versible degradation of the CdSe.[2b] This effect is alleviated by any factor which increases the rate of sulfur dissolution in polysulfide solution, such as an increase in $[S^{2-}]$ or addition of Se^{2-} to the electrolyte. Thus, in the CdSe/polysulfide system, NR can be looked upon as a measure of the stabilizing influence of the electrolyte on the photoelectrode. In the course of several accelerated output stability experiments (corresponding to at least a month under day-night AM1 conditions), the NR of the PEC was checked. It was found that the most stable PEC (as judged by remaining output after passing a fixed number of coulombs) also gave the lowest NR.[11] The earlier reported difference in stability between single-crystal and thin layer polycrystalline CdSe photoelectrode PEC's[2b] is also reflected in lower NR's for the latter, more stable system. The cause for this lies probably in lower real current densities on the high surface area, polycrystalline electrodes.

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(4) The cell was kept in the dark for 10 min prior to illumination, to ensure complete decay of any, previous, light-induced processes.
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(12) This research was supported in part by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel.

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Preparation of a Porphyrin–Iron–Carbene Model for the Cytochrome P 450 Complexes Obtained upon Metabolic Oxidation of the Insecticide Synergists of the 1,3-Benzodioxole Series

Sir:

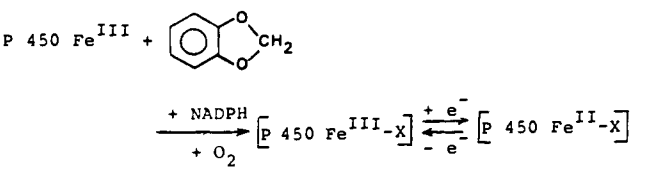
Evidences have been presented in favor of the formation of cytochrome P 450–iron–carbene complexes during reductive metabolism of polyhalogenated compounds.[1-3] These compounds do react with ferroporphyrins, in the presence of an excess of reducing agent, leading to stable iron(porphyrin)(carbene) complexes.[4-7] (eq 1). The iron–carbene structure of one of them has been definitely established by an X-ray analysis.[8]

$$Fe^{II}(P) + RR'CX_2 \xrightarrow[-2\ X^-]{+2\ e^-} Fe^{II}(P)(CRR') \qquad (1)$$

P = porphyrin or cytochrome P 450

Various derivatives of 1,3-benzodioxole are well-known insecticide synergists. Their use in combination with an insecticide results in a marked increase in toxicity, presumably because of their ability to inhibit the enzymes responsible for insecticide detoxication.[9] The benzodioxole derivatives are oxidatively metabolized in vivo and in vitro by cytochrome P 450 dependent monooxygenases with formation of very stable complexes of this cytochrome in the ferrous state, characterized by a Soret peak at 455 nm.[10] After aerobic removal of the reducing agent (NADPH), the Soret band shifts to 438 nm which has been explained by the formation of the corresponding ferric complexes.[10c-d] The latter are also obtained by reaction of cytochrome P 450 with benzodioxole derivatives in the presence of cumene hydroperoxide.[10d]

Scheme I



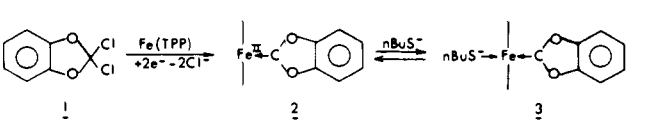
The great stability of the iron–metabolite (X) bond in these complexes is probably at the origin of the synergistic action of the benzodioxole derivatives (Scheme I). It has been proposed[11] that the iron ligand present in these complexes is the 1,3-benzodioxole-2-carbene[12] formed by oxidation of the methylene group of 1,3-benzodioxole.

The present paper describes the isolation and characterization of an iron(II)(porphyrin)(1,3-benzodioxol-2-carbene) complex, obtained by reduction of 2,2-dichloro-1,3-benzodioxole according to eq 1, and brings indirect evidence for the presence of this carbene as ligand in the benzodioxole-derived cytochrome P 450–iron(II) complexes (Scheme I).

Addition of deaerated 2,2-dichloro-1,3-benzodioxole (**1**)[13a] to an NMP[14] solution of Fe^{II}(TPP) results in an immediate oxidation of the iron, giving Fe^{III}(TPP)(Cl). Progressive addition of 2 equiv of compound **1**[13b] to a CH_2Cl_2–NMP (20/1) solution of Fe(TPP) vigorously stirred in the presence of an excess of iron powder as a reducing agent leads to the formation of a new species characterized in visible spectroscopy (in benzene) by peaks at 412 and 516 nm. After filtration and two crystallizations from CH_2Cl_2–CH_3OH, purple crystals of complex **2** are obtained (yield, ≃50%). Its following characteristics—λ 412 nm (ϵ 2×10^5), 516 (18×10^3), 540 (sh), in benzene; ^{1}H NMR (C_6D_6, Me_4Si) 8.82 (s, 8 H), 8.02 (m, 8 H), 7.27 ppm (m, 12 H), for the protons of the porphyrin ring; ^{13}C NMR (C_6D_6, Me_4Si) 148.3, 143.7, 134.5, 133.8, 128.1, 126.8, 122.3 ppm, for the carbons of the porphyrin ring—are indicative of a low-spin iron(II)–porphyrin complex with an axial symmetry. They are similar to those which have been reported for the pentacoordinated Fe(TPP)(CS)[6] and Fe(TPP)(carbene)[4,5,7] complexes. The presence of the axial 1,3-benzodioxole-2-carbene ligand in complex **2** is indicated by its mass spectrum which exhibits two intense peaks at *m/e* 120 and 240 corresponding to the $C_7H_4O_2$ carbene and to the olefin obtained by its dimerization.[15a] Moreover, the only signals which appear in addition to those of the porphyrin in the ^{1}H and ^{13}C NMR spectra of complex **2**—^{1}H NMR δ 5.23 (m, 2 H), 4.8 ppm (m, 2 H); ^{13}C NMR 107.2, 122.5, 147.4 ppm—are those which are expected for a benzodioxole-derived carbene[15c] bound to iron and held in a close proximity to the porphyrin ring[15b] (Scheme II). Complex **2** is stable in deaerated solution, but slowly oxidized to the μ-oxo[Fe^{III}(TPP)]$_2$O complex in the presence of oxygen ($t_{1/2}$ in benzene at 27 °C, ≃0.5 h).

In the cytochrome P 450 complex where the iron(II) is

Scheme II



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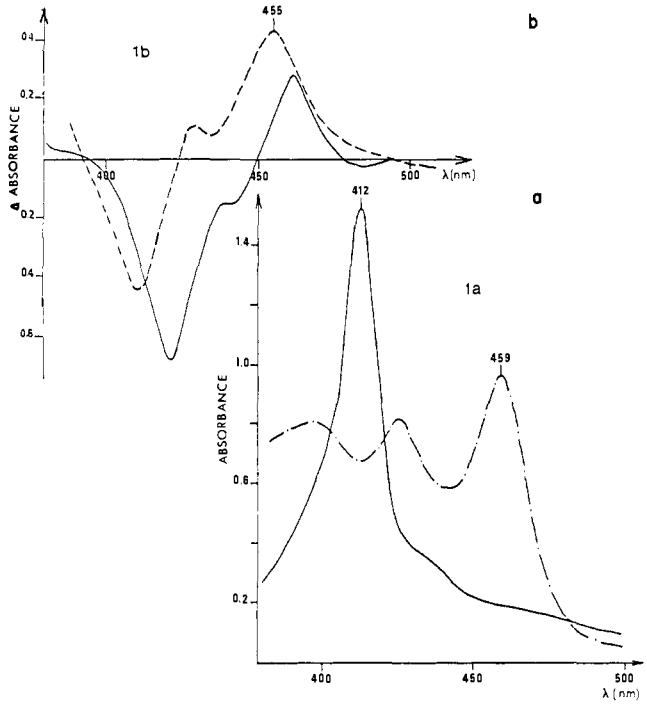

Figure 1. (a) —, electronic spectrum, at 20 °C, of complex **2**, 7.8×10^{-6} M in toluene; -·-, spectrum at −10 °C, 0.3 min after addition of 150 μL of a DMF solution of *n*-BuSK (10^{-1} M) and dibenzo-18-crown-6 ether (5×10^{-2} M) to the 3-mL cuvette containing complex **2** (for this last spectrum, $A \times 1/2$). (b) -·-, difference spectrum of rat liver microsomes (cytochrome P 450, 3 μM) after addition of 10^{-3} M 1,3-benzodioxole and 10^{-3} M NADPH to the sample cuvette, 5-min incubation, and, then, addition of $Na_2S_2O_4$ to both cuvettes ($A \times 1/10$ for this difference spectrum); —, difference spectrum corresponding to 7.8×10^{-6} M complex **2** in toluene in the sample cuvette, 7.8×10^{-6} M Fe(TPP)(Cl) in toluene in the reference cuvette, and, then, addition of *n*-BuSK to both cuvettes (conditions of Figure 1a).

bound to a benzodioxole metabolite, the endogenous ligand of the iron, trans to the metabolite, is very probably a thiolate (cysteinate). This is suggested by its unusually red-shifted Soret peak (455 nm), which seems to be a characteristic of the iron(II)(porphyrin or hemoprotein)(RS^-)(L) complexes where a thiolate ligand is trans to various ligands (L) like CO,[16] isocyanides,[17] carbenes,[1-3] nitrosoalkanes,[18] nitrosoarenes,[19] thioethers,[20] phosphines,[21] and other phosphorus derivatives.[22] In order to obtain an actual model of the cytochrome P 450-iron(II)-benzodioxole metabolite complex, we have added alkyl thiolates, in the presence of a crown ether, to complex **2**.[23]

Complex **2**, like other iron(porphyrin)(carbene) complexes, is unstable to nucleophiles like pyridine, alkylamines, and thiolates, because of irreversible reactions between these nucleophiles and the carbene ligand.[4,5,8,27] However, the electronic spectrum of complex **2** in toluene, recorded at 25 °C just after addition under argon of *n*-butyl thiolate in excess, in the presence of dibenzo-18-crown-6 ether, exhibits a new peak at 459 nm which disappears within a few minutes. At −10 °C, the proportion of the 459-nm-absorbing species is higher (≃70%) and its destruction is slower (Figure 1a). These data suggest the formation of the model complex **3** immediately after thiolate addition,[24] followed by the destruction of the iron-carbon bond upon reaction with thiolate in excess. Accordingly, after disappearance of the 459-nm peak, addition of CO to the solution leads to the formation of the Fe(TPP)(CO)(*n*-BuS^-) complex, characterized by peaks at 375 and 449 nm.[16]

Figure 1b compares the visible difference spectra of the microsomal cytochrome P 450-iron(II)-benzodioxole-derived metabolite complex vs. microsomal cytochrome P 450 and of complex **2** vs. Fe(TPP)(Cl) just after addition of excess *n*-BuS^- to both cuvettes. Their similarity indicates that complex **3** is a model for the cytochrome P 450-iron(II)-benzodioxole-metabolite complex, strongly supporting the 1,3-benzodioxole-2-carbene nature of this metabolite.

Because of the strength of the iron-carbon bond in several previously described iron(porphyrin)(carbene) complexes,[4,5,7,8] these data could explain the inactivation of cytochrome P 450 by the benzodioxole carbene metabolite and, thus, the severe inhibition of the detoxifying monooxygenases of the insects.

The formation of the cytochrome P 450-benzodioxole-derived carbene complex is the first example of the involvement of an iron-carbene bond after the NADPH- and O_2-dependent oxidation of a substrate by cytochrome P 450. This should be an important point in the understanding of the mechanism of oxygen activation and oxidation of some substrates by cytochrome P 450. If one admits the proposition[26] that the active oxygenating cytochrome P 450 complex involves an oxo ligand, the formation of the carbene complex by 1,3-benzodioxole oxidation corresponds formally to the replacement of this oxo ligand by the 1,3-benzodioxole-2-carbene (eq 2).

$$\text{Cyt P 450 Fe}^{III} \xrightarrow[+\,2H^+\ -H_2O]{+\,O_2\,+\,2e^-} [\text{cyt P 450 Fe}^{V}{=}O] \xrightarrow[-\,H_2O]{+\,\text{benzodioxole}} \left[\text{cyt P 450 Fe}{=}C\begin{matrix}O\\O\end{matrix}\!\!\bigcirc\right] \quad (2)$$

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(13) (a) Prepared according to H. Gross, J. Rusche, and M. Mirch, *Chem. Ber.*, **96**, 1382 (1963). (b) **1** should be freshly distilled and added over a period of 10 h.
(14) NMP is used for *N*-methylpyrrolidone, TPP for the dianion of *meso*-tetraphenylporphyrin.
(15) (a) Upon heating of the sample (Varian CH 7 mass spectrometer), a spectrum corresponding to $C_7H_4O_2$ (*m/e* 120) and $C_{14}H_8O_4$ (*m/e* 240) appeared suddenly at 120 °C; this is due to the thermal decomposition of complex **2**. No peaks corresponding to the porphyrin were observable at this temperature. At 220 °C, the peaks of Fe(TPP) (M^+ 668) appeared. (b) The signals of the ortho and meta aromatic protons of the benzodioxole ligand were, respectively, shifted downfield by 1.65 and 1.22 ppm relative to those of pyrocatechol carbonate. (c) We could not detect the ^{13}C NMR signal of the carbenic carbon even with a C_6D_6 solution saturated with complex **2** (≃10^{-2} M) in the presence of $Cr^{III}(acac)_3$ (Bruker WH 90, sweep width 6000 Hz, 20 000 45° pulses, 8 K point memory blocks, acquisition time 2 s). This has been previously encountered with such quaternary carbenic carbons far from any proton.[4,7]
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(23) This procedure has been used to obtain the visible spectra of model complexes of CO–[16] and NO–iron(II)–cytochromes P 450: J. O. Stern and J. Peisach, *FEBS Lett.*, **62**, 364 (1976).
(24) The 459-nm peak is not due to the complex $Fe^{III}(TPP)(n\text{-}BuS^-)_2$,[25] which could be formed by oxidation of the iron by oxygen traces, since an EPR study at 110 K of the experiment failed to reveal any significant formation of $Fe^{III}(TPP)$ low-spin complex.[25] Moreover, the addition of n-BuS^- to $Fe^{III}(TPP)(Cl)$ and $Fe^{II}(TPP)$, under identical conditions, does not lead to the 459-nm peak formation.
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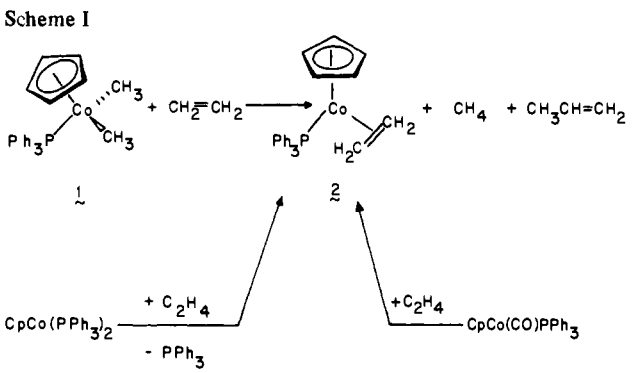
Reaction of a Metal Alkyl with Ethylene as a Model for Ziegler–Natta Polymerization. Evidence for the Olefin Insertion Mechanism

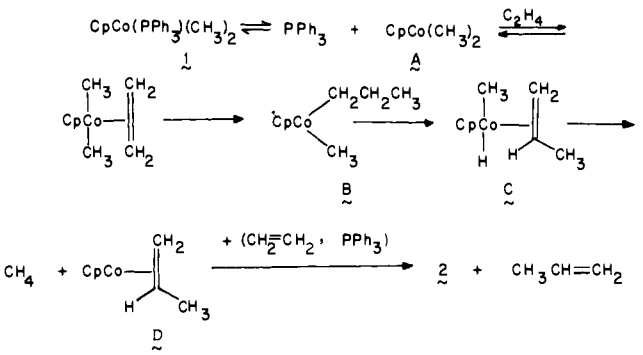
Sir:

Dimerization, oligomerization, and Ziegler–Natta polymerization of ethylene and other olefins are among the most important homogeneous catalytic processes.[1] It has long been assumed that these reactions involve insertion of olefin into the metal–carbon bond of an intermediate metal alkyl.[2,3] Green and his co-workers have pointed out recently, however, that there are no unambiguous examples—in either early or late transition metal complexes—in which a well-characterized metal–alkyl–olefin compound has been observed to undergo this insertion reaction.[4] This has led them to suggest an alternative mechanism for apparent insertion reactions which involves α-elimination to form a transient carbene complex. In this note, we report that the well-characterized[3e,5] cobalt complex **1** (Scheme I) reacts cleanly with ethylene, giving propylene and methane as products. We have carried out a

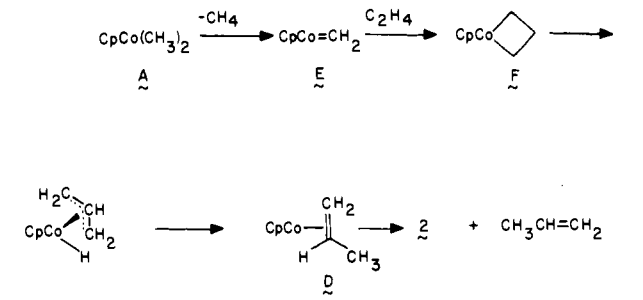
Scheme I



Scheme II



Scheme III



labeling study which demonstrates (in agreement with the classical view) that insertion, rather than α-elimination, is the critical step in the mechanism of this reaction.

When a 0.13 M benzene-d_6 solution of **1** was heated under 4 atm (5 equiv) of ethylene for 30 h at 76 °C in a sealed NMR tube, the absorptions characteristic of **1** (δ 4.49, 0.61 ppm) and ethylene (5.27) were replaced by those from methane (0.22) and propene (1.58, CH_3), as well as by a new cyclopentadienyl signal (5.50, 5 H) and two new multiplets at 1.11 (2 H) and 2.09 (2 H) ppm. A complex with these absorptions can be isolated free of starting **1** by repeated crystallizations from benzene–hexane, although it slowly decomposes in solution (N_2 atmosphere, 20 °C) with loss of ethylene. η^5-Cyclopentadienylbis(triphenylphosphine)cobalt(I)[6] and ethylene react thermally and η^5-cyclopentadienyl(triphenylphosphine)carbonylcobalt(I)[5a] and ethylene react upon photolysis (Scheme I) to give NMR absorptions identical with those observed in the reaction of ethylene with **1**. The structure of this material is assigned as the new olefin complex,[7] **2**, on the basis of these observations. In a quantitative experiment, heating 2 mL of a 0.127 M benzene solution of **1** under 11 atm (20 equiv) of ethylene at 54 ± 1 °C for 121 h gave methane (91%), propene (84%), **2** (103%), and unreacted ethylene. No (<0.5%) propane was observed.[8]

The observed products can be explained by either a classical mechanism involving insertion of ethylene into a metal–carbon bond (Scheme II), or by the Green–Rooney alternative involving α-elimination (Scheme III). In the former, coordination of ethylene to the unsaturated intermediate A generated by phosphine dissociation, followed by insertion into a cobalt–methyl bond, gives the propyl–methyl complex B. β-Hydrogen elimination in B generates a hydrido–methyl–olefin complex which reductively eliminates methane, and ethylene and phosphine displace propene from the initially formed, unsaturated, olefin complex D. In the alternative (Scheme III), intermediate A is converted into carbene complex E by α-elimination and reductive elimination of methane. Addition of ethylene to the M=C bond gives metallacycle F; this then undergoes β-elimination and a second reductive elimination, generating D which leads to **2** and propene as before (Scheme II).

Because our system involves characterizable complex **1**, it

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