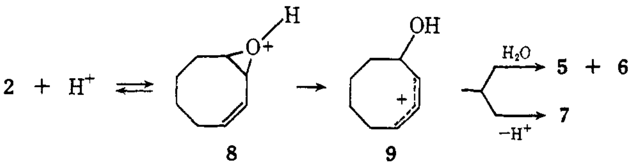
Table I. Values of k_0, k_{H^+}, k_{OH^-}, and k_{HA} for Aqueous Hydrolysis of **1** and **2** at 25°[a]

	1	**2**
$k_0 \times 10^4$, sec^{-1}	2.2 ± 0.3[b,d]	
k_{H^+}, M^{-1} sec^{-1}	$1.64 \pm 0.04 \times 10^4$[b,e]	3.55 ± 0.06[h]
$10^3 k_{OH^-}$, M^{-1} sec^{-1}	1.48 ± 0.03[b]	
$10^2 k_{H_2PO_4^-}$, M^{-1} sec^{-1}	7.4 ± 0.5[b,f]	
$10^2 k_{(CH_3)_2AsO_2H}$, M^{-1} sec^{-1}	3.4 ± 0.2[c,g]	

[a] The reactions were monitored spectrophotometrically in the thermostated cell compartment (±0.15°) of a Gilford 2400 spectrophotometer. The reaction of **1** was followed by decrease of absorbance at 220–227 nm, and reaction of **2** was followed by increase of absorbance at 230 nm due to formation of **7**. [b] $\mu = 1.0$, maintained with KCl. [c] $\mu = 1.0$, maintained with NaCl. [d] Average of ten runs at pH 10–12. [e] Average of five runs at pH 5.65 in cyanomethylamine buffer. [f] pH 5.79. [g] Identical slopes were obtained at pH 5.75 and 6.08 from plots of k_{obsd} *vs.* [HA]. [h] $\mu = 0.1$ (NaCl).

and 44% 2-cyclohexene-*trans*-1,4-diol (**4**).[8,9a] The related epoxide **2** yielded approximately equal amounts of 1,2- and 1,4-diols **5** and **6**[9b] and conjugated dienol **7**.[9a] The products from hydrolysis of **1** and **2** can be rationalized by loss of a proton from or collapse of solvent with intermediate allyl cations (*i.e.*, Scheme I).

Scheme I



Inverse kinetic solvent isotope effects (k_{D_2O}/k_{H_2O}) of 2.3 and 2.1 were observed for the hydronium ion catalyzed hydrolyses of **1** and **2**, respectively.

Catalysis by dihydrogen phosphate ion ($H_2PO_4^-$) and cacodylic acid ($(CH_3)_2AsO_2H$) in the hydrolysis of **1** requires a mechanism in which general acid is involved in the rate-determining step. The kinetic isotope effect ($k_{H_2PO_4^-}/k_{D_2PO_4^-}$) was found to be 2.3 and provides additional evidence for the involvement of $H_2PO_4^-$ at the transition state of the rate-determining step. The product distribution from hydrolysis of **1** in 1 *M* KH_2PO_4 solution ([HA]/[A$^-$] = 5) was the same as the product distribution in nonbuffered solution at pH 5.5, and suggests that a common intermediate (presumably an allyl cation) is formed from catalysis by both hydronium ion and dihydrogen phosphate ion. The ability of phosphate and cacodylate buffers to catalyze the hydrolysis of **1**, while amine acids do not provide detectable catalysis, most likely results from the bifunctional nature of dihydrogen phosphate ion and cacodylic acid. One possibility is that C–O bond breaking is concurrent with proton transfer from the general acid,[10] and the phosphate ion is able to provide electrostatic stabilization[11] of the partially formed allylic cation at the transition state.

In the pH-independent range (pH 9–12),[8] the product mixture contained 98% of the *trans*-1,2-diol **3**, and only 1–2% of *trans*-1,4-diol **4**.[12] Formation of predominately trans 1,2-product **3** from **1** in the pH-independent range suggests considerable nucleophilic involvement of water at the transition state. The solvent isotope effect (k_{H_2O}/k_{D_2O}) of 1.26 at pH (pD) 11.7–11.8 is also consistent with a nucleophilic attack of water on the epoxide.

The lack of buffer catalysis or a significant pH-independent term in the hydrolysis of **2** is probably related to the fact that **2** is much less reactive than **1** to acid-catalyzed hydrolysis.[10] If the ratio ($k_{H^+}/k_{H_2PO_4^-}$) for the hydrolysis of **2** is approximately equal to that same ratio (*ca.* 2×10^5) for the hydrolysis of **1**, then the value of $k_{H_2PO_4^-}$ for **2** would be *ca.* 2×10^{-5} M^{-1} sec^{-1}, and could not be detected experimentally by the spectroscopic method used in this study. Other highly reactive epoxides might also be expected to show buffer catalysis, and this possibility is being further explored.

Acknowledgment. This work was supported in part by the Research Corporation. Discussions with Drs. V. P. Vitullo and R. M. Pollack are appreciated.

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[8] Product analyses were carried out throughout the pH range by injecting an ethanol solution of 1 in a nonbuffered solution maintained at constant pH for *ca.* 10 half-lives with a Radiometer pH-Stat. After the pH of the reaction solution was changed to *ca.* 7–9, it was analyzed directly by glpc on a 1/8-in., 5% hyprose column.

[9] (a) Products **3**, **4**, and **7** were hydrogenated to known saturated compounds. (b) Structures **5** and **6** were assigned on the basis of nmr spectra. Stereochemistry was not determined.

[10] It has been suggested that release of ground-state strain leads to general acid catalyses in acetal hydrolysis: T. F. Fife, *Accounts Chem. Res.*, 5, 264 (1972).

[11] B. M. Dunn and T. C. Bruice, *J. Amer. Chem. Soc.*, **93**, 5725 (1971); V. P. Vitullo and N. R. Grossman, *J. Org. Chem.*, **38**, 179 (1973).

[12] 3-Cyclohexene-*cis*-1,2-diol, prepared from the reaction of osmium tetroxide with 1,3-cyclohexadiene, possessed a glpc retention time different from 3 and 4 and was shown to be stable throughout the pH range studied.

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Metal Complex Promoted Decomposition of the Carbene Precursor Chlorodifluoroacetate

Sir:

As part of an investigation into the synthesis of new carbene complexes and carbenoid systems, we have undertaken a study of the reactions of nucleophilic metal complexes with known carbene precursors. Reactions of this type have been reported before,[1-3] such as by Mango and Dvoretzsky on the catalytic decomposition of diazomethane by $IrCl(CO)(PPh_3)_2$,[1] but few well characterized organo transition metal products have been obtained. Our studies have focussed on the use of trihaloacetate ions and in particular chlorodifluoroacetate as the carbene precursors. These studies have led to the establishment of a novel reaction sequence whose principal features include (1) two distinctly different metal-promoted pathways for the decomposition of CF_2ClCOO^-, (2) the formation of difluoromethyl complexes, and (3) evidence for the intermediacy of a metallocarbanion. In addition, the de-

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[1] F. D. Mango and I. Dvoretzky, *J. Amer. Chem. Soc.*, **88**, 1654 (1966).

[2] P. Hong, N. Nishii, K. Sonogashira, and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, 993 (1972).

[3] Reactions of carbenes and carbene precursors with metal hydride complexes have also been reported as in T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 104 (1956); and K. S. Chen, J. Kleinberg and J. A. Landgrebe, *J. Chem. Soc., Chem. Commun.*, 295 (1972).

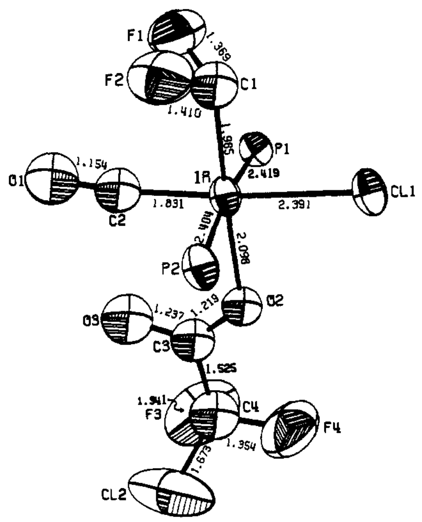


Figure 1. A perspective drawing of the inner coordination geometry of $IrCl(OCOCF_2Cl)(CHF_2)(CO)(PPh_3)_2$ (I) with phenyl rings omitted for clarity. The estimated standard deviations for the bond lengths are: Ir–Cl(1), Ir–P(1), Ir–P(2), 0.005; Ir–O(2), 0.010; all others *ca.* 0.02 Å. Important bond angles (deg) are: P(1)–Ir–P(2), 171.8 (2); Cl(1)–Ir–C(2), 174.6 (6); C(1)–Ir–O(2), 176.6 (6); C(1)–Ir–Cl(1), 89.2 (5); C(1)–Ir–P(1), 94.3 (6); C(1)–Ir–P(2), 93.2 (6); C(1)–Ir–C(2), 85.4 (8); Ir–C(1)–F(1), 115 (1); Ir–C(1)–F(2), 115 (1); F(1)–C(1)–F(2), 100 (1).

composition of monodentate, oxygen-coordinated α-chloro- and α-bromocarboxylates in these systems indicates that they may serve as a source of carbene.

Refluxing $NaCF_2ClCOO$ and $IrCl(CO)L_2$ (L = PPh_3; 5:1 molar ratio) in "dry" diglyme under N_2 results in decoloration of the initially yellow solution and precipitation of NaCl within 7 min. If the reaction is stopped at this point and filtered to remove NaCl, complex I is obtained in excellent yield upon the addition of hexane. If refluxing is continued or if a solution of I in diglyme is refluxed, complex II is isolated upon hexane addition. The structures of I and II have been determined by single-crystal X-ray diffraction methods. Intensity data were collected by the θ–2θ scan technique and the structures solved by standard Patterson and Fourier methods. Least-squares refinements of the structures assuming a fixed geometry for the phenyl rings of the phosphine ligands and anisotropic thermal parameters for the nongroup atoms have converged to discrepancy factors R and R' of 0.056 and 0.075 for I and 0.058 and 0.070 for II (3836 and 1645 reflections included, respectively).

I has a unit cell with dimensions a = 18.31 (2), b = 12.15 (1), c = 10.92 (1) Å; α = 106.98 (5), β = 94.75 (5), γ = 108.98 (5)°; V = 2154 Å^3; space group $P\bar{1}$; ρ_{exptl} = 1.60 (2), ρ_{calcd} 1.57 g/cm^3; Z = 2 with one molecule of benzene per molecule of I. II has a unit cell of dimensions a = 10.47 (1), b = 14.45 (2), c = 24.58 (2) Å; β = 97.68 (5)°; V = 3686 Å^3; space group $P2_1/c$; ρ_{exptl} = 1.65 (2), ρ_{calcd} = 1.65 g/cm^3; Z = 4.

The structures of complexes I and II are illustrated in Figures 1 and 2, respectively, with important bond distances and angles summarized in the captions. Both complexes are diamagnetic, possess octahedral geometries, and are complexes of Ir(III). The salient features of the structures are the appearance of a coordinated difluoromethyl group in each and the difference in the ligands in the sixth coordination position trans to $-CHF_2$. In I, this ligand is monodentate O-coordinated chlorodifluoroacetate while in II it is a chloride ion. The formulation of the difluoromethyl group is based on the bond angles around the donor C atoms (see figure captions), the neutral charge of each complex, and deuterium substitution as described below.

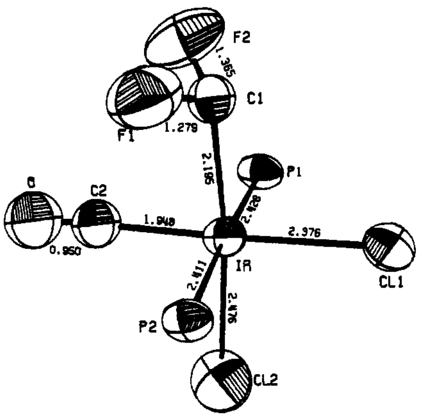
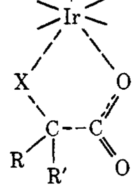


Figure 2. A perspective drawing of the inner coordination geometry of $IrCl_2(CHF_2)(CO)(PPh_3)_2$ (II) with phenyl rings omitted for clarity. The estimated standard deviations for the bond lengths are: Ir–Cl(1), Ir–P(1), Ir–P(2), 0.008; Ir–Cl(2), 0.010; all others *ca.* 0.03 Å. Important bond angles (deg) are: P(1)–Ir–P(2), 177.0 (3); Cl(1)–Ir–C(2), 177.6 (9); C(1)–Ir–Cl(2), 173.7 (8); C(1)–Ir–Cl(1), 92.7 (8); C(1)–Ir–P(1), 93.0 (9); C(1)–Ir–P(2), 89.8 (9); C(1)–Ir–C(2), 86 (1); Ir–C(1)–F(1), 111 (2); Ir–C(1)–F(2), 109 (2); F(1)–Ir–F(2), 108 (3).

The change in the sixth position ligand in going from I to II is of particular interest. Since I yields II quantitatively, it is clear that the Cl^- ion in II originates from the CF_2ClCOO^- ligand in I. The decomposition of the coordinated chlorodifluoroacetate appears to proceed in a concerted manner with no evidence for an initial decarboxylation step. Similar decompositions are observed with other complexes of O-coordinated α-halocarboxylates including $IrHCl(OCOCF_2Cl)(CO)L_2$ and $IrHCl(OCOCHBrCH_3)(CO)L_2$, and we propose the decomposition to proceed *via* the cyclic transition state **1** to account for these observations. This concerted mechanism differs from that found by Armbrecht, *et al.*,[4] for the decomposition of $R_3Sn(OCOCCl_3)$ to R_3SnCl in which a trichloromethyltin intermediate is observed. However, this is not surprising in view of the fact that the anions CF_2XCOO^- (X = Cl, Br, I) decompose in a concerted manner to yield CF_2 whereas other trihaloacetate ions such as CCl_3COO^- decompose in a stepwise fashion with a trihalomethide ion as an intermediate.[5] **1** implies that O-coordinated



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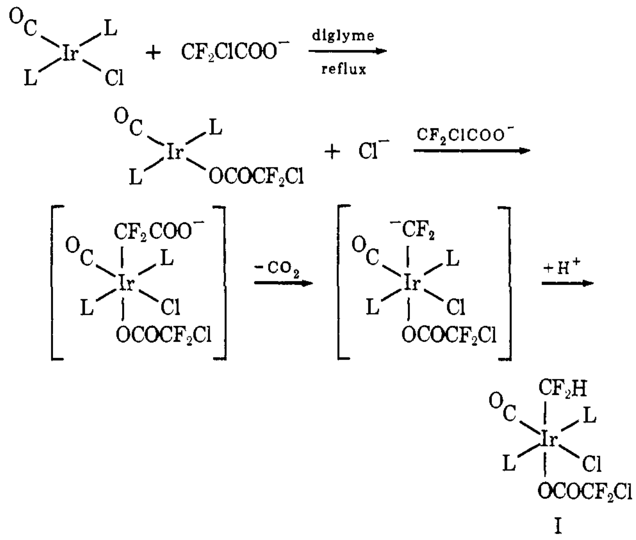
[4] F. M. Armbrecht, Jr., W. Tronich, and D. Seyferth, *J. Amer. Chem. Soc.*, **91**, 3218 (1969).

[5] J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964, p 47.

α-halocarboxylates may serve as a source of carbene. However, attempts to trap CF_2 by converting I to II in the presence of olefins have proven unsuccessful to date. Further efforts in this direction are in progress.

The appearance of the $-CHF_2$ group in I and II was somewhat unexpected, and, in light of the aprotic nature of the solvent, the source of the proton proved of interest. It seems that although the diglyme had been dried by refluxing over $LiAlH_4$, sufficient water remained to serve as the proton source. This was demonstrated by drying diglyme to which D_2O had been added and repeating the reaction outlined above. The deuterium analog of II, $IrCl_2(CDF_2)(CO)L_2$, was thus obtained (ν_{C-H} 2940, ν_{C-D} 2200 cm^{-1}). The abstraction of a proton from water to yield difluoromethyl is taken as evidence for the intermediacy of a metallocarbanion, and the reaction sequence given in Scheme I is proposed to explain the formation of I. Support for the initial step involving replacement of the chloride in the parent complex by the acetate is obtained from the reports[6-8] of a number of closely related complexes which were synthesized by different routes. However, attempts to synthesize the directly analogous complex $Ir(OCOCF_3)(CO)L_2$ by allowing $IrCl(CO)L_2$ to react with $NaCF_3COO$ were unsuccessful.

Scheme I



Finally, we note that continued refluxing of II in diglyme yields a mixture of $IrCl(CO)L_2$ and $IrHCl_2(CO)L_2$ after 1 hr indicating the possibility of a cyclic reaction sequence between the Ir(I) complex and excess $NaCF_2ClCOO$. Such a sequence is being investigated to determine its synthetic utility.

Acknowledgment. We wish to thank the National Science Foundation (Grants GP-23139 and GP-35667X) for support of this work.

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(9) Alfred P. Sloan Foundation Fellow, 1972–1973.

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Reverse Osmosis in Organometallic Synthesis

Sir:

When a solution of a dissociable complex is forced against a selectively permeable membrane under pressure, ligand and solvent diffuse through the membrane but the metal-containing species are retained. Thus, reverse osmosis concentration of a solution of the equilibrium mixture results in selective removal of the free ligand and provides a solution to the long-standing problem of removal of nonvolatile dissociated ligands from solutions of organometallic complexes.[1]

Solutions of homogeneous catalysts often contain detectable quantities of coordinatively unsaturated species, as illustrated for dihydridotetrakis(triphenylphosphine)ruthenium(II).[3] Ligand-deficient complexes such as **2**[3] are commonly the active species for catalysis.[4] Removal of the dissociated ligand by reverse osmosis enhances catalytic activity. Whether or not the ligand-deficient complex can be isolated depends on the particular system and the conditions employed. For example, **2** is too unstable to be isolated but if nitrogen is used as the pressuring gas, the dinitrogen complex $RuH_2(N_2)(PPh_3)_3$[5] (**3**) can be readily isolated. This illustrates the use of reverse osmosis to replace a dissociated ligand (triphenylphosphine) by a more labile one (dinitrogen). The dinitrogen complex **3** had been previously detected in nitrogen-saturated solutions of **1** but could not be isolated from these solutions because of the presence of the dissociated triphenylphosphine.[3] Preparation and isolation required a different route.[5]

$$\underset{\mathbf{1}}{RuH_2(PPh_3)_4} \rightleftharpoons \underset{\mathbf{2}}{RuH_2(PPh_3)_3} + PPh_3$$

In an illustrative experiment, a 0.02 *M* tetrahydrofuran solution (200 ml) of **1** was pressured with nitrogen (80–100 atm) in a reverse osmosis cell[6] fitted with a membrane[7] of the polyimide obtained from *p,p'*-diaminodiphenyl ether and pyromellitic dianhydride. A solution (170 ml) of triphenylphosphine in tetrahydrofuran (THF) was removed by permeation. Slow addition of hexane to the residual solution precipitated crystalline $RuH_2(N_2)(PPh_3)_3$ in 41% yield.

In addition, two new dinitrogen complexes have been isolated by this technique. Both new complexes were

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(1) The principles of reverse osmosis, many kinds of reverse osmosis apparatus, and diverse membrane forms have been discussed recently.[2] These publications provide a detailed introduction to many qualitative and mathematical aspects of reverse osmosis and membrane technology. However, in our experience, the use of reverse osmosis for preparative purposes requires neither elaborate apparatus nor complex mathematics.

(2) (a) C. E. Reid in "Desalination by Reverse Osmosis," J. Merton, Ed., Massachusetts Institute of Technology Press, Cambridge, Mass., 1966; (b) A. S. Michaels and H. H. Bixler, *Progr. Separation Purification*, 1, 143 (1968); (c) A. S. Michaels, *ibid.*, 1, 297 (1968); (d) N. N. Li and R. B. Long, *ibid.*, 3, 153 (1970); (e) H. K. Lonsdale, *ibid.*, 3, 191 (1970); (f) R. E. Kesting, "Synthetic Polymeric Membranes," McGraw-Hill, New York, N. Y., 1971; (g) S. Sourirajan, "Reverse Osmosis," Academic Press, New York, N. Y., 1970.

(3) T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **92**, 3011 (1970).

(4) C. A. Tolman, *Chem. Soc. Rev.*, 1, 337 (1972).

(5) W. H. Knoth, *J. Amer. Chem. Soc.*, **94**, 104 (1972).

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(7) C. W. Alegranti and M. Panar, manuscript submitted for publication.