experiment. Randomization of the deuterium throughout the Np group and OsH positions (none into L) of **1b**-d_7 was readily followed by ^{1}H NMR during thermolysis in C_6D_{12}. Mass spectral analysis of NpH resulting from thermolysis of **1b**-d_7 in C_6D_6 also indicated extensive internal scrambling of the deuterium label within the neopentyl group, presumably through intermediate **5**.

Pyrolysis of **1b** in neat Me_4Si at 80 °C results in a much slower reaction, first order in **1b** (k_{obsd} = 4.8 × 10^{-6} s^{-1}), leading to formation of **1c** but with competitive formation of **6**[5] (path 4, Scheme I). Reaction of **1b** at 80 °C in cyclopentane + ca. 12 mol % of methane leads to formation of only **6** with k_{obsd} = 2.2 × 10^{-6} s^{-1}. We are examining the scope and mechanism of the tetraalkylsilane activation in lieu of the intermolecular alkane activation.

Compound **6** apparently arises from two independent paths. Pyrolysis of **1b** in cyclopentane at 80 °C to produce **6** is retarded by the addition of excess L up to a point, after which the rate becomes independent of [L] (k_{obsd} = 6.8 × 10^{-7} s^{-1}). A kinetic isotope effect, k_H/k_D, of 1.7 is observed in the absence of added L (using $[(CD_3)_3P]_4Os(H)[CH_2C(CH_3)_3]$), but *no* isotope effect is found in the presence of a large excess of added L′. These results are most consistent with the operation of path 5 in the absence of added L and path 6 in its presence. All reactions of **4** are suppressed by a large excess of free L, to the point that the very slow direct reductive elimination of NpH from **1b** becomes evident.

This $L_4Os(II)$ system is a rare example of soluble, mononuclear, noncyclopentadienyl-containing metal complexes which undergo a rich variety of C–H bond activation reactions that are amenable to close mechanistic scrutiny. Comparison of this chemistry to that of other reported molecules may afford answers to some of the remaining intriguing questions regarding this important reaction type. Additional investigations of the scope and mechanism of C–H bond activation in this system and analogous Os(II) complexes with other phosphine ligands are under way.

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Naturally Occurring Benzoporphyrins: Bacterial Marker Pigments?

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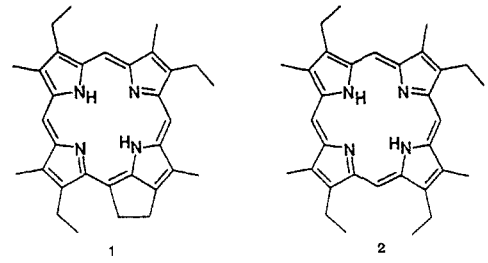
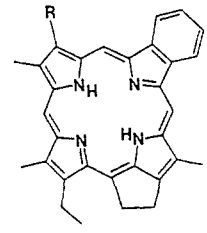
The occurrence of sedimentary porphyrins with rhodo-type electronic spectra,[1] showing a bathochromic effect and intensity increase in band III, in comparison with those of other widely occurring porphyrins of structural types represented by **1** and **2**, has been recognized for over 50 years.[2] Mass spectrometric studies[3] of isolated fractions enriched in rhodo-type components, and subsequent comparison of electronic spectra with those of synthesized compounds,[4] indicated that these components might be monobenzoporphyrins. Other evidence was given by oxidation of isolated fractions to mixtures of products containing 1*H*-benzopyrrole-2,5-dione.[5] It has been suggested that a sedimentary



1 2



3a : R = C_2H_5
3b : R = CH_3

Diels–Alder reaction involving a vinyl β-substituent and β–β′ double bond of one of the tetrapyrroles with a dienophile and subsequent aromatization could account for the formation of the proposed benzene ring.[6]

An alternative suggestion is intramolecular cyclization of two β-substituents, e.g., a methyl and an adjacent propionic acid chain, followed by dehydration and dehydrogenation.[7,8] In this paper we report (i) the first isolation of individual components of this type from a crude oil (Boscan; Cretaceous, Venezuela), (ii) confirmation that these components, the two most abundant rhodoporphyrins in the oil, are monobenzoporphyrins, and (iii) their structural assignment as **3a,b** by ^{1}H NMR, using decoupling and nuclear Overhauser effect (NOE) studies at 400 MHz. Attention was focused on isolating components containing an exocyclic ring (cf. **1**) to identify the specific pyrrole carrying the rhodofying moiety and to attempt to provide information about a possible origin for the sedimentary components in terms of precursor biological pigments, since no tetrapyrrole with a benzene ring (or dihydro or tetrahydro counterpart) at β,β′ positions has been reported in organisms.

The isolation procedure was developed from that used previously[9] and involved flash silica chromatography[10] of the crude oil, followed by demetalation (methanesulfonic acid 98%, N_2, 100 °C, 4 h) of the porphyrin-containing fraction (mainly V = 0). Further flash chromatography afforded a fraction enriched in rhodoporphyrins (ca. 15%). Two stages of preparative HPLC, involving normal phase (Spherisorb S 5W; 250 × 10 mm i.d.), followed by reverse phase (Spherisorb S 5 ODS2; 250 × 10 mm i.d.), allowed isolation of a number of components including **3a** and **3b** (ca. 1% of total porphyrins). Both **3a** and **3b** have mass ($M^{+\cdot}$, m/z 484 and 470, respectively) and electronic spectra (λ_{max} 505, 542, 574, 628 nm; relative intensity 69, 100, 43, 23, Soret 407 nm) consistent with rhodoporphyrins containing an exocyclic alkano ring.

Examination of the Zn^{II} complex of **3a** by ^{1}H NMR (Figure 1, Table I) revealed the presence of 2β-ethyls, 3β-methyls, and 3-meso protons. The presence of a β,β′-fused benzene ring and the CH_2CH_2 moiety in the alkano ring was confirmed by decoupling and NOE difference experiments. Furthermore, con-

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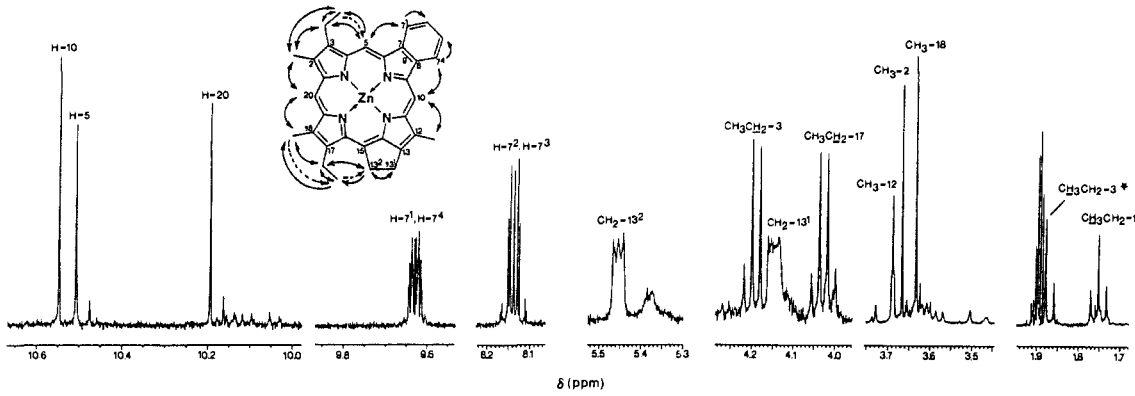

Figure 1. Partial 400-MHz ^1H spectrum of **3a** (Zn^{II} complex) in $(CD_3)_2CO/3\%$ C_5D_5N. The free induction decay was Gaussian-multiplied and zero-filled to give 0.18-Hz digital resolution after Fourier transformation. The two regions containing the methyl group resonances (ca. 1.7–1.9 and ca. 3.5–3.7 ppm) are shown at ca. 0.33 of the gain used for the other regions. Arrows indicate enhancements: 5% < NOE < 20% (dotted arrows ca. 2–4%). * Signal partially overlapping with ^{13}C satellites of solvent signal.

Table I. ^1H NMR Data at 400 MHz for **3a** (Zn^{II} Complex) in $(CD_3)_2CO/3\%$ C_5D_5N

δ	multiplicity[a]	NOE[b]	assignment
10.548	s	9.630, 3.688	H-10
10.507	s	9.630, 4.190	H-5
10.194	s	3.668, 3.635	H-20
9.630	m (8.140)	10.548, 10.507, 8.140	H-7^1, H-7^4
8.140	m (9.630)	nd	H-7^2, H-7^3
5.455	m (4.148)	4.148, 4.030, 1.754	13^2-CH_2
4.190	q (7.1, 1.880)	10.507, 3.668, 1.880	3-CH_3CH_2
4.148	m (5.455, 3.688)	5.455	13^1-CH_2
4.030	q (7.1, 1.754)	5.455, 3.635, 1.754	17-CH_3CH_2
3.688	t (1.0, 4.148)	10.548	12-CH_3
3.668	s	10.194, 4.190, 1.880	2-CH_3
3.635	s	10.194, 4.030, 1.754[c]	18-CH_3
1.880	t (7.1, 4.190)	10.507,[c] 4.190, 3.668	3-CH_3CH_2
1.754	t (7.1, 4.030)	5.455,[c] 4.030, 3.635	17-CH_3CH_2

[a] (J = Hz, δ coupled nuclei.) [b] Chemical shifts where enhancements seen when δ signal irradiated; n.d., not determined. [c] Weak enhancement observed.

nection between the CH_2CH_2 moiety and 12-CH_3 (3.655 ppm) could also be established by decoupling experiments (Table I). The structure of **3b** was established in the same way, the spectrum of the Zn^{II} complex being essentially similar to that of **3a** except for the absence of the resonances at 4.190 and 1.880 ppm (3-CH_3CH_2) which were replaced by an appropriate increase in intensity of a CH_3 singlet (3,18-CH_3) at 3.625 ppm. The results confirm that **3a** is 13,15-ethano-3,17-diethyl-2,12,18-trimethylmonobenzo[*g*]porphyrin and **3b** is 13,15-ethano-17-ethyl-2,3,12,18-tetramethylmonobenzo[*g*]porphyrin.

It is clear from the presence of the exocyclic alkano ring that both compounds have arisen from degradation of chlorophylls rather than from tetrapyrroles such as cytohemes. The position of the benzene ring excludes an origin for this feature from a Diels–Alder type of reaction involving C-2,3 and a vinyl substituent at C-3. Furthermore, intramolecular cyclization involving 18-CH_3 and a propionic acid chain at C-17 can be excluded. It is difficult to envisage how a rearrangement of a known chlorophyll could give rise to **3a,b**. In the absence of other information at present, it is tempting to suggest that they could have originated from a precursor related in some way to bacteriochlorophylls *d*,[11] where structural modifications occur on β-substituents of the appropriate pyrrole ring. Furthermore, a tetrahydrobenzoporphyrin component has been found[8] in a limestone with a milder thermal history than the source rock of Boscan crude. The position of this structural feature was not established, so it is possible that such a component could aromatize in sediments to give **3a**. The stage at which the aromatization occurred is unknown, although it could have occurred at an early stage of diagenesis, since rhodoporphyrins have been reported recently[12] in sediments with a very mild thermal history.

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Reaction of Malondialdehyde with Guanine Nucleosides: Formation of Adducts Containing Oxadiazabicyclononene Residues in the Base-Pairing Region

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Malondialdehyde (MDA) is the simplest β-dicarbonyl compound and a widespread natural product.[1,2] It is generated during peroxidation of polyunsaturated fatty acids and is also formed as a result of enzymatic and nonenzymatic degradation of prostaglandin endoperoxides.[1] It is reactive toward protein and nucleic acids and is toxic and mutagenic.[3] In *Salmonella typhimurium*, MDA and acroleins substituted with good leaving groups at the β-position induce frame-shift mutations and structure–activity studies indicate that both carbonyl equivalents of MDA or the β-substituted acroleins are required.[4] It is unusual for frame-shift

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