transients but requires that the catalyst acts only as an oxygen sink as far as the CO_2 formation is concerned. The only other possibility appears to be that CO_2 formation occurs on catalyst sites to which oxygen is transferred slowly but CH_4 rapidly.

The role of the oxygen in the formation of the methyl radicals is more difficult to interpret at this time. It is a striking feature of the reaction that all product formation, both oxygenates and higher hydrocarbons, ceases instantly when helium replaces oxygen in the feed.[7] Furthermore, it appears from recent work[7] that the rate of lattice oxygen exchange determines the catalyst activity. These results seem to suggest that the lattice oxygen atoms themselves cannot be a significant source of reactant oxygen and that molecular, gas-phase oxygen is somehow involved. This aspect is currently under study in our laboratory. A similar and related aspect of this reaction is that the formation of all the reaction products is very fast compared to the time scale of the transients, while there is now convincing evidence that large amounts of methane are present on the catalyst which desorb much more slowly and which at present seem to have no obvious role in the reaction mechanism.[5] It is tempting to speculate that most of the chemistry involved occurs at the gas/solid interface, the only function of the catalyst being the production of reaction intermediates.

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Carbon Monoxide and Carbon Dioxide Carbon–Metal Bond Insertion Chemistry of Alkyliron(III) Porphyrin Complexes

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Migratory insertion reactions represent one of the major classes of reactivity exhibited by organometallic species. In general, for metal–alkyl complexes, the process involves transfer of a cis ligand (such as CO) into a metal–carbon bond. Insertion reactions are also known for which prior coordination of the inserting group is not feasible. Among the reactions for which this "direct insertion" process is likely are the CO, isonitrile, aldehyde,[1] and alkene[2] insertions into hydridorhodium(III) porphyrins, and the light-driven CO_2 insertion into the methylindium(III) porphyrin complex.[3] Indirect evidence also exists for SO_2 insertion[4] and for dioxygen insertion[5] into an alkyliron(III) porphyrin bond. Metalloporphyrin derivatives are poor candidates for *migratory* insertion by virtue of the fact that cis ligation of two axial ligands is highly unfavorable. Accordingly, Halpern and co-workers have recently proposed a novel free radical mechanism for alkene insertion into Rh–Rh and Rh–H bonds of rhodium octaethylporphyrin.[2]

The first evidence is presented here for CO and CO_2 insertion reactions of alkyliron(III) porphyrin complexes. Spectroscopic results are consistent with generation of the respective acyl and carboxylatoiron(III) porphyrin complexes. An additional feature that renders this chemistry distinctly different than that of classical organometallic compounds is the paramagnetism of the iron(III) center in both the parent alkyl complex and in the insertion products.

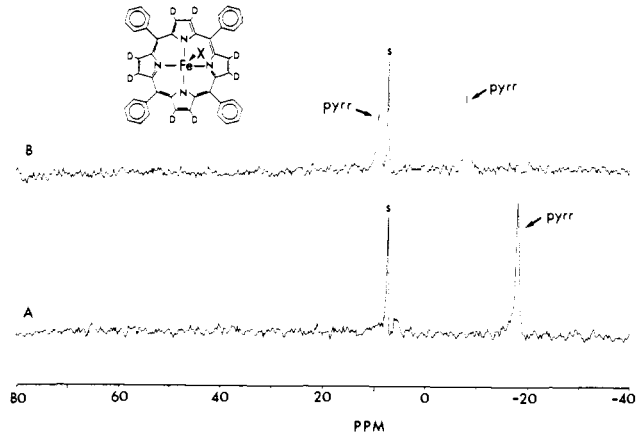

Figure 1. Deuterium NMR spectra of (TPP-d_8)Fe(III) species, 55 MHz, 25 °C, benzene solution, $(CD_3)_4Si$ reference. The deuterium pyrrole signals are denoted "pyrr", and the natural abundance solvent signal is labeled "s": (A) (TPP-d_8)FeBu and (B) product of (TPP-d_8)FeBu with CO.

Lithium alkyls were generated in hexane solution from the corresponding chlorinated hydrocarbon and lithium metal or, in the case of the *n*-butyl derivative, purchased (Aldrich) as a hexane solution. All reactions were performed in an inert atmosphere chamber filled with argon. Alkyliron(III) tetraphenylporphyrin complexes were prepared by combination of stoichiometric amounts of the lithium alkyl derivatives in hexane with a benzene or toluene solution of chloroiron(III) tetraphenylporphyrin ((TPP)FeCl) at a concentration of 2.0–5.0 mM.[6,7] In order to readily distinguish the pyrrole proton (deuterium) signal, it was most convenient to utilize (TPP-d_8)FeCl (deuteriated at the pyrrole positions). Formation of the alkyl complex was monitored by deuterium NMR spectroscopy, in which case the pyrrole deuteron signal at 79 ppm for the high-spin chloroiron(III) porphyrin was replaced by one in the −16 to −19 ppm region characteristic of the low-spin alkyliron(III) complex[6] as shown in Figure 1.

Insertion reactions were carried out under anaerobic conditions in NMR tubes. Carbon monoxide was gently bubbled through the benzene solution of the alkyliron porphyrin for 3–5 min, and an atmosphere of CO at ambient pressure was maintained in the septum-sealed tube. Optical spectra were recorded before and after the NMR measurements by removal of a small portion of the NMR sample inside the inert atmosphere chamber. Light was not required to effect the reactions.

Evidence for reaction between (TPP)Fe–alkyl and CO is found in changes for both optical and NMR spectra. Bands at 392, 412 (Soret), 518, and 552 nm for the red (TPP)FeBu complex[8] were replaced by bands at 406 (Soret), 513, 560, 603, and 637 nm upon equilibration with CO. The solution remained red in color. With CO addition the deuterium NMR spectrum for (TPP-d_8)FeBu with a pyrrole deuteron signal at −17.2 ppm was converted to one with a new pyrrole deuteron signal at −8.2 ppm (Figure 1). A second pyrrole signal at 8.7 ppm was attributable to the iron(II) porphyrin–carbon monoxide byproduct.[9] For solutions in which partial conversion had taken place, both −17.2 and −8.2 ppm

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(9) The iron(II) product, (TPP)Fe(CO), presumably results from homolytic rupture of the iron(III)–alkyl bond with loss of the alkyl radical from the solvent cage and subsequent coordination of CO by the iron(II) product. Addition of α-(4-pyridyl 1-oxide)-*N*-*tert*-butylnitrone to the reaction mixture yielded a "trapped" alkyl radical species detectable by ESR spectroscopy. In benzene solution the insertion product predominates, whereas in the highly solvating THF solvent the iron(II) carbonyl species is the major product.

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signals were evident, indicating that the species were not interconverted rapidly on the NMR time scale and that CO does not rapidly coordinate to the alkyliron(III) porphyrin. Pyrrole deuteron signals for the CO adducts of (TPP)Fe-ethyl and (TPP)-Fe-neopentyl complexes were at -8.0 and -7.1 ppm, respectively. The (TPP)Fe-norbornyl complex was resistant to CO insertion under the conditions cited above. Absence of splitting or asymmetry of the signal rules out alkyl group migration to the pyrrole nitrogen sites. The upfield position and relatively narrow line width for the new pyrrole signal are indicative of a low-spin iron(III) tetraphenylporphyrin product. Electron spin resonance spectra at 5 K confirm the low-spin character with g values of 2.56, 2.38, and 1.88.

The proton NMR spectrum of the product formed between (TPP)FeBu and CO revealed two new signals at 18.6 and -1.3 ppm approximately one-fourth the intensity of the pyrrole signal at -8.2 ppm. On the basis of comparisons with the acetyl and butyryl analogues, these signals are assigned to the β and γ protons of $-C(O)CH_2CH_2CH_2CH_3$, respectively (the α-CH_2 signal is broadened beyond detection, and the $-CH_3$ signal overlaps with diamagnetic region signals). The red solution persists for hours under anaerobic conditions but is otherwise highly oxygen and moisture sensitive. The green (TPP)Fe-O-Fe(TPP) is formed upon exposure to the atmosphere. Addition of HCl vapor to the red CO adduct of (TPP)FeBu elicited conversion to the parent (TPP)FeCl species.

Following addition of CO to (TPP)FeBu, IR spectra (toluene solvent) revealed appearance of a new solvent sensitive band at 1817 cm^{-1} (1765 cm^{-1} with ^{13}CO). These overall results are suggestive of CO insertion into the Fe-C bond of the original alkyl complex, with subsequent formation of a novel acyl-iron(III) porphyrin complex. Acyliron(III) porphyrin complexes have not

$$(TPP)Fe\text{-}CH_2(CH_2)_2CH_3 + CO \rightarrow (TPP)Fe\text{-}C(=O)(CH_2)_3CH_3$$

been reported,[10] and hence an independent synthetic route was devised. Addition of butyryl chloride to the iron(I) tetraphenylporphyrin anion[11] produced a small amount of the species with a -8.2 ppm pyrrole peak. However, the putative acyliron(III) product was prepared as the predominant species by addition of the acyl chloride to the corresponding iron("0") tetraphenylporphyrin dianion with subsequent iodine oxidation of the iron(II) derivative to an iron(III) complex spectroscopically identical to the CO insertion product.

The CO insertion reaction is first-order in CO pressure at pressures less than 1 atm and first-order in alkyliron(III) porphyrin. Among mechanistic speculations is the possibility for a CO-assisted homolytic scission of the iron-alkyl bond with attack of the immediate Fe-CO product by a caged alkyl radical. This process would account for appearance of significant amounts of (TPP)Fe(CO) as a byproduct.

A parallel insertion reaction with CO_2 would be expected to produce a carboxylate complex, and this is indeed confirmed on the basis of spectroscopic comparisons with known carboxylatoiron(III) porphyrin derivatives. Following addition of CO_2 to a benzene solution of (TPP)FeBu, the red solution with a pyrrole deuteron signal at -17.2 ppm was converted over a period of hours to a green species with a pyrrole deuteron signal at 80 ppm. The proton NMR spectrum of this complex revealed meta-phenyl signals at 12.7 and 11.7 ppm as expected for a high-spin (TPP)$Fe^{(III)}$ carboxylate complex.[12] A broad signal at 20.7 ppm is assigned to a β-CH_2 group of the carboxylate ligand on the basis of a recent spectroscopic study of carboxylate complexes.[13] The green solution exhibited optical spectral bands at 410, 572, and 610 nm, consistent with spectra observed for oxygen-ligated (TPP)$Fe^{(III)}$ complexes. The net reaction observed for CO_2 insertion is thus summarized by

$$(TPP)Fe\text{-}CH_2(CH_2)_2CH_3 + CO_2 \rightarrow (TPP)Fe\text{-}OC(=O)(CH_2)_3CH_3$$

The reactivity of alkyliron(III) porphyrins (and possibly the aryl analogues) suggests that a large number of new coordination complexes are feasible through addition of other ligand types. Investigation of the low-spin iron(III) derivatives is also of interest in terms of developing the organometallic chemistry of paramagnetic species.

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Preparation of Complex Aminoglycosides: A New Strategy

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Aminoglycosides are widely distributed in nature and are found in a large variety of biologically important molecules. A few examples of these are aminopolysaccharides, such as blood group determinants and antigenic determinants on cell surfaces,[1] aminoglycoside antibiotics,[2] glycoproteins, glycolipids,[3] and nucleoside antibiotics (i.e., tunicamycin).[4] In the past, synthesis of these molecules has generally required two separate strategies, one for the preparation of the appropriate aminosugar and another for the glycosidation of this sugar.

Recently, we have described a new mild, highly stereoselective and efficient method for the preparation of aminosugars which involve the cycloaddition of an azodicarboxylate onto a glycal.[5] Herein, we report that the cycloadducts obtained by this reaction are powerful and versatile glycosylating agents and can be used to prepare a variety of complex glycosides. This allows both the aminosugar and the glycoside preparation to be combined in a single, mild, simple, and efficient strategy for the first time.

A wide variety of glycals smoothly undergoes a [4 + 2] cycloaddition with dibenzyl azodicarboxylate to give dihydrooxadiazines of the general formula **1**. Previously, we have described this reaction with several furanoid glycals[5] and since have found that this reaction proceeds well with all furanoid and pyranoid glycals attempted, with the exception of those bearing an allylic acyloxy function (i.e., R = Ac, Scheme I). This work will be described in detail at a later date.

In our initial work, we noted that when the cycloadducts were treated with *p*-TsOH in methanol, they underwent stereospecific opening at C-1 with inversion of stereochemistry. Therefore, it was felt that these dihydrooxadiazines may provide entries to more complex aminoglycosides as well as to the parent aminosugar. However, the analogy, while very tempting, is not direct since the

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