the isomer **1a** (TT) and **1b** (CT) at 255 °C via the intermediate (*E*,*E*)-1,5-cyclodecadiene conformations **7**, which require two endocyclic bond rotations (EBR) of 180° from one crossed double-bond conformation to the other (**7a** ⇄ **7b**, Scheme II). This process at 255 °C has the unique property of having $\Delta G^{\ddagger}_{\text{Claisen}} \gg \Delta G^{\ddagger}_{\text{Cope}}$.[6] Examination of molecular models of **7a**, which has the required C–O bond situated equatorially to the ring, reveals severe transannular interactions of H_a with H_b when the proper orbital overlap is attained for Claisen rearrangement.[7]

In contrast, the isomer **2a** (TC, entry 6) is largely converted into **10** along with Cope isomerization (via **9a** ⇄ **9b**, double EBR) to the isomer **2b** (CC). The Cope-Claisen aldehyde **10** can arise from conformation **9b** of the (*E*,*Z*)-1,5-cyclodecadiene having the starred carbon axially oriented in the chair-like transition state of the Claisen rearrangement rather than in the preferred equatorial position as is the case in unconstrained rearrangements.[8] The reduced strain associated with the (*E*,*Z*)-1,5-cyclodecadiene **9b** relative to the *E*,*E* isomer **7a** permits the Claisen rearrangement to become a viable process at 255 °C.

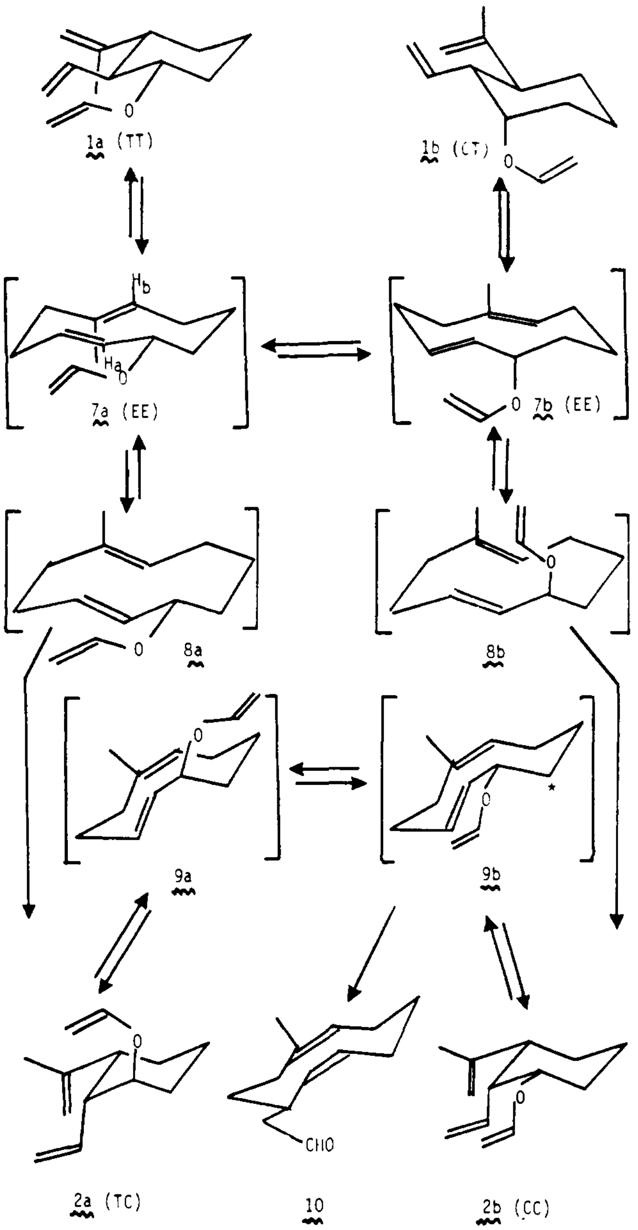
At 207 °C (entry 7), thermolysis of isomer **2a** (TC) produces an equilibrium mixture of the **2a** and **2b** isomers without effecting Claisen rearrangement ($\Delta G^{\ddagger}_{\text{Claisen}} \gg \Delta G^{\ddagger}_{\text{Cope}}$).[9]

Table I

entry	isomer	temp, °C	time, h	products, % yield 1a	1b	2a	2b	10	5	olefins
1[a,b]	1a	312	3					21	11	43
2[a,b]	1b	312	3					26	11	40
3[a,b]	2a	312	3					70	12	18
4[b,c]	1a	255	3	55	45					
5[b,c]	1b	255	3	55	45					
6[b,c]	2a	255	3			24	9	58	9	
7[b,c]	2a	207	2.5			75	25			

[a] Absolute yields. [b] GLC analysis, 6 ft × 1/8 in. 5% Carbowax 20M Anakrom ABS 110/120 on a Perkin-Elmer 3920 FID chromatogram. [c] Relative yields.

Scheme II



Crossover from the trans series **1** to the cis series **2** occurs only at higher temperatures (onset ~280 °C, 3 h) without the accumulation of the isomers **2a** (TC) and **2b** (CC). The crossover process is effectively irreversible ($\Delta G^{\ddagger}_{2\to 1} \gg \Delta G^{\ddagger}_{2\to 10}$). If the higher energy crossover pathway which involves a single EBR process is concerted, it would require a boat-like transition (**8**) wherein the olefin termini are separated to a larger extent than in the transition state for the isomerization **7a** ⇄ **7b**. The presence of diradical intermediates in the crossover cannot be discounted at this time.

Acknowledgments. We express our thanks to the National Institutes of Health (CA 16432) and Hoffmann-La Roche for financial support of this work. The Bruker 270-MHz instrument is supported by National Institutes of Health Research Grant No. 1-P08-PR00798 from the Division of Research Sources.

References and Notes

(1) F. E. Ziegler and J. J. Piwinski, *J. Am. Chem. Soc.*, **101**, 1611 (1979).
(2) The nomenclature refers to the relative stereochemistry of C_1–C_2, C_2–C_3.

(3) **1a:** NMR ($CDCl_3$, 270 MHz) δ 6.28 (1 H, dd, J = 14 and 7 Hz), 5.56–5.41 (1 H, m), 5.09–4.98 (2 H, m), 4.72–4.65 (2 H, m), 4.24 (1 H, dd, J = 14 and 1.5 Hz), 3.93 (1 H, dd, J = 7 and 1.5 Hz), 3.51 (1 H, td, J = 10 and 4 Hz, H_{C_1}–H_{C_2} trans), 2.20–1.22 (8 H, m), 1.63 (3 H, s). **1b:** NMR ($CDCl_3$, 270 MHz) δ 6.27 (1 H, dd, J = 14 and 7 Hz), 5.84–5.66 (1 H, m), 5.03–4.92 (2 H, m), 4.72 (1 H, br s), 4.69 (1 H, br s), 4.29 (1 H, dd, J = 14 and 1.5 Hz), 4.01 (1 H, q, J = 3 Hz, H_{C_1}–H_{C_2} cis), 3.96 (1 H, dd, J = 7 and 1.5 Hz), 2.46 (1 H, td, J = 12 and 3 Hz), 2.14–1.21 (7 H, m), 1.60 (3 H, s). **2b:** NMR ($CDCl_3$, 270 MHz) δ 6.35 (1 H, dd, J = 14 and 7 Hz), 5.84–5.68 (1 H, m), 5.19–5.03 (2 H, m), 4.79 (1 H, br s), 4.63 (1 H, br s), 4.30 (1 H, dd, J = 14 Hz and 1.5 Hz), 4.03 (1 H, dd, J = 7 and 1.5 Hz), 3.87 (1 H, dt, J = 12 and 4 Hz, H_{C_1}–H_{C_2} cis), 2.97–2.88 (1 H, m), 2.12–2.03 (1 H, m), 1.96–1.21 (6 H, m), 1.71 (3 H, s).

(4) **2b:** MS (70 eV) *m/e* (rel intensity) 192 (M^+, 1.2), 149 (56), 148 (31), 93 (91), 81 (100).

(5) For related Cope isomerizations, see K. Morikawa and Y. Hirose, *Tetrahedron Lett.*, 869 (1969); G. L. Lange, M. A. Huggins, and E. Neidert, *ibid.*, 4409 (1976); P. A. Wender and J. C. Lechleiter, *J. Am. Chem. Soc.*, **99**, 267 (1977); J. R. Williams and J. F. Callahan, *J. Chem. Soc., Chem. Commun.*, 404 (1979).

(6) In similarly substituted Claisen and Cope rearrangements, the former reaction usually has a smaller $\Delta G^{\ddagger}$ at a specific temperature. See S. J. Rhoads and N. R. Raulins, *Org React.*, **22,** 1 (1975).

(7) A referee has suggested that the strain energy associated with the (*E,E*)-1,5-cyclodecadiene **7** and its *E,E* Claisen product could also account for a high $\Delta G^{\ddagger}_{\text{Claisen}}$.

(8) F. E. Ziegler, *Acc. Chem. Res.*, **10,** 227 (1977), and references cited therein.

(9) Strictly speaking, these data do not rule out the possibility of the formation of the *E,E* isomer of **10** from the trans isomers 1 in an undetectable amount, since the associated strain (cf. note 7) could allow a retro-Claisen rearrangement.[10]

(10) (a) M. Rey and A. Dreiding, *Helv. Chim. Acta*, **48,** 1985 (1965); (b) S. J. Rhoads and R. D. Cockroft, *J. Am. Chem. Soc.*, **91**, 2815 (1969); (c) M. T. Hughes and R. O. Williams, *Chem. Commun.*, 587 (1968).

Frederick E. Ziegler,* John J. Piwinski
Sterling Chemistry Laboratory, Yale University
New Haven, Connecticut 06520

Received August 13, 1979

Nitrogen 1s Photoelectron Spectra of Octaethylporphyrin and Tetraphenylporphine Complexes of Lanthanides

Sir:

X-ray photoelectron spectroscopy (ESCA) has been proved to be a powerful method for the elucidation of structure and bonding in complex molecules of f transition elements.[1] In our previous work on ESCA spectra for a series of lanthanide (Ln) and actinide (An) compounds, $Ln(OH)_3$,[2] $H(LnPc_2)$, and $AnPc_2$,[3] we gave our attention to the satellite phenomena in Ln $3d_{5/2}$ and An $4d_{5/2}$ spectra. The observations suggested that f orbitals [either half-occupied or vacant orbital(s)] played an important role in the core ionization process which gave sharp variations in the satellite intensity of the spectra. As an extension of our ESCA study of f transition metal complexes, we now focus on lanthanide complexes of octaethylporphyrin (OEP), Ln(OEP)(OH) (Ln = Eu, Gd, Yb, and Lu), and of tetraphenylporphine (TPP), Ln(TPP)(acac) (Ln = Sm, Gd, Er, and Yb; acac = acetylacetonate).

We report here new findings derived from our observations of nitrogen 1s photoelectron spectra of Ln(OEP)(OH) and Ln(TPP)(acac). For a comparison, we measured also N 1s spectra of H_2TPP and H_2OEP. N 1s spectra have been shown to be a source of valuable information on the geometry of both porphyrins and metalloporphyrins.[4-8] Besides the geometrical viewpoint, we found a noticeable correlation between the line width (fwhm) of the N 1s signal and the number of unpaired electrons in the lanthanide–porphyrin complexes. This indicates that unpaired valence electrons are not localized in the lanthanide 4f orbitals but are bound in MO's delocalized over N and lanthanide orbitals, and that the induced spin density on the N atoms provides an exchange interaction with the ionized N 1s core.

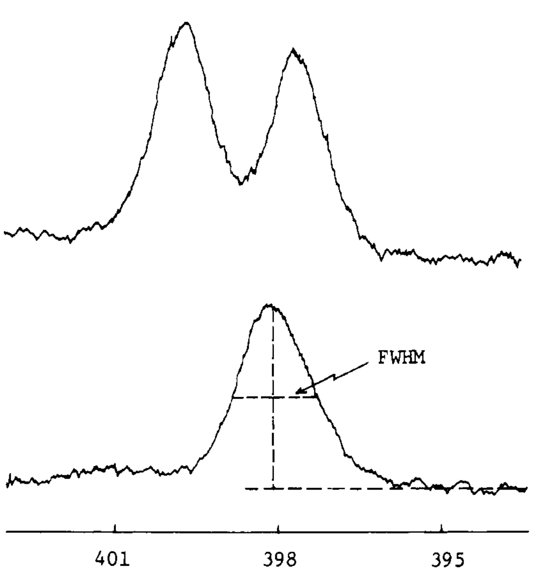


Figure 1. Typical N 1s signals of free-base prophyrin (top) and lanthanide porphyrin (bottom). The fwhm of a N 1s peak for each lanthanide porphyrin was estimated with a procedure shown by broken lines.

Octaethylporphyrin complexes Ln(OEP)(OH) have been prepared by T. Saran Srivastava. We synthesized and purified tetraphenylporphine complexes Ln(TPP)(acac) by the method described by Wong et al.[9] though the Sm compound seems to decompose gradually to metal-free TPP in chloroform. X-ray photoelectron spectra were obtained with a Hewlett-Packard 5950-Å ESCA spectrometer employing Al Kα X-ray excitation. The charging effects were neutralized by using an electron flood gun. The samples were prepared by carefully brushing each compound on double-stick scotch tape. We observed neither any visible evidence of decomposition nor change in the photoelectron spectra of the lanthanide porphyrins during the course of experiments performed, except for the case of Sm(TPP)(acac).[10] The spectra were calibrated using a C 1s binding energy at 284.8 eV which arises from the carbon atoms having hydrocarbon character in the porphyrin rings.

The N 1s spectrum measured for either H_2OEP or H_2TPP exhibits a doublet due to the selective protonation of two of the central nitrogens. Observed binding energies of each doublet are 399.7 and 397.7 eV for H_2OEP and 400.0 and 398.0 eV for H_2TPP, and individual peaks have fwhm values of ~1.2_5 eV. These binding energies are in agreement with those obtained previously by other groups[5,6,8] and differ only slightly from others which could be because of the use of different reference lines. We note here that our fwhm values (1.2_5 eV) are close to the value of 1.1 eV given by Niwa et al.[5] which is the narrowest N 1s signal obtained for porphyrins in the solid state. This seems to warrant the subsequent discussion concerning the N 1s line width of lanthanide porphyrins.

In complexing a lanthanide ion with OEP or TPP, the N 1s spectrum collapses to a single peak with a binding energy value directly in between the corresponding porphyrin doublet. This is schematically drawn in Figure 1, where the N 1s spectra of free-base and metal-incorporated porphyrins are typified by those of H_2OEP and of Yb(OEP)(OH), respectively. The single N 1s peak indicates the existence of four equivalent nitrogens in the lanthanide porphyrins and thus the equalized four Ln–N interactions. The situation is achieved only when a lanthanide is located equidistant between the four nitrogen atoms.

The binding energies and the fwhm values determined for a series of lanthanide porphyrins are summarized in Table I. No significant difference in the binding energies can be seen between the lanthanide porphyrins studied, indicating that the

0002-7863/80/1502-0882$01.00/0