

Spectroscopic Evidence for Agostic Interactions in Organocobalt Porphyrins

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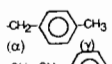
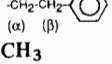
It has been recently discovered that an unusual mode of bonding is often present in coordinatively unsaturated (i.e. sixteen- and seventeen-electron) organometallic complexes [1]. This type of interaction, which involves the bridging of a pendant methyl or methylene proton to a transition metal has been termed agostic (from Greek *agostos*: to hold to one's self), and has been casually referred to as 'an organometallic chemist's hydrogen bond' [2]. This type of bonding is similar to the B–H–B and M–H–M bonding modes seen in inorganic chemistry. However, agostic interactions are unique in that the possibility of such bonding modes opens the field for exploring the reactivities of sp^3 -hybridized hydrocarbon compounds that are often considered un-

activated when bound to a transition metal. Agostic interactions have even been implicated in the hydrogenase/nitrogenase metalloenzyme system [3]. Herein we wish to report that the unusual proton chemical NMR signal positions in the 360 MHz proton and proton-decoupled NMR spectra of five-coordinate organocobalt porphyrins (sixteen-electron species) can be explained by agostic interactions, and we provide spectroscopic evidence for such interactions. We note that the proton NMR chemical shift assignments for similar compounds in the past have been either assigned incorrectly in the literature, or the explanations given for the unusual order of chemical shifts has been unproven or puzzling [4].

The diamagnetic penta-coordinate organocobalt-(III) porphyrins that we have studied were synthesized according to Perrée-Fauvet and Gaudemer [5] and were previously used as the starting material for our dioxygen insertion studies into metal–carbon bonds [6]. Our well-resolved ^1H NMR spectra of the organocobalt porphyrins brought to our attention a systematic behavior in which the β -protons on the alkyl ligand coordinated to the Co(III) are the highest upfield in the proton NMR spectrum, while the α -protons exhibit anomalously broad resonances. Because of the large diamagnetic ring current present in the porphyrin ligand, it has in the past been

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TABLE 1. 360 MHz ^1H NMR spectral characteristics of organocobalt porphyrins in C_6D_6

Alkyl group (R)	Co(III) (OEP) (R)					
	H_α	H_β	H_γ	H_δ		
CH_3	–5.20 ppm					
CH_2CH_3	–4.08 ppm (br)					
CH_2CH_3 (+ pyr- d_5)	–4.35 (q, 2H)	–5.47 (t, 3H)	–5.24 (t, 3H)			
$\text{CH}_2\text{CH}_2\text{OH}$	–4.36 (br)	–3.08 (t, 2H)	OH not detected			
$\text{CH}_2\text{CH}_2\text{NH}_2$	–6.17 (br)	–2.75 (br)	N–H not detected			
$\text{CH}_2\text{CH}_2\text{COCH}_2\text{CH}_3$	–2.71, 6.71 (br)	–9.22 (br)	+2.54 ppm (q, 2H)	+0.36 ppm		
$\text{CH}_2\text{C}_6\text{H}_5$	–2.67 (br)	3.15 (2H)	5.56 (2H)	7.09 (2H)		
$\text{CH}_2\text{C}(\text{CH}_3)_3$	–4.40 (br)		–2.89 (9H)			
Alkyl group (R)	Co(III) (TPP) (R)					
	H_α	H_β	H_γ	H_δ	H_ϵ	H_η
	–2.63 (s)		1.60 (s)	3.17 (d)	5.65 (d)	
	–3.38 (m)	–3.38 (m)		5.07 (d)	6.45 (m)	6.45 (m)
CH_3	–4.75 (s)					
CH_2CH_3	3.53 (q)					
$\text{CH}_2\text{CH}_2\text{CH}_3$	–3.62 (t)	–4.43 (t)	–4.64 (t)			
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	–3.56 (t)	–4.64 (m)	–1.35 (m)	–0.73 (t)		
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	–3.68 (t)	–4.81 (m)	–1.48 (m)	–0.55 (m)	0.00 (m)	+0.40 (m)
$\text{CH}_2-\text{CH}-\text{CH}_3$ CH_3	–3.73 (d)	–5.15 (m)	–2.04 (d)			

assumed that the closer the coordinated alkyl protons are to the porphyrin ring, the higher upfield are these resonances, due to the closeness in distance of these protons to the ring current of the porphyrin macrocycle [4]. This assumption means that the α -protons in organocobalt porphyrins should be the furthest upfield. Indeed, as seen in Table 1, this is true when $R = -CH_2C_6H_5$, or $-CH_2C(CH_3)_3$ [1]. However, when $R = -CH_2CH_3$, $-CH_2CH_2CH_3$ and $-CH_2CH_2CH_2CH_2CH_3$, the β -protons are the highest upfield, suggesting that these protons are now closer to the porphyrin ring than the α -protons. A possible bonding situation resulting in the β -protons becoming closer to the porphyrin ring is via an agostic interaction of the β -protons with the Co(III), as depicted in Fig. 1. Indeed, agostic interactions most often involve β -carbon hydrogens. When an axial ligand (such as pyridine- d_5) is added to the five-coordinate complexes (thus forming coordinatively saturated eighteen-electron six-coordinate species), the order of chemical shifts for the coordinated alkyl protons is changed (see Table 1), and there is no broadening of the α -hydrogen resonances (see Fig. 2). Since an

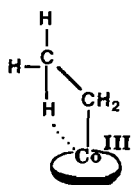


Fig. 1. Possible bonding scheme for interaction of β -protons with Co(III) porphyrin to form an agostic interaction.

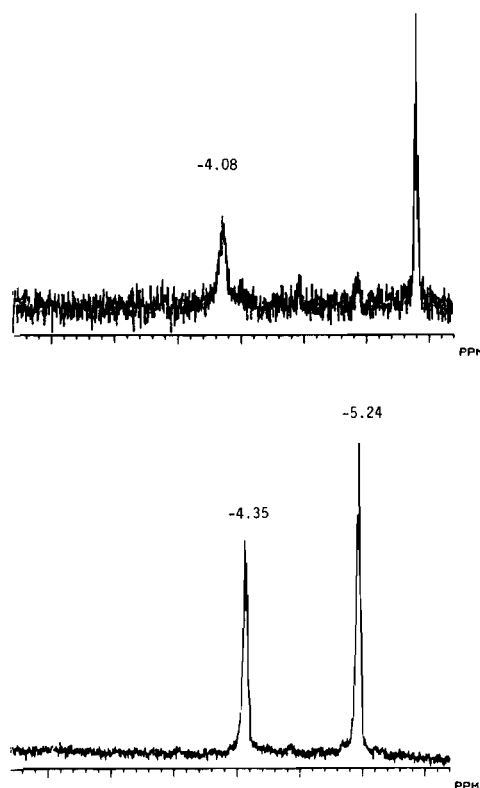


Fig. 2. 360 MHz 1H NMR spectrum of Co(III)(OEP)($-CH_2CH_3$) in C_6D_6 (top) at ambient temperature, and spectrum of Co(III)(OEP)($-CH_2CH_3$) in the C_6D_6 with a ten-fold excess of pyridine- d_5 (bottom) at ambient temperature. Only the region of the coordinated alkyl proton resonances is shown.

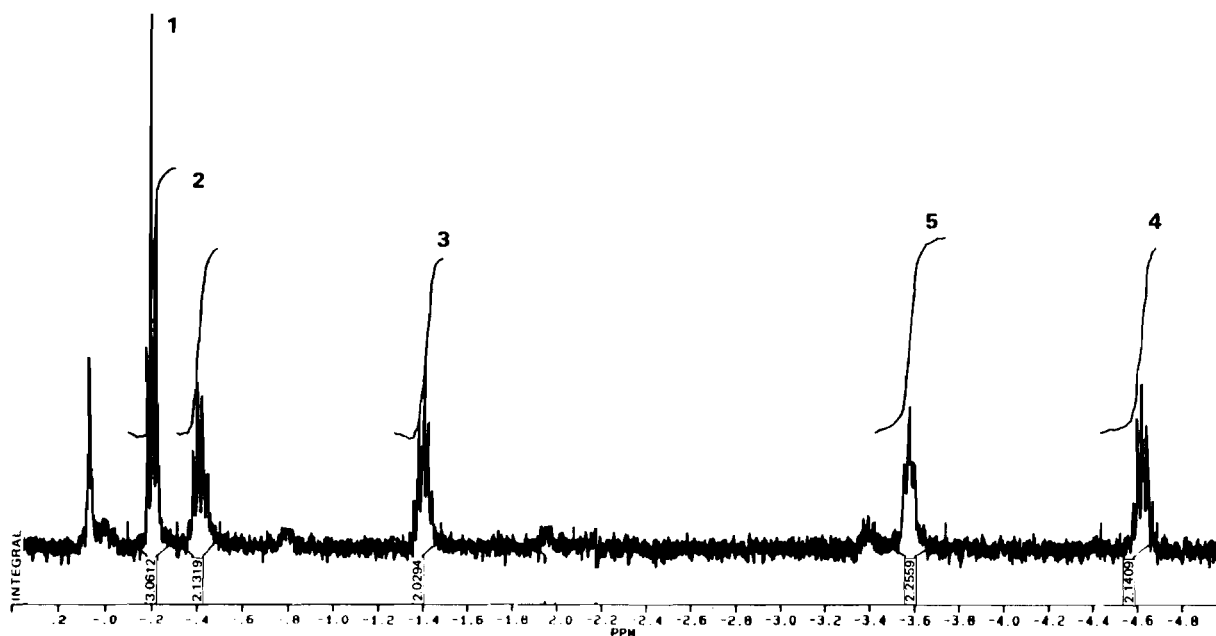


Fig. 3. 360 MHz 1H NMR spectrum of Co(III)(TPP)($-CH_2CH_2CH_2CH_2CH_3$) in C_6D_6 at ambient temperature in the region of the coordinated alkyl proton resonances only. The coordinated alkyl protons are numbered 5, 4, 3, 2, 1 starting from the α -methylene protons.

eighteen-electron species is now formed, the metal is less capable of perusing an agostic interaction to increase its coordination number. The assignment of the proton chemical shifts has been made by careful integration and decoupling experiments. Figure 3 depicts a typical ^1H NMR spectrum (360 MHz) of an organocobalt(III) porphyrin (where $\text{R} = -\text{CH}_2\text{CH}_2-\text{CH}_2\text{CH}_2\text{CH}_3$ and porphyrin = tetraphenylporphyrin, in the region of the alkyl proton resonances only).

When 2-phenylethyl is used as the axial alkyl ligand, the unusual β -proton chemical shift is not seen. However, the α - and β -protons are isochronous since one signal is seen for both, and this molecule exhibits a special case where the α - and β -proton are at equivalent distances from the porphyrin ligand. This can be explained by the steric repulsion between the phenyl group and the porphyrin ligand, making the alkyl protons inaccessible for an agostic interaction (see Fig. 1; they appear in the expected order: $C_{\alpha\text{-H}} > C_{\beta\text{-H}} > C_{\gamma\text{-H}}$) [7].

Perrée-Fauvet and Gaudemer postulated that the unusual β -proton chemical shift in organocobalt(III) tetraphenylporphyrins is due to 'an aromatic solvent effect' [5], whereas Ogoshi *et al.* have guessed that this shift as well as the α -proton broadening is due to the electronegativity of the Co(III) ion and quadrupolar relaxation [7]. It is interesting to compare the protons in the alkyl group R for $\text{Rh}(\text{OEP})\text{R}$, as they appear in the expected order: $C_{\alpha\text{-H}} > C_{\beta\text{-H}} > C_{\gamma\text{-H}}$. None of these explanations adequately explains the β -proton chemical shifts of the five-coordinate versus the six-coordinate (pyridine adducts) of the organocobalt(III) porphyrins nor the anomalous broadening of the α -proton resonances. An agostic interaction of the protons in the five-coordinate species explains adequately the positions of the alkyl proton resonances with reference to the distance of these protons from the porphyrin macrocycle. Indeed, Ogoshi has used isoshielding tensors in organorhodium(III) porphyrins to correlate proton chemical shifts of coordinated alkyl protons with the distance of these protons from the porphyrin ring in $(\text{OEP})\text{Rh}(\text{III})(\text{R})$ complexes, where OEP = octaethylporphyrinato

dianion*. Furthermore, an agostic interaction is also verified by the fact that when we deliberately coordinatively saturate our sixteen-electron complexes $[(\text{porphyrin})\text{Co}(\text{III})(\text{R})]$ by adding a sixth axial ligand (pyridine- d_5), and obtain an eighteen-electron complex, the β -proton chemical shift is now at lower field and the α -proton resonances are very sharp, thus losing the agostic interaction and increasing the covalency of the Co(III) ion [8]. This observation is the first of its kind in organometallic porphyrin chemistry, and will perhaps be discovered to be more prevalent in bio-organometallic chemistry where activation of hydrocarbons is involved.

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*Efforts are currently under way to use Green's method of partial deuteration to detect the agostic interaction as well as to try to crystallize the complex for X-ray diffraction analysis. Additional support for a β -agostic interaction of the $-\text{CH}_2\text{CH}_3$ group is provided by infrared spectrophotometry and cyclic voltammetry. We have detected low-energy C-H stretching absorptions in the 2500–3000 cm^{-1} frequency range, the usual $\nu(\text{C}-\text{H})$ absorption frequency range for agostic compounds [8]. In addition, $E_{1/2}$ for a series of $\text{Co}(\text{OEP})(\text{R})(\text{L})$ complexes where $\text{R} = -\text{CH}_3$, $-\text{CH}_2\text{CH}_3$ and $-\text{CH}_2\text{C}(\text{CH}_3)_3$ and $\text{L} = \text{pyridine}$ showed the $\text{Co}^{\text{III/II}}$ potentials to be -0.853 , -1.013 and -1.110 V versus SCE, respectively.