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Nuclear Magnetic Resonance Spectroscopy. Carbon-13 Spectra of the Silver(I) Complexes of Cyclopentene and Cyclohexene[1]

Sir:

In recent years, proton magnetic resonance spectroscopy has been utilized to investigate the nature of the species arising when alkenes are dissolved in solutions containing either silver(I)[2] or mercury(II)[3] ions. We report here on the use of high-resolution nmr spectra of ^{13}C (cmr) in natural abundance[4] in examining such complexes.

The cmr spectra of cyclopentene and cyclohexene in aqueous silver nitrate solution[5] reveal that the unsaturated carbon resonances in both compounds are shifted to higher fields by 4.4 ppm, relative to those of the free cycloalkenes (see Table I). The remaining carbon resonances are shifted downfield slightly. These shifts seem best rationalized on the basis of a small increase in the σ character of the bonds at the unsaturated carbons,[6] although steric interactions[2c] with the silver ion cannot be definitely ruled out. As with the proton chemical shifts of silver–alkene complexes,[2b] there is no significant concentration effect on the ^{13}C chemical shifts.

Table I. Carbon Chemical Shifts of Cycloalkene–Silver Nitrate Complexes in Aqueous Solution at 15.1 MHz

	δ (CS$_2$)[a]	δ (CS$_2$)[a]	$\Delta\delta$
Cyclopentene		Cyclopentene–AgNO$_3$ Complex	
C1, C2	62.2	66.6	+4.4
C3, C5	160.2	158.3	−1.9
C4	169.7	168.3	−1.4
Cyclohexene		Cyclohexene–AgNO$_3$ Complex	
C1, C2	65.6	70.0	+4.4
C3, C6	167.3	165.8	−1.5
C4, C5	169.7	169.4	−0.3

[a] In parts per million relative to carbon disulfide.

The downfield shift of vinyl protons on formation of a silver(I) complex is usually explained as resulting from proton deshielding arising from π-electron donation from the alkene to the silver(I) ion.[2] Dewar[7] has proposed that the complexes are formed as the result of σ overlap between the bonding alkene π orbital with a vacant s or sp hybrid orbital on the silver(I) ion and π overlap of an occupied d orbital on the ion with an antibonding alkene π orbital. The net effect appears to be that the π-electron density decrease at carbon is not balanced by the d-electron contribution, thus making σ bonding more important than π bonding.[2c] Thus, an increase in the σ character of the bonds at the alkene carbons is expected and the ^{13}C results tend to bear this out. An increase in the σ character of the bonds to the unsaturated carbons would be expected to decrease the couplings between alkenic carbons and the directly attached hydrogens, but actually there is very little change upon complexation. The lack of appreciable change in the ^{13}C–H coupling constants suggests an alternative explanation of the chemical-shift changes, namely that the π-orbital energy of the alkene is reduced by coordination with silver ion, so as to produce small changes in the excitation energy.

With regard to interaction of mercury(II) ion with alkenes, evidence has been presented[3b,c] and challenged[3a] for direct observation of proton resonances of mercurinium ions. We have found that the cmr spectra of methanol solutions containing equimolar amounts of cyclopentene or cyclohexene and mercury(II) acetate gave no resonances corresponding to alkenic carbons and, indeed, were best explained as arising from 1-acetoxymercuri-2-methoxycyclopentane or 1-acetoxymercuri-2-methoxycyclohexane.

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[1] Supported by the National Science Foundation.

[2] (a) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 2519 (1960); (b) J. Schug and R. J. Martin, *J. Phys. Chem.*, **66**, 1554 (1962); (c) H. W. Quinn, J. S. McIntyre, and D. J. Peterson, *Can. J. Chem.*, **43**, 2896 (1965).

[3] (a) W. Kitching, A. J. Smith, and P. R. Wells, *Aust. J. Chem.*, **21**, 2395 (1968); (b) Y. Saito and M. Matsuo, *Chem. Commun.*, 961 (1967); (c) V. Sokolov, U. Yustynyuk, and O. Reutov, *Dokl. Akad. Nauk SSSR*, **173**, 1103 (1967).

[4] (a) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967); *ibid.*, **90**, 3543 (1968); (b) F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **60**, 1152 (1968); (c) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, in press.

[5] The samples were prepared by saturating either a 2 *M* or saturated silver nitrate solution with cycloalkene. Cyclopentene and cyclohexene were chosen for study because of their high solubility in silver nitrate solutions (H. J. Taufen, M. J. Murray, and F. F. Cleveland, *ibid.*, **63**, 3500 (1941)).

[6] It is well known that there is a large chemical shift difference between sp^2- and sp^3-hybridized carbons, the sp^3 carbons being upfield by about 100 ppm (J. B. Stothers, *Quart. Rev.* (London), **19**, 144 (1965)).

[7] M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951).

Isoporphyrins

Sir:

The discovery of phlorins and the recognition of their stability prompted Woodward[1] to suggest that tautomeric structures of porphyrin with a saturated bridging carbon atom [isoporphyrin (**1**)] might exist. We report here the synthesis of a metalloisoporphyrin.

Controlled-potential oxidation of zinc *meso*-tetraphenylporphyrin (ZnTPP), at 1.1 V *vs.* sce, in dichloromethane–tetrapropylammonium perchlorate brings about two successive reversible one-electron oxidations. The first step generates a π cation radical[2] which is stable in nucleophilic solvents[3] and can be isolated in

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[1] R. B. Woodward, *Ind. Chim. Belge.*, **27**, 1293 (1962).

[2] R. H. Felton, D. Dolphin, D. C. Borg, and J. Fajer, *J. Amer. Chem. Soc.*, **91**, 196 (1969).

[3] Stable cations of metallooctaethylporphyrins have been reported by J.-H. Fuhrhop and D. Mauzerall, *ibid.*, **91**, 4147 (1969).

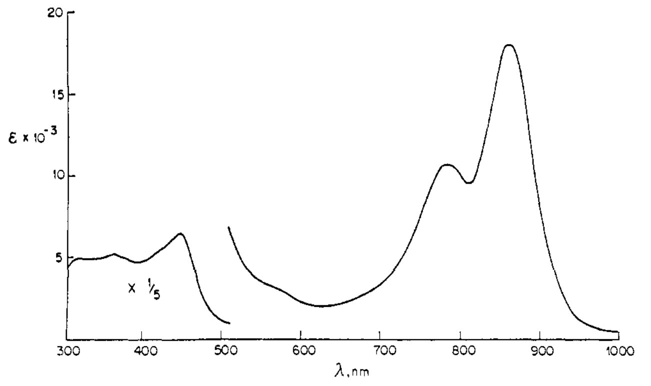


Figure 1. Optical absorption spectrum of isoporphyrin **3** in CH_2Cl_2.

crystalline form.[4] Removal of the second electron[4] yields the π dication **2**, which is stable, in the absence of nucleophiles, and can be quantitatively reduced back, *via* the cation radical, to ZnTPP, *viz.*

$$\text{ZnTPP} \underset{}{\overset{-e}{\rightleftharpoons}} \text{ZnTPP}^{+} \underset{}{\overset{-e}{\rightleftharpoons}} \text{ZnTPP}^{2+}$$

Addition of methanol to the magenta solution ($\lambda_{max}^{CH_2Cl_2}$ 350 nm (ϵ 6 × 10^4)) of the dication[5] caused it immediately to turn green. Solvent was removed under reduced pressure and the residue shaken with benzene; filtration removed tetrapropylammonium perchlorate and the other product of the reaction, protonated (demetalated) *meso*-tetraphenylporphyrin (**4**). Addition of cyclohexane to the green filtrate gave **3** as dark green needles with a purple metallic luster (optical absorption spectrum, Figure 1). Compound **3** is stable in glacial acetic acid, but the addition of KI to such solutions brings about a rapid and quantitative reduction and demetalation to give TPPH_4^{2+} (**4**).

The dication **2**, which has lost two electrons, should be a powerful electrophile, and its reaction with methanol can be viewed as nucleophilic attack at a *meso* carbon atom to give **3**. Upon electrophoresis the

$$\text{ZnTPP}^{2+}(\text{ClO}_4^-)_2 + \text{CH}_3\text{OH} \longrightarrow \text{ZnTPPOCH}_3^+\text{ClO}_4^- + \text{H}^+ + \text{ClO}_4^-$$

isoporphyrin migrates toward the cathode while ZnTPP remains stationary. The infrared spectrum (KBr) confirms identification of **3** as a perchlorate salt and contains *inter alia* bands at 618 and 1110 cm^{-1} which are absent in ZnTPP but present in perchlorate salts of 1,19-disubstituted tetradehydrocorrins.[6] *Anal.* Calcd for $C_{45}H_{31}N_4OZnClO_4$ (**3**): C, 66.84, H, 3.87; N, 6.93. Found: C, 66.58; H, 4.01; N, 6.82.

Assignment of the isoporphyrin structure **3** is supported by the nmr spectrum (Figure 2). In the parent ZnTPP, phenyl protons fall into two groups: *ortho* protons appear as a multiplet at 8.25 ppm, *meta* and *para* protons as a multiplet at 7.83 ppm. The difference in chemical shifts between these protons and those of benzene and the deshielding of the *ortho* compared with the *meta* and *para* protons result from the porphyrin ring current. In ZnTPP, the ring current also deshields the eight equivalent β protons, which appear at 9.05 ppm. Disruption of the aromatic system and consequent loss of ring current cause the phenyl protons of **3** to appear as a multiplet centered at 7.04 ppm. Similarly the β protons of **3** are no longer equivalent and appear as two overlapping AB quartets at higher field. Two AB quartets are consistent with the C_2 symmetry of **3**. A similar upfield shift of the β protons of zinc *meso*-tetraphenylphlorin (which also lacks a ring current) has been observed.[7]

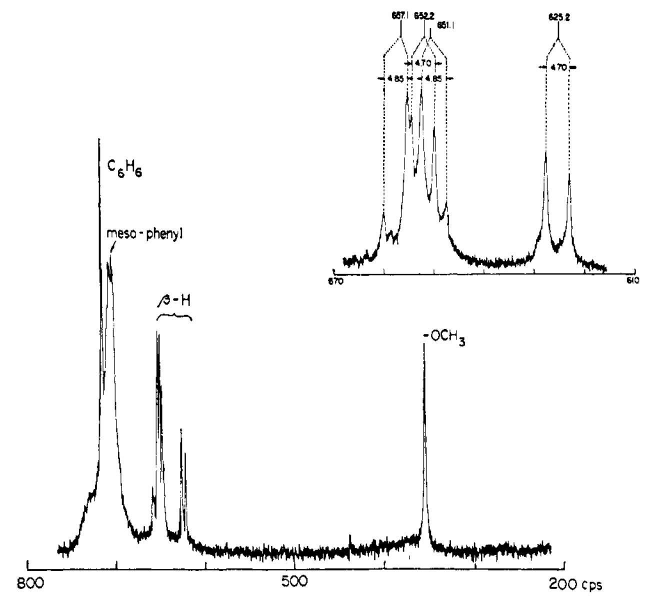
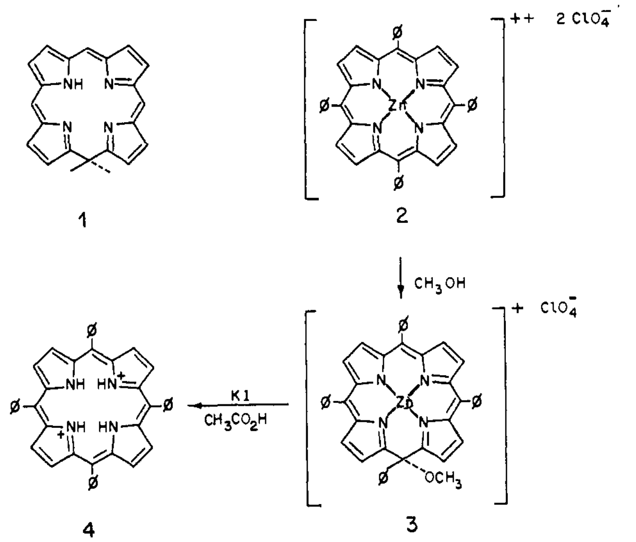


Figure 2. Nmr spectrum (100 MHz) of isoporphyrin **3** in C_6D_6. Relative intensity of the β protons to the methoxy protons is 8:3.



The absorption spectrum of isoporphyrin **3** (Figure 1) is consistent with a theoretically computed spectrum. (The SCF MO calculations have been described previously.[4,8]) Calculated transition energies (and dipole oscillator strengths) of the isoporphyrins are as follows: 828 (0.24), 380 (0.21), 362 (1.22), 337 (0.20), and 330 nm (0.60). Overlap of the transitions in the ultraviolet accounts for the intense, but generally

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[4] J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Amer. Chem. Soc.*, in press.

[5] Treatment of this dication with water gave the corresponding hydroxyisoporphyrin, which required two electrons for reduction to ZnTPP. Isoporphyrins of CuTPP and MgTPP have also been prepared under similar conditions.

[6] D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, and I. T. Kay, *J. Chem. Soc., C*, 30 (1966).

[7] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 818 (1963).

[8] J. Fajer, B. H. J. Bielski, and R. H. Felton, *J. Phys. Chem.*, **72**, 1281 (1968).

featureless, absorption in this region. In accord with the observed addition of nucleophiles at the *meso* position, each *meso* carbon atom of the porphyrin dication has a calculated excess positive charge of 0.32 electron.

The isoporphyrin described here represents direct evidence of nucleophilic attack upon the porphyrin nucleus. Formation of the isocyclic ring of chlorophyll (reported by Cox, *et al.*[9]) may also proceed through an isoporphyrin intermediate. These authors showed that a magnesium porphyrin substituted with a β-keto ester side chain was oxidized, by iodine in methanolic sodium carbonate, to a porphyrin containing an isocyclic ring. This ring formation was envisaged as a coupling between a porphyrin cation radical and an enolate radical. However, in view of the low oxidation potential[10] ($E_{1/2}$ = 0.77 V *vs.* sce) at which magnesium porphyrin dications may be formed, we suggest that formation of the isocyclic ring involves attack of the β-keto ester *enolate anion* onto the *porphyrin dication.*[11] The resulting isoporphyrin can in this case lose a proton to form a neutral *meso*-substituted porphyrin.

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(9) M. T. Cox, T. T. Howarth, A. M. Jackson, and G. M. Kenner, *J. Amer. Chem. Soc.*, **91**, 1232 (1969).

(10) A. Stanienda and G. Biebl, *Z. Physik. Chem.* (Frankfurt), **52**, 254 (1967).

(11) Aside from direct oxidation of magnesium porphyrins to the dication state, disproportionation of the π cation radical also affords a small yield of the dication, *viz.* $2\text{Mg(porphyrin)}^+ \rightleftarrows \text{Mg(porphyrin)} + \text{Mg(porphyrin)}^{2+}$.

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On the Exchange of Trimethylamine with Trimethylamine–Borane in Benzene. A Caveat Concerning the Interpretation of Nuclear Magnetic Resonance Data

Sir:

A recent publication in this journal[1] presented conclusive nmr evidence concerning the rapid exchange at room temperature of trimethyamine–trimethylborane and of trimethylphosphine–trimethylborane with the corresponding free Lewis base. The same paper also stated that trimethylamine–borane exchanged with trimethylamine in benzene solution, whereas mixtures of the same components in glyme (1,2-dimethoxyethane) showed no evidence of exchange even at 80°. The conclusions concerning exchange were based on the temperature dependence of the chemical shift of trimethylamine–borane when mixed with trimethylamine in benzene, and on the lack of such a temperature dependence in glyme. These results were surprising, since they seemed to require a specific and strong participation of the solvent in the assumed exchange process, and since they were at odds with the observation that tertiary amine–boranes only slowly equilibrate with other amines in benzene solution and at room temperature.[2] It was, therefore, decided to examine more closely the nmr behavior of trimethylamine–borane and of trimethylamine in benzene over wide concentration and temperature ranges.

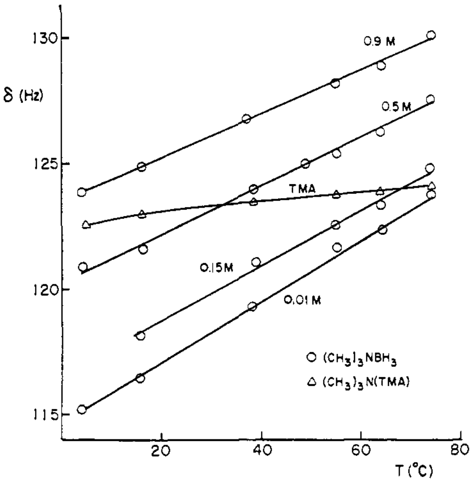

Figure 1. Temperature and concentration dependence of the chemical shifts of trimethylamine–borane and of trimethylamine. (The chemical shift of trimethylamine is independent of concentration and nearly independent of temperature.)

All spectra were run at 60 MHz on a Varian A-60A spectrometer, on solutions prepared from sublimed trimethylamine–borane and solvents dried over molecular sieve 3A. Side bands generated from internal tetramethylsilane and placed in close proximity to the peaks of interest were used to minimize errors in the determination of chemical shifts. Chemical shift data are referred to internal tetramethylsilane and correspond to the methyl protons in free or coordinated trimethylamine; they are quoted in hertz downfield from the reference, with a probable error no larger than ±0.2 Hz. Temperatures were calibrated by the chemical shift differences in methanol or ethylene glycol.

The following facts were established. The chemical shift of trimethylamine in benzene is independent of concentration in the range 0.01–0.9 *M*, only slightly dependent on temperature in the range 4–74°, and independent of admixed trimethylamine–borane. The chemical shift of trimethylamine–borane in benzene, on the other hand, depends on all of the above variables. First, there is a downfield shift with increasing concentration. Second, at fixed concentration, there is a downfield shift with increasing temperature. The temperature coefficient of the shift is larger at the lower concentrations and the combined effect of concentration changes in the range 0.01–0.9 *M* and temperature changes from 4 to 74° can produce chemical shift differences as large as 15 Hz. The results are given in Figure 1. Finally, mixtures of trimethylamine–borane and trimethylamine gave chemical shifts for the borane adduct which were *always downfield* relative to the shift

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(1) A. H. Cowley and J. L. Mills, *J. Amer. Chem. Soc.*, **91**, 2911 (1969).

(2) G. E. Ryschkewitsch, unpublished results.