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Preliminary communication

NOVEL TITANIUM(III) PORPHYRINS WITH ARYL AXIAL LIGANDS. REDOX STOICHIOMETRY TUNED BY AXIAL LIGATION

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Summary

Aryltitanium(III) porphyrin complexes have been prepared by anaerobic treatment of fluorotitanium(III) tetraphenylporphyrin with various aryl Grignard reagents. They react with dioxygen to give oxotitanium(IV) tetraphenylporphyrin and the corresponding biaryl.

Organometalloporphyrins of the transition series, i.e. porphyrin complexes which have an axial transition metal—carbon bond to an organic ligand, have been known for group VIII metals for several years [1]. However, such compounds have not previously been described for early transition metals, and unsuccessful attempts to isolate organoniobium(V) porphyrins have led to the conclusion [2] that the porphyrin ligand is much less effective than the cyclopentadienyl ligand in giving organoniobium derivatives. We now report the synthesis of some titanium(III) porphyrins with aryl axial ligands which demonstrate the possibility of formation of stable metal—carbon bonds in early transition metal-porphyrin complexes.

The fluorotitanium(III) complex of tetraphenylporphyrin, TiF(tpp) [3], was treated with an aryl or benzyl Grignard reagent as detailed by Teuben for the arylation of chlorotitanocene [4]. All operations were conducted in a glove box under argon maintained at 1—5 ppm O_2 (reaction 1):

$$\mathrm{TiF(tpp)} + \mathrm{ArMgBr} \xrightarrow{C_6H_5CH_3/THF} \mathrm{TiAr(tpp)} + \mathrm{MgBrF} \qquad (1)$$

The reaction was monitored by the disappearance of the characteristic EPR spectrum of the fluoro complex [3] and concomitant appearance of the spectrum shown in Fig. 1. The three aryltitanium(III) porphyrins thus obtained ($Ar = C_6H_5$, o-$CH_3C_6H_4$, $CH_2C_6H_5$) have been isolated as purple oxygen-sensitive crystals. Their toluene solutions exhibit very similar nine-line EPR spectra, reflecting interaction of the unpaired electron with the four equivalent

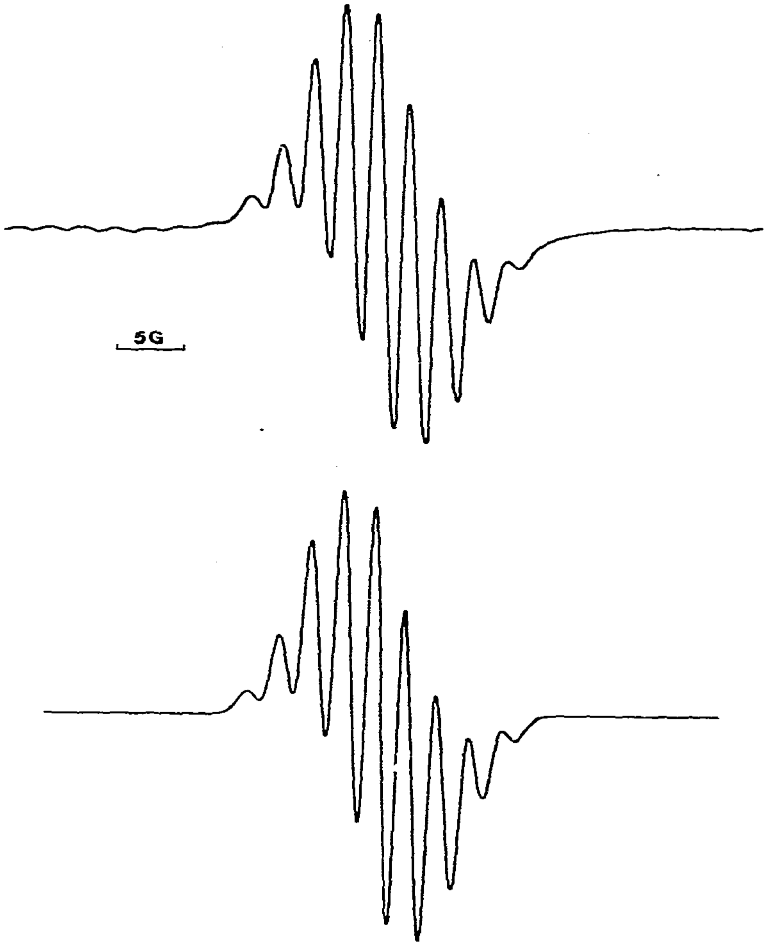

Fig. 1. (Top) Electron paramagnetic resonance spectrum of Ti(o-$CH_3C_6H_4$)(tpp) in toluene at room temperature. Conditions of EPR spectroscopy: microwave frequency, 9.52 GHz; magnetic field central value 3338 G; microwave power, 20 mW; modulation amplitude, 0.16 G; magnetic field sweep rate, 25 G min^{-1}; time constant, 0.3 s; instrument gain, 3.2×10^2. This spectrum shows hyperfine interaction with the four equivalent porphyrin nitrogens with a splitting of 2.3 G; g value: 1.967. (Bottom) Calculated spectrum with $4 \times (a_N = 2.3$ G).

nitrogen nuclei of the porphyrin. Electronic absorption spectra in toluene solution support the formulation of these compounds as five-coordinate complexes of the type TiAr(tpp). Satisfactory elemental analyses were not obtained, presumably due to the high oxygen sensitivity of these compounds and the presence of residual magnesium halides. However, the structure assigned to these compounds on the basis of their EPR and UV-visible spectra was corroborated by the identification of their autoxidation products (vide infra).

Addition of various ligands (pyridine, *N*-methylimidazole, THF) to a toluene solution of Ti(C_6H_5)(tpp) leaves its UV-visible and EPR spectra unchanged, pointing to a preference of titanium(III) for five-coordination in this complex. This behaviour contrasts with that observed for TiF(tpp), which readily affords six-coordinate complexes [3]. A phenyl group as an axial ligand probably leads to increased negative charge at the titanium(III) ion relative to fluoride, thus explaining the decreased tendency of the phenyl complex to bind σ-donor ligands.

Similar arguments can be used to account for the influence of the axial ligand on the reactions observed with dioxygen. The fluoro complex TiF(tpp) has been shown previously to react with O_2 in dichloromethane to afford a 1/1 mixture of $\mathrm{Ti(O_2)(tpp)}$ and $\mathrm{TiF_2(tpp)}$ [3]. The reaction of the phenyl complex $\mathrm{Ti(C_6H_5)(tpp)}$ with O_2 in toluene leads to entirely different products, however. The only metalloporphyrin which is obtained is the oxo complex TiO(tpp) [5]; moreover, biphenyl (separated by HPLC and identified by IR) is formed in the process. Detection of the latter suggests intermediate formation of phenyl radicals, implying the following two-step mechanism:

$$\begin{tikzcd}[column sep=small]
\mathrm{Ti(C_6H_5)(tpp)} + \mathrm{O_2} \rightarrow \mathrm{Ti(O_2)(tpp)} + \mathrm{C_6H_5}\cdot \arrow[dr] & & (2) \\
& (\mathrm{C_6H_5})_2 & \\
\mathrm{Ti(C_6H_5)(tpp)} + \mathrm{Ti(O_2)(tpp)} \rightarrow 2\mathrm{TiO(tpp)} + \mathrm{C_6H_5}\cdot \arrow[ur] & & (3)
\end{tikzcd}$$

Binding of O_2 to the titanium(III) ion in a first step affords the peroxo complex $\mathrm{Ti(O_2)(tpp)}$ and a phenyl radical (reaction 2). This reaction is a two-electron reduction of dioxygen by the titanium(III) complex $\mathrm{Ti(C_6H_5)(tpp)}$ and it requires redox assistance from the phenyl axial ligand. The peroxo complex itself is a two-electron oxidant [6] which undergoes oxygen-atom abstraction from another $\mathrm{Ti(C_6H_5)(tpp)}$ molecule in a second step, leading to two molecules of the oxo complex (reaction 3); this has been checked in separate experiments. The benzyl complex $\mathrm{Ti(CH_2C_6H_5)(tpp)}$ behaves similarly upon exposure to dioxygen.

In contrast to the two-electron reduction of dioxygen in two successive one-electron steps which has been observed in the reaction TiF(tpp) + O_2 [3], the above process is a four-electron reduction of dioxygen in two successive two-electron steps. The possibility of "tuning" the redox stoichiometry of metalloporphyrins by controlling the axial ligand located *trans* to the dioxygen binding site is thus confirmed [7]. Various possible implications in catalysis will be explored.

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