is possible to carry out labeling experiments which clearly distinguish these two alternatives. This involves treatment of appropriately labeled **1** with labeled and unlabeled ethylene, and analysis of the isotopic distribution in the methane and propene produced. In methane formed by the insertion pathway, three of the hydrogens derive from the initial methyl group and the fourth originates in the ethylene. A complete methyl group is also transferred to the ethylene. In the α-elimination pathway the fourth hydrogen originates on the second methyl group, and a methylene group is transferred to the ethylene.

When **1**-d_{21} (completely deuterated phosphine and methyl groups) was treated with ethylene, mass spectral analysis of the product methane[9,10] showed that it was identical with CD_3H synthesized by quenching a portion of the CD_3MgI, used to prepare **1**-d_{21}, with H_2O. Similar analysis of the propene produced showed it to be ≥96% propene-d_3. In a second experiment, reaction of **1**-d_{21} with ethylene-d_4 gave 95% CD_4. These results demonstrate that (a) the new methane hydrogen is derived from the ethylene and from no other hydrogen source in the system (cyclopentadienyl ring, solvent, phosphine) and (b) a complete methyl group is transferred to the ethylene. This clearly establishes insertion, rather than α-elimination, as the mechanism responsible for ethylene methylation by complex **1**.

It is still certainly possible that Ziegler-Natta polymerization and/or other apparent insertion reactions take place by the α-elimination route. However, in our opinion, those in favor of this mechanism must now shoulder the burden of proof for establishing it.

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(9) Heating 2 mL of 0.14 M 1-d_{21} (≥97.6 atom % D in methyl, ≥98.4% in phosphine phenyl; by NMR) in benzene-h_6 at 54 ± 1 °C for 120 h under 11 atm (27 equiv) of ethylene. Mass spectra (50 eV), *m/e* (relative intensity, corrected for background and ^{13}C contributions): synthetic CD_3H, 19 (100.0), 18 (39.9), 17 (44.1), 16 (4.0), 15 (2.1), 14 (1.9); methane from **1**-d_{21} and ethylene, 19 (100.0), 18 (39.5), 17 (43.5), 16 (3.9), 15 (2.1), 14 (1.9).

(10) At higher temperature, **1** decomposes slowly in benzene solution ($t_{1/2} \sim$ 120 h, 70 °C) to give a mixture of methane and ethane (6:1) and as yet uncharacterized organometallic products. The methane produced by decomposing 1-d_{21} (completely deuterated phosphine and methyl groups) in benzene-d_6 is mostly CD_3H (>80%). This side reaction accounts for ≤2% of the products formed under the milder ethylene reaction conditions.

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Titanium(III) Porphyrins and Their Dioxygen Adducts

Sir:

There is wide current interest in the reactions of low-valent metalloporphyrin complexes with molecular oxygen.[1] We report here a convenient synthetic procedure for the isolation of coordinatively unsaturated titanium(III) porphyrins, some mechanistic implication for their autoxidation, and the stabilization of a reversible titanium(III)-dioxygen adduct by immobilization in a host crystal lattice.

Stirring a suspension of $Ti(F)_2(TPP)$[2,3] with zinc amalgam in dry, oxygen-free benzene gives a pink solution from which the five coordinate d^1 complex Ti(F)(TPP), **1**, can be isolated as purple crystals.[4,5] Hyperfine splittings in the EPR spectrum of **1** in CH_2Cl_2 at room temperature (Figure 1) indicate substantial interaction of the unpaired electron with the axial fluoride ligand and weaker interactions with the four equivalent porphyrin nitrogens (Table I).[6] Consistent with the presence of a vacant coordination site in **1**, changes in the EPR and UV-visible spectra are observed upon addition of ligands

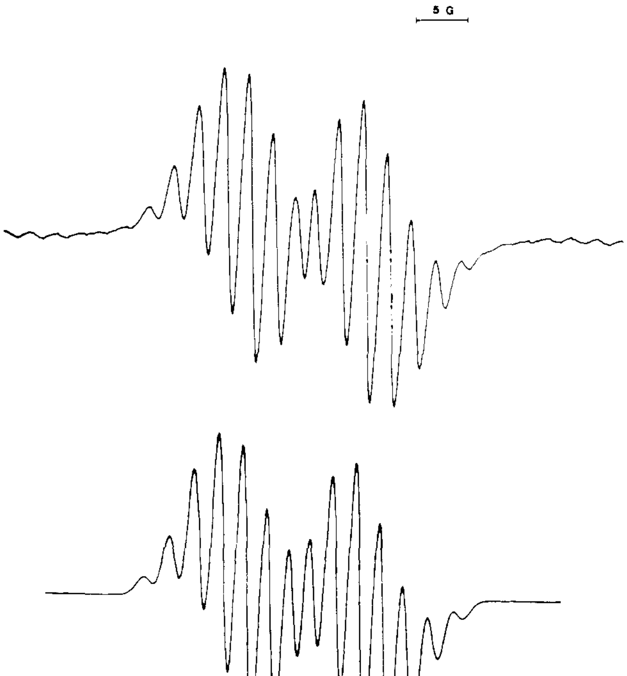

Figure 1. Experimental (top) and simulated (bottom) EPR spectra of Ti(F)(TPP) in dichloromethane at 25 °C.

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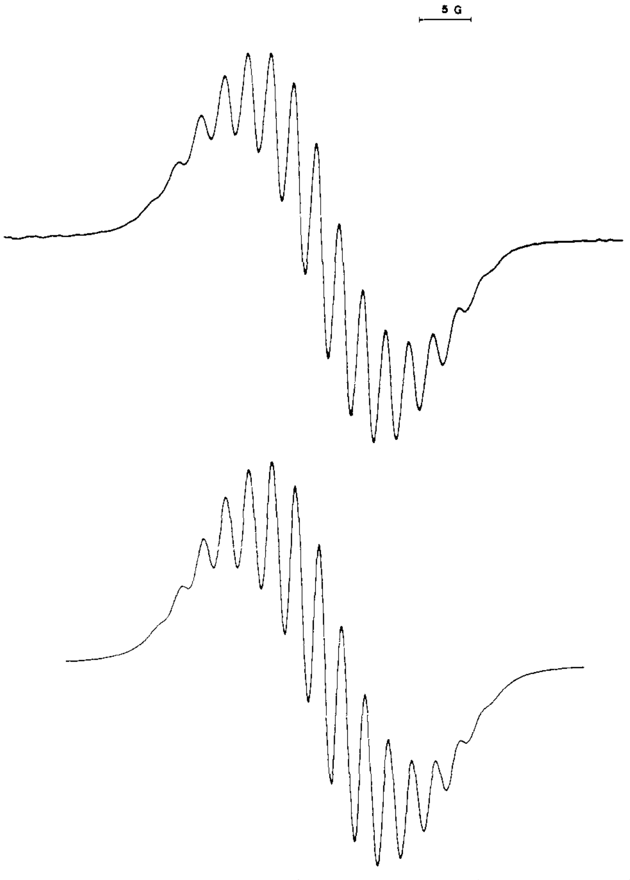


Figure 2. Experimental (top) and simulated (bottom) EPR spectra of $[Ti(F)_2(TPP)]^-$ in 10^{-1} M CH_2Cl_2-Bu_4NPF_6 at 25 °C.

Table I. EPR Parameters of Titanium(III) Porphyrin Complexes

complex	g	a_F, G	a_N, G	a_L (nucleus), G
Ti(F)(TPP)	1.972	11.1	2.29	
$[Ti(F)_2(TPP)]^-$	1.968	6.7	2.20	6.7 (F)
Ti(F)(OEP)	1.973	10.9	2.34	
$[Ti(F)_2(OEP)]^-$	1.971	6.3	2.25	6.3 (F)
Ti(F)(THF)(TPP)	1.965	9.6	2.35	
Ti(F)(Py)(TPP)	1.964	9.5	2.2	1.0 (N)
Ti(F)(1-MeIm)(TPP)	1.961	9.8	2.5	1.0 (N), 0.7 (N)
Ti(F)(NMP)(TPP)	1.963	9.8	2.4	0.7 (N)
$Ti(F)(PBu_3)(TPP)$	1.970	9.0	2.35	0.84 (P)

(L). These are accounted for by the formation of six-coordinate complexes of the type Ti(F)(L)(TPP). Values of the hyperfine splittings obtained from a comparison of experimental and simulated EPR spectra for several such complexes are listed in Table I.

Upon electrochemical reduction in dichloromethane with 10^{-1} M Bu_4NPF_6 or Bu_4NClO_4 as electrolyte, and upon chemical reduction with sodium anthracenide in benzene-THF, $Ti(F)_2(TPP)$ retains both its axial fluoride ligands and gives the anionic Ti(III) complex $[Ti(F)_2(TPP)]^-$, **2**, whose experimental and simulated EPR spectra are shown in Figure 2. The latter is also obtained, as expected, upon addition of Et_4NF to **1**. These observations indicate a strong preference of titanium(III) porphyrins for six coordination, the five-coordinate **1** being obtained only with fluorine atom abstracting reductants such as $Cr(acac)_2$ or zinc amalgam.

The orbital in which the unpaired electron resides in all the titanium(III) porphyrin complexes is reasonably thought to be the metal $3d_{xy}$ level. Numerous EPR studies on the isoelectronic vanadium(IV) complex V(O)(TPP),[7] and on the $4d^1$ molybdenum(V) compounds Mo(O)(OR)(TPP)[8] or $[Mo(O)(TPP)]_2O$[9] have been interpreted in terms of a singly occupied d_{xy} orbital. Extended Hückel calculations on V(O)(TPP)[10] gave support to this assignment and placed the 3d orbitals in the order $d_{x^2-y^2} > d_{z^2} \gg d_{xz}, d_{yz} > d_{xy}$. This result can be applied safely to the five-coordinate Ti(F)(TPP). In the six-coordinate complexes Ti(F)(L)(TPP), the presence of an additional axial ligand raises the d_{xz}, d_{yz} orbital pair to higher energies relative to d_{xy}, again resulting in a $(3d_{xy})^1$ ground state. The small value of the hyperfine coupling from the four equivalent porphyrin nitrogen nuclei, a_N = 2.2–2.5 G, is also consistent with this ground state, and compares well with the range found in vanadium(IV) and molybdenum(V) porphyrins (2.3–2.8 G). The substantially higher value of the coupling from the axial ligand in Ti(F)(TPP) or Ti(F)(OEP) reflects in fact a small electron spin density at the fluorine nucleus whose magnetic moment is large,[11] in agreement with the proposed electron configuration. Finally, the fluorine coupling (6.3–6.7 G) observed for $[Ti(F)_2(TPP)]^-$ or $[Ti(F)_2(OEP)]^-$ is comparable with the value (7.5 G) found for *trans*-$[Ti(F)_2(H_2O)_4]^+$.[12]

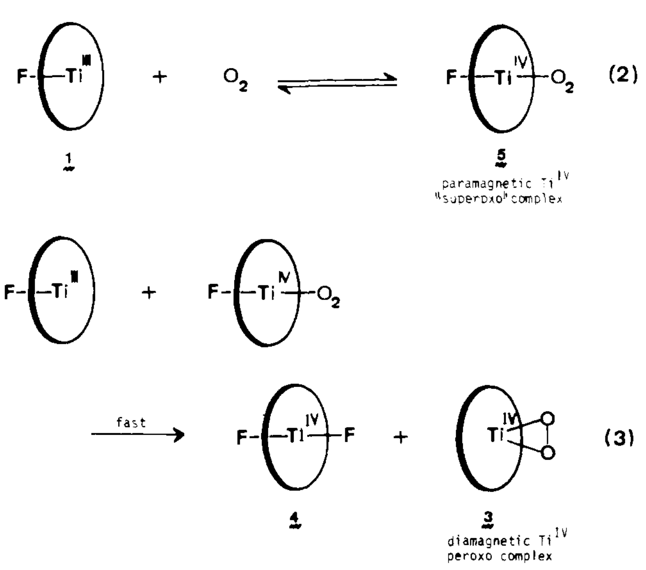
When exposed to oxygen, solutions of Ti(F)(TPP) in dichloromethane or benzene rapidly autoxidize giving a mixture of the known peroxo Ti(IV) complex $Ti(O_2)(TPP)$,[13] **3**, and of $Ti(F)_2(TPP)$, **4**, in roughly equal amounts, as deduced from UV-visible spectroscopy and voltammetry:

$$2Ti(F)(TPP) + O_2 \rightarrow Ti(O_2)(TPP) + Ti(F)_2(TPP) \quad (1)$$

Autoxidation of Ti(F)(L)(TPP) is somewhat slower, reflecting a kinetic stabilization by L which is present in excess and presumably prevents rapid dissociation to the dioxygen binding species **1**.

Autoxidation of **1** also occurs in the solid state, albeit slowly. Interestingly, this process involves a migrating fluorine atom. Crystals of **1** were ground and exposed to air, and IR spectra of samples dispersed in KBr were recorded to monitor the reaction. The characteristic Ti–F stretch of **1** at 680 cm^{-1} slowly decreased while bands at 900 and 647 cm^{-1}, corresponding, respectively, to O–O stretch of **3** and Ti–F stretch of **4**, gradually increased with time. No band attributable to an expected transient six-coordinate superoxo Ti(IV) complex, **5**, was observed. Such an intermediate, when formed in the crystal lattice of **1**, probably lies close enough to its nearest Ti(III) neighbor to undergo fluorine atom abstraction and subsequent rearrangement to **3** (Scheme I). We have tried to stabilize **5** by slowing down reaction 3 at low temperatures. However, even at −80 °C in toluene, no EPR resonance corresponding to the hypothetical paramagnetic **5** was found; the only observed resonance was that of **1** slowly decaying to the diamagnetic

Scheme I



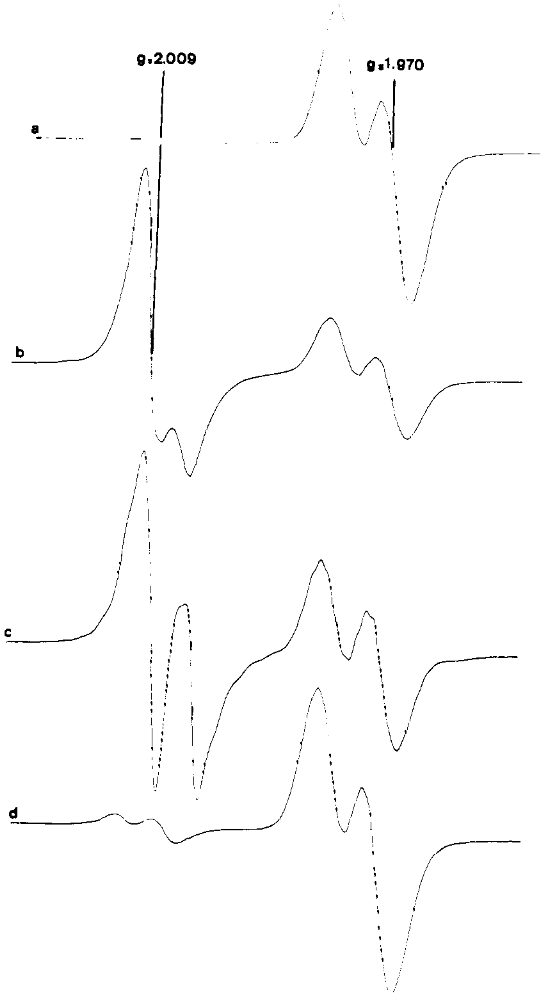


Figure 3. EPR spectra of Ti(F)(TPP) ~1% in Ti(O)(TPP) host crystals: (a) under argon at 20 °C; (b) under dioxygen at 20 °C (the new signal at g = 2.009 corresponds to the dioxygen adduct $Ti(O_2)(F)(TPP)$, **5**); (c) under dioxygen at −196 °C; (d) after evacuation overnight at 20 °C. Conditions of EPR spectroscopy: microwave frequency, 9.1 GHz; microwave power, 20 mW; modulation amplitude, 0.16 G; magnetic field sweep rate, 50 G/min^{-1}; time constant, 0.25 s; instrument gain, 250 (a, b, d), 200 (c).

compounds **3** and **4**. The high stability of $Ti(O_2)(TPP)$ and the preference of **1** for six coordination probably are strong driving forces for reaction 3. Reasoning that combined immobilization and dilution of the dioxygen binding sites of **1** might afford the desired kinetic stabilization of **5**, we grew crystals from a CH_2Cl_2 solution containing Ti(O)(TPP),[14] **6**, and Ti(F)(TPP) in an ~100:1 ratio. EPR examination of the ground crystals under Ar at room temperature shows that **1** is indeed present in low concentration in the lattice of the diamagnetic, probably isostructural **6** (Figure 3a). Upon admission of O_2, a new two-line signal grows at lower field (g = 2.009), while the resonance of **1** decreases in intensity (Figure 3b). Evacuation of the sample for a few hours restores the signal of **1** almost quantitatively (Figure 3d). Eight such oxygenation-deoxygenation cycles have been performed without any noticeable alteration in the EPR signal of **1**. The fact that the new paramagnetic species obtained under O_2 appears at the expense of **1**, and the observation that **1** is recovered upon evacuation of the sample, led to the safe conclusion that the new species is **5**, a dioxygen adduct of **1**. It would seem reasonable to assign to this dioxygen adduct the superoxo titanium(IV) formalism. At 77 K, however, the EPR signal of **5** reveals additional hyperfine structure, presumably from the porphyrin nitrogen nuclei (Figure 3c). Moreover, oxygenation of **1** with a ^{17}O–^{18}O mixture enriched to 25.29% ^{17}O results only in a small broadening of the EPR signal of **5** at 77 K. These observations indicate a substantial spin density on the porphyrin and only a small spin density on the dioxygen ligand,[15] and they suggest a significant contribution of a peroxo-porphyrin cation radical–titanium(IV) resonance form to the electronic configuration of **5**. Efforts are underway at this time to elucidate further the nature of the dioxygen adduct **5**.

The reactions of Ti(III) complexes with dioxygen have been studied for several years.[16] However, we believe this is the first demonstration that a mononuclear peroxo Ti(IV) complex can be prepared using O_2 and low-valent Ti rather than the more obvious H_2O_2 and Ti(IV) route. Moreover, this is the first report of a Ti(III) complex which gives a reversible dioxygen adduct. Finally, we note that the existence of two distinct mononuclear dioxygen complexes of a synthetic metalloporphyrin formally differing by one electron is unprecedented, and that it is conceptually reminiscent of cytochrome P-450 oxygenation and subsequent reduction.

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(2) Abbreviations: TPP = *meso*-tetraphenylporphyrinato; OEP = octaethylporphyrinato; Et_4N = tetraethylammonium; Bu_4N = tetrabutylammonium; acac = acetylacetonato; PBu_3 = tri-*n*-butylphosphine; THF = tetrahydrofuran; Py = pyridine; NMP = *N*-methylpyrrolidone; 1-MeIm = *N*-methylimidazole; EPR = electron paramagnetic resonance.

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Detection of Thiobenzoylphenylmethylene by Electron Spin Resonance Spectroscopy

Sir:

Ketocarbenes have been implicated in a large variety of reactions involving the thermal and photochemical decom-