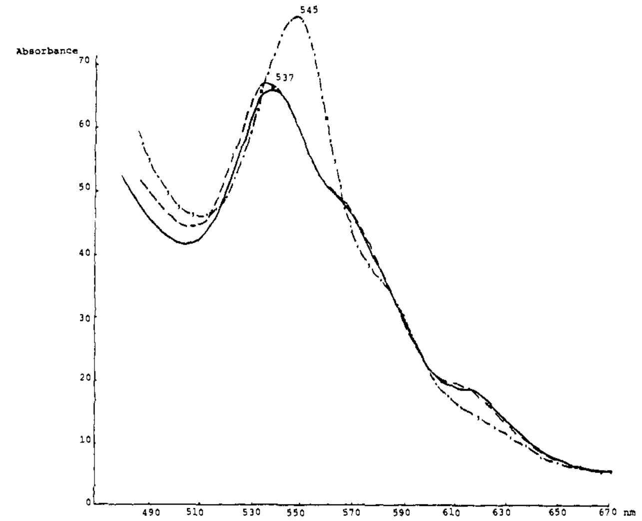
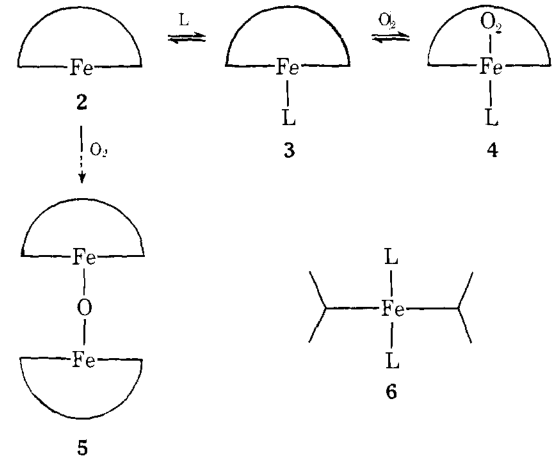


Figure 1. Visible spectrum of the Fe^{II} porphyrin in dry pyridine: (——) under argon, (– — ·) under oxygen, (– – –) under argon after three oxygenation–deoxygenation cycles.

−20° pyridine solutions of adduct **4** are stable for several days.[12]

In this system the stability of the dioxygen adduct **4** is largely dependent on the nature[13] and concentration of the coordinating base, L. Thus a 5% concentration of 1-methylimidazole in benzene provides a 5-hr lifetime (25°) whereas rapid autoxidation occurs in a solution of 5% pyridine in benzene. A rationale for these observations is presented in Scheme I. Assuming that the predominant species in anaerobic solution is the pentacoordinate complex **3**, it may react with oxygen reversibly to octahedral adduct **4** or it may dissociate to square planar complex **2.** Experiment has shown that in benzene solution, in the absence of ligand L, the species **2** is instantaneously autoxidized, most certainly by oxygenation of the unprotected face. A large excess of L shifts the equilibrium toward pentacoordinate complex **3** and consequently reduces the rate of autoxidation. In the previously described system[4] the presence of an octahedral species, **6,** results in a lower concentration of the sensitive square planar species, such as **2.** Consequently in our system, Scheme I, the absence of octahedral species, such as **6,** which are geometrically impossible renders this system much more sensitive toward irreversible autoxidation.[14] An analogous explanation can be offered for the rapid autoxidation of an extremely hindered porphine prepared by Collman,[4] which also forms a pentacoordinate ferrous complex with nitrogenous ligands.

Scheme I



In agreement with this general Scheme I, we have shown that decay of **4,** over two half-lives follows clean first-order kinetics (25°, benzene, 5% 1-methylimidazole). Such behavior is in complete accord with dissociation of **4** to the autoxidizable square planar species **2.**

In summary these results support the thesis that steric inhibition of the bimolecular process, eq 1, provides a means of stabilizing ferrous dioxygen complexes of porphyrins. However, they also indicate that the position of the equilibria is important in determining the lifetimes of such species.

Acknowledgments. We thank the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, Eli Lilly & Co., and Hoffmann-La Roche for their generous financial support.

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(5) J. Almog, J. E. Baldwin, R. L. Dyer, and M. Peters, preceding communication.
(6) The analogous mesotetraphenylporphineiron(III) chloride has λ_{max} ($CHCl_3$) 509.5 nm, μ 5.87BM; E. B. Fleischer and T. S. Srivastava, *J. Amer. Chem. Soc.*, **91**, 2404 (1969).
(7) All magnetic moments were determined in the solid state at 25° unless otherwise stated. We thank Mr. S. Koch for these determinations.
(8) J. P. Collman and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 2048 (1973).
(9) The analogous mesotetraphenylporphineiron(II) has λ_{max} 534, and 563 nm (in toluene with *N*-methylimidazole).[8]
(10) Manometric determination[1] revealed an uptake of 0.9 ± 0.1 mol of dioxygen per mole of complex. We thank Dr. R. L. Dyer for this measurement. The solution so obtained is diamagnetic; *cf.* J. Löliger and R. Scheffold, *J. Chem. Educ.*, **49**, 646 (1972).
(11) (a) The μ-oxo dimer of *meso*-tetraphenylporphineiron(III) complex has λ_{max} ($CHCl_3$) 408 and 571 nm: (b) Compound **5** could be reconverted to the ferric chloro species by treatment with hydrogen chloride in chloroform.
(12) We have made many attempts to crystallize the adduct **4;** however, to date all our efforts have only produced the less soluble precursor **2** as a crystallizable species.
(13) Use of a 5% solution of imidazole in benzene results in instantaneous autoxidation; *cf.* (a) V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Amer. Chem. Soc.*, **95**, 1142 (1973); also ref 3a.
(14) Accurate models of I show that nitrogen ligands, such as pyridine or 1-methylimidazole cannot enter the cavity of **1.**

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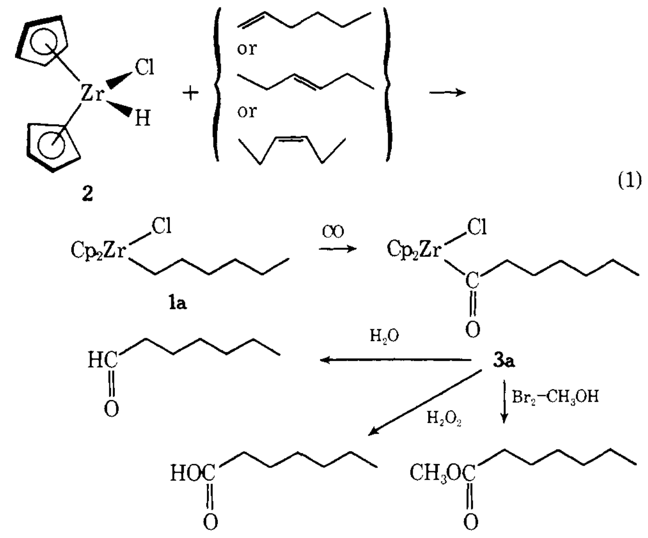
Hydrozirconation. II. Oxidative Homologation of Olefins *via* Carbon Monoxide Insertion into the Carbon–Zirconium Bond

Sir:

We have recently reported[1] the preparation of di(η^5-cyclopentadienyl)(chloro)alkylzirconium(IV) complexes, $(\eta^5\text{-}C_5H_5)_2Zr(Cl)R$ (**1**), which are inexpensively and conveniently produced by reaction of the corresponding hydride,[2] **2,** with olefins (hydrozirconation). These alkylzirconium compounds are versatile intermediates for organic synthesis in that they react with a variety of electrophilic reagents to generate organic products in high yield and under mild conditions. We now wish to report our results concerning another aspect of the chemistry of **1** which expands in scope the utility of these complexes as reagents for organic synthesis. We have found that **1** undergoes a clean and high yield insertion of CO into the C–Zr bond[3] to produce the first examples of zirconium-acyl complexes, (η^5-$C_5H_5)_2Zr(Cl)(C(O)R)$ (**3**), which, in turn, can be readily converted, depending on subsequent procedures, to an aldehyde, a carboxylic acid, or an ester (reaction 1).



(1)

In striking contrast to the failure of (η^5-$C_5H_5)_2Zr(CH_2Ph)_2$ to undergo reaction with CO even under drastic reaction conditions[4] (whereas insertion occurs readily for the Ti analog), we find that reaction of **1** with CO occurs faster and in higher yield than was reported for Ti counterparts.[5] At no stage during the reaction between **1** and CO could a zirconium carbonyl species be detected; a reasonable reaction sequence to postulate[6] involves rapid, reversible CO coordination favoring the coordinatively unsaturated form followed by slow alkyl migration to coordinated CO.

The synthesis of a representative acyl, **3a,** was as follows. A solution of 2 mmol **1a** (which can be prepared from **2** and 1-hexene or cis or trans internal hexenes) was stirred in 5 ml of benzene[7] under 20 psi of CO at room temperature. Conversion of **1a** to **3a** was complete in several hours. The colorless acyl complex was identified by its spectral properties[8] (nmr [C_6D_6]: $\delta_{C_5H_5}$ 5.8; $\delta_{CH_2\text{-}C(O)\text{-}}$ 2.8 (t, J = 7 Hz); ν_{CO} = 1550 cm^{-1}). Other, similar zirconium alkyls also underwent CO insertion; relative rates are cycloalkyl > n-alkyl.[9,10]

Protonolysis of **3** immediately yields aldehyde; addition of dilute aqueous HCl to a benzene solution of **3a** at room temperature immediately gave n-heptaldehyde (99%). Oxidative cleavage of the acyl-zirconium bond was effected in two ways. Treatment of a solution of **3a** first with aqueous NaOH and then with 30% H_2O_2 gave, upon acidification, n-heptanoic acid (77%), or Br_2 in methanol, slowly added to a solution of **3a** at room temperature, gave methyl n-heptanoate (51%). Results obtained starting with other representative olefins are summarized in Table I. In no case were products isomeric with those shown in Table I observed.[11,12]

Cleavage mechanisms for the Zr–C bond in **1** and **3** may not parallel those postulated for other transition metal alkyls or acyls. Protonation of most transition metal alkyls is generally envisioned to occur by oxidative addition of proton to the metal followed by reductive loss of alkane.[13] Reaction of **1** with dilute aqueous acid yields the alkane quantitatively,[1] but it is unlikely that this occurs through initial oxidative addition of proton to the formally d^0 Zr(IV) center. It is entirely possible that, for d^0 complexes **1** and **3,** direct electrophilic attack of proton of the carbon atom occurs to give the alkane or aldehyde, respectively.[14] Several instances of oxidative cleavage of the M–C(O)R bond have been studied from a mechanistic standpoint.[15,16] In them, a process involving oxidation of the metal atom by various oxidizing agents followed by nucleophilic displacement by solvent of the metallic moiety at the acyl carbon has been suggested.[15] For Zr(IV) acyls, oxidation of the metal is unreasonable and the ester or acid products described herein may result, here too, from direct electrophilic attack by H_2O_2 or Br_2 on the acyl carbon atom.

Table I

Olefin[a]	Work-up	Product	% yield[b]
1-Hexene or 3-hexene	1. dil HCl	n-Heptanal	99
	2. Br_2–CH_3OH	Methyl n-heptanoate	51
	3. NaOH–H_2O_2	n-Heptanoic acid	77
2-Methyl-2-butene	1.	4-Methylpentanal	71
	2.	Methyl 4-methylpentanoate	50
	3.	4-Methylpentanoic acid	26
Cyclohexene	1.	Cyclohexanecarboxyaldehyde	97
	2.	Methyl cyclohexanecarboxylate	57

[a] Preliminary results show that 1-hexyne can be converted to *trans*-2-heptenal in good yield.[10] [b] Yields were determined by vpc and are based on (η^5-$C_5H_5)_2Zr(R)Cl$ species.

When followed by CO insertion, hydrozirconation is reminiscent, with one outstanding difference, of hydroformylation or hydrocarboxylation.[17] In these latter sequences, an olefin and a transition metal hydride react to give a mixture of isomeric metal alkyls in which the metal is attached to one of various carbons in the alkyl chain;[17] rapid, reversible β-hydride elimination and readdition tends to attach the metal to an internal carbon,[18] even when a terminal olefin is the starting material. Subsequent reactions, therefore, lead to a mixture of organic products. Hydrozirconation proceeds opposite to this trend in that **1** reacts with a variety of olefins to yield that species in which the zirconium is attached to the least hindered carbon of the alkyl chain (see reaction 1). Clearly, this facet of hydrozirconation makes it the method of choice when internal olefins are available but terminal oxidative homologation, such as terminal hydroformylation, is desired. We are now studying other types of insertion reactions involving C–Zr species.[19]

Acknowledgments. The authors wish to acknowledge generous support for this work provided by the National Science Foundation (GP 43026X). They also thank D. W. Hart and J. A. Labinger for helpful suggestions and comments.

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(4) G. Fachinetti and C. Floriani, *J. Chem. Soc., Chem. Commun.*, 654 (1972).
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(7) Solvents were distilled from sodium benzophenone ketyl under argon. For benzene, this was made possible by admixing 5% tetraglyme. The zirconium alkyls were prepared under argon.
(8) These data compare favorably with those reported for their Ti analogs (ref 5).
(9) A parallel trend for CO insertion into the Fe–C bond has been reported: M. Green and D. J. Westlake, *J. Chem. Soc. A*, 367 (1971).
(10) Preliminary results show that the alkylzirconium species insert CO faster than do alkenyl analogs.

(11) Our detection ability would reveal <0.1% yield of such products.

(12) These work-up procedures are simple compared with those described for hydroboration sequences in which mixtures of products can be obtained and in which a final reduction step is necessary to generate the aldehyde; see, for example, H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N.Y., 1972, Chapter XVII.

(13) For example, see U. Belluco, G. Deganello, R. Pietropaolo, and P. Uguagliati, *Inorg. Chim. Acta, Rev.*, **4**, 7 (1970), and references cited therein.

(14) Similar reactions occur for Ti analogs; see J. X. McDermott and G. M. Whitesides, *J. Amer. Chem. Soc.*, **96**, 947 (1974).

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(18) For example, see R. A. Schunn, *Inorg Chem.*, **9**, 2567 (1970).

(19) NOTE ADDED IN PROOF. Yields of carboxylic acids or esters produced from **3** can be substantially improved by treatment of **3** with NBS (to give the acyl bromide) followed by water or alcohols, respectively.

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Gas Phase Nucleophilic Reactions of Aromatic Systems

Sir:

Gas phase ion–molecule reactions have attracted the attention of a wide range of chemists as a means to investigate the interplay of structure and reactivity in the absence of a solvent. A particular point of interest along these lines, and as yet little explored, is to what extent substituent effects observed in solution can be regarded as a true manifestation of intrinsic behavior.[1]

Nucleophilic displacement of halides in aromatic systems provide a particularly good case for a direct comparison of substituent effects in solution and in the gas phase. These reactions are known to be subject to dramatic rate enhancements in solution in the presence of electron attracting groups.[2,3] In an extreme case, acceleration factors of 10^8 have been reported for polyfluoro compounds with respect to the monofluoro species.[4,5] In the gas phase, the present communication shows that attack by alkoxide ions on fluoro-substituted benzenes gives rise to a fast ion–molecule reaction leading to a substituted phenoxide ion. Icr techniques have been used to study these processes.[6]

Methoxide and ethoxide ions react slowly with fluorobenzene in the gas phase *via* reaction 1. (See Table I.) Hydroxide ions in turn undergo preferentially the acid–base reaction (2). Observation of $C_6FH_4^-$ as originating *only* from

$$RO^- + C_6H_5F \longrightarrow F^- + C_6H_5OR \qquad (1)$$

$$R = CH_3,\ C_2H_5$$

$$OH^- + C_6H_5F \longrightarrow H_2O + C_6FH_4^- \qquad (2)$$

OH^-, and the inability to detect F^- by collision induced decomposition,[7] is taken as partial support against a benzyne mechanism for reaction 1.

When these same nucleophiles are used with hexafluorobenzene, fluoride displacement suffers no appreciable acceleration. Reaction 3 is found instead to be fast and to

$$RO^- + C_6F_6 \longrightarrow C_6F_5O^- + RF \qquad (3)$$

yield a somewhat unexpected product.[8] Typical rate constants for these reactions are shown in Table I, whereas the rate constant for production of F^- is estimated as an upper limit, since it cannot be detected under the conditions used to measure k_3.

Table I

Reaction	$10^{10}k$, cm³/mol sec
$CH_3O^- + C_6H_5F \rightarrow F^- + C_6H_5OCH_3$	0.4
$CH_3O^- + C_6F_6 \rightarrow C_6F_5O^- + CH_3F$	16
$F^- + C_6F_5OCH_3$	0.4[a]
$i\text{-}C_3H_7O^- + C_6F_6 \rightarrow C_6F_5O^- + C_3H_7F$	14
$CH_3O^- + C_6F_5H \rightarrow C_6F_5^- + CH_3OH$	13
$i\text{-}C_3H_7O^- + C_6F_5H \rightarrow C_6F_5^- + C_3H_7OH$	10

[a] See text. The actual rate constant may be considerably lower than this value.

Table II. k_{5a}/k_{5b} for Difluorobenzenes

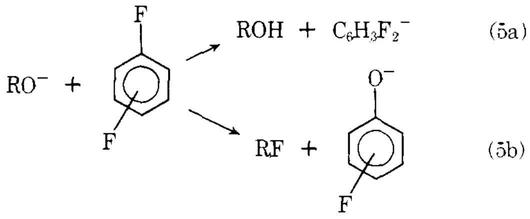
RO^-	Ortho	Meta	Para
CH_3O^-	3.2	10	46
$C_2H_5O^-$	1.1	8.2	1.5
$i\text{-}C_3H_7O^-$	0.14	19	0.51

Reactions of partially fluorinated benzenes with alkoxide ions are helpful to understand under what conditions the three reactivity channels are operative. Pentafluorobenzene, 1,2,3,4-tetrafluorobenzene, and 1,3,5-trifluorobenzene yield exclusively the conjugate base of these aromatics. Upper limits estimated for fluoride displacement show again no substantial rate enhancement over reaction 1.

$$RO^- + C_6F_{6-n}H_n \longrightarrow ROH + C_6F_{6-n}H_{n-1}^- \qquad (4)$$

$$n = 1\text{–}3$$

The formation of phenoxide ion finally becomes competitive in some of the difluorobenzene isomers. In this case,



relative rate constants are much more important than absolute values, and can be determined accurately because of the proximity in mass number of the products. (See Table II.) Since these relative rate constants will depend strongly on the relative acidities of the alcohols and the difluorobenzenes, appropriate mixtures of the alkyl nitrite, the difluorobenzenes, and the alcohol can be used to establish the preferred direction of reaction (5a) by double resonance techniques.[9] The acidity order determined in this fashion is m-$C_6H_4F_2$ > i-C_3H_7OH > o-$C_6H_4F_2$ > C_2H_5OH ≥ p-$C_6H_4F_2$ > CH_3OH. Fluoride displacement is again unimportant in the difluorobenzenes.

These examples allow some conclusions to be made: (a) gas phase nucleophilic attack on the ring is feasible only when the acidity of the aromatic compounds is less or comparable to that of the alcohol;[10] (b) electron-attracting substituents[11] do not speed up halide displacement as in solution but do accelerate the overall reactivity of the aromatic substrate through a new pathway which leads to a substituted phenoxide.

While the first conclusion is not surprising in view of recent observations in ion–molecule reactions,[12,13] the formation of a phenoxide ion as opposed to F^- is indeed remarkable. The preference for the phenoxide ion formation can be