complexation, the conformations of **1a**–**3a** are essentially the same, as was predicted from molecular model examination.[2]

Comparisons of the distances and bond angles of Table I provide interesting conclusions. (1) Oxygen–oxygen repulsions in the free ligand (**1a**) deform the aryl groups and their attached atoms from their normally coplanar arrangements. Although the usual van der Waals oxygen-to-oxygen distance is 2.80 Å, the pseudoortho distances in **1a** are 2.92 Å. This is attributed to the enforced orientations of the electron pairs and the accumulation of six contiguous pseudoortho oxygen relationships. (2) Introduction of Li^+ into the hole shrinks the diameter from 1.62 Å to a filled-hole diameter of 1.48 Å,[10] which provides a pseudoortho oxygen–oxygen distance at 2.78 Å, slightly below the usual van der Waals distance. The hole shrinkage must increase the oxygen–oxygen repulsions, an effect compensated for by introduction of the positive charge and relaxation of the angle strains in the aryl support structures. For example, the distance the oxygens are bent out of the best planes of their attached aryls decreases from 0.20 in **1a** to 0.07 Å in **2a**. Likewise, the angles of aryl folds around their $O{-}Ar{-}CH_3$ axes decrease from 6.3 in **1a** to 2.6° in **2a**. Thus some of the strong binding that **1** shows for Li^+ is associated with compensation for oxygen–oxygen repulsion and relaxation of deformation strain in the support structure. (3) Introduction of Na^+ into the hole expands its diameter from 1.62 Å in **1a** to a filled-hole diameter of 1.75 Å in **3a**.[11] The resulting pseudoortho oxygen–oxygen distance is 3.00 Å, well above the usual van der Waals distance. The hole expansion must relieve oxygen–oxygen repulsion, and the positive charge therefore becomes less important in compensating for these repulsions in **3a** than in **2a**. Some relief of angle strain in the support structure of **1a** is seen in passing to **3a**. Thus the distances the oxygens are bent out of the best planes of their attached aryls decrease from 0.20 in **1a** to 0.12 Å in **3a**. Likewise the angles of the aryl folds around the $O{-}Ar{-}CH_3$ axes decrease from 6.3 in **1a** to 4.8° in **3a**. (4) Interestingly, the average distances that the carbons of the attached aryls are bent out of the best planes of their parent aryls are identical (0.16 Å) in the three structures. In contrast, the Ar–Ar best plane dihedral angles go from 52 to 56 to 61° for the empty, Li^+, and Na^+ filled spherands, respectively, in spite of the fact that the hole diameters increase in a different order (**2a** < **1a** < **3a**). The dihedral angles within the $CH_3OC_6H_2$ units between the C–O–C planes and the best aryl planes are 62 in **1a**, 85 in **2a**, and 84° in **3a**. These differences probably reflect adjustments to the differing demands of molecular packing. Although $Ar{-}O{-}CH_3$ bond angles are normally about 118°, they are 115, 112, and 113° in **1a**, **2a**, and **3a**, respectively. This trend is compatible with the intuitive generalization that the larger the number of ligands attached to an element, the smaller the bond angles must be to spatially accommodate those ligands.

These results demonstrate that a moderately strained and highly organized hexameric host can be assembled by oxidation with $Fe(AcAc)_3$ of monomeric, dimeric, or trimeric aryldilithium. High-energy aryl radicals are probably intermediates that couple to produce aryl–aryl bonds in these syntheses. It seems likely that only highly exothermic reactions will produce spherands as strained as **1**. The immediate open-chain precursor of the lithiospherium salt (**2**) was probably the open-chain hexaaryl diradical, which possesses 1024 different possible conformations.[12] Only two of these (enantiomerically related) could lead directly to the enforced conformation of cycle **1** or its complexes. The Li^+ present in the medium probably provided much of the organization this diradical needed to ring close. Its very short life insured its high dilution.

Supplementary Material Available: Position and vibration parameter for the spherand, lithiospherium chloride, and sodiospherium methyl sulfate (3 pages). Ordering information is given on any current masthead page.

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[10] The diameter of the hole organized and occupied by Li^+ in the [2.1.1]cryptand complex of LiI (six heteroatoms) is about 1.50 Å [Moras, P. D.; Weiss, R. *Acta Crystallogr. Sect. B* **1973**, *b29*, 400–403].

[11] The diameter of the hole organized and occupied by Na^+ in benzo-15-crown-5·H_2O·NaI (six heteroatoms) is 1.97 Å [Bush, M. A.; Truter, M. R., *J. Chem. Soc. Perkin, Trans. 2* **1972**, 341–344]. This and other diameters are calculated by averaging the $O{-}M^+$ distances and subtracting the radius of an O atom (1.40 Å) [Pauling, L. C. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260].

[12] The open-chain hexameric diradical is constitutionally like ended. It contains five potentially chiral elements associated with Ar–Ar rotations and six associated with $CH_3O{-}Ar$ rotations, eleven in all. The number of stereoisomers (conformers) for a constitutionally like-ended system containing an odd number of potential chiral elements is 2^{n-1} [Mislow, K. "Introduction to Stereochemistry", W. A. Benjamin: New York, 1965; p 88].

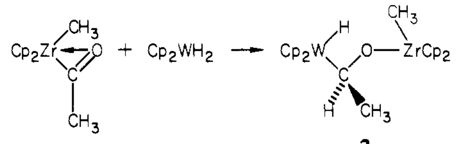
Transition-Metal-Mediated Hydrogenation of CO to Olefins: Intermediacy of Coordinated Carbenes

John A. Marsella, Kirsten Folting, John C. Huffman, and Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center
Indiana University, Bloomington, Indiana 47405

Received May 18, 1981

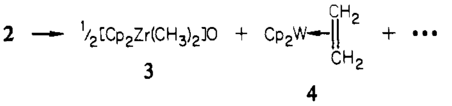
We recently reported that the reaction of $Cp_2Zr(CH_3)[\eta^2\text{-}C(O)CH_3]$ (**1**) with several transition-metal hydrides yields products arising from hydrogen transfer to the unsaturated carbon of the η^2-acetyl unit.[1a] For example, Cp_2MoD_2 gave $Cp_2Zr(CH_3)(OCD_2CH_3)$ immediately on mixing. At that time, we noted that the reaction of **1** and Cp_2WH_2 permits detection of a bimetallic complex (**2**), the consequence of a single hydrogen transfer by a dihydrido complex. We report here the identity of the unexpected products of further reaction of **2**. We also report the first detailed observation of a stoichiometric synthesis of ethylene incorporating carbon from CO and the intermediacy (and structure) of a W(II) carbene complex in the reaction which ultimately forms ethylene.



(1)

1 2

Treatment of a solution of $Cp_2Zr(CH_3)_2$ and Cp_2WH_2 in C_6D_6 (unreactive at 25 °C) with CO (1 atm) leads to the formation of **2**; this reaction is characterized by a color change from yellow to orange.[1b] The lifetime of **2** in solution is limited and resonances due to $[Cp_2Zr(CH_3)]_2O$ (**3**)[2] and $Cp_2W(\eta^2\text{-}C_2H_4)$ (**4**)[3] soon appear (eq 2). The use of ^{13}CO leads to carbon-13 incorporation in the ethylene ligand of **4** (i.e., $H_2{}^{13}C^{12}CH_2$). Additional resonances are observed in the zirconium cyclopentadienyl region as eq 2 proceeds and the ^1H NMR resonances of $CH_4 + C_5H_6$ also appear. The cyclopentadienylzirconium compounds responsible for these additional resonances have not been identified; however, similar resonances are observed when either $Cp_2Zr(CH_3)_2$ or **3** is hydrolyzed with water. We have established, by comparison to an



(2)

3 4

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[1] (a) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 1747. Marsella, J. A.; Huffman, J. C.; Caulton, K. G. *ACS Symp. Ser.* **1981**, *No. 152*. (b) Cp_2ZrMe_2 reacts rapidly with CO to form $Cp_2Zr[C(O)Me]Me$. Formation of **2** has also been demonstrated by using isolated samples of $Cp_2Zr[C(O)Me]Me$.

[2] (a) This new complex may also be synthesized from $[Cp_2ZrCl]_2O$ and CH_3Li. ^1H NMR (C_6D_6): δ 5.73 (s, 10 H, Cp_2Zr), 0.23 (s, 3 H, CH_3). MS; heaviest ion observed *m/e* 471, corresponding to M-15; $[Cp_4{}^{90}Zr_2(CH_3)O]^+$. (b) This complex has also been referenced in a recent publication: Hunter, W. E.; Atwood, J. L.; Fachinetti, G.; Floriani, C. *J. Organomet. Chem.* **1981**, *204*, 67.

[3] (a) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. (b) Thomas, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 1838.

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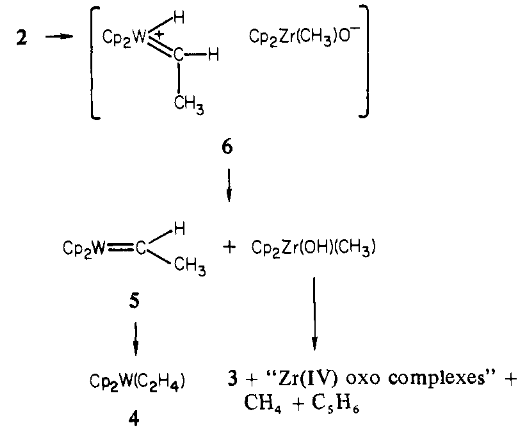
Scheme I



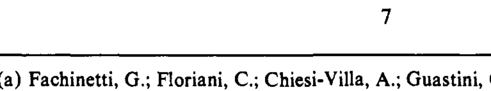
authentic sample, that $(Cp_2ZrO)_3$[4] is *not* a product of these reactions. By proton NMR spectroscopy, the formation of **4** is nearly quantitative, while **3** accounts for approximately two-thirds of the original zirconium cyclopentadienyl peak intensity.

Periodic spectroscopic monitoring of the course of reaction **2** allows detection of an intermediate whose C_5H_5 resonances are in the region characteristic of tungsten complexes. This complex exhibits two closely spaced singlets (each of intensity 5) at δ 4.59 and 4.63 (relative to Me_4Si), a doublet at δ 1.03 (J = 7 Hz, intensity 3), and a quartet at δ 10.3 (J = 7 Hz, intensity 1). We assign these resonances to a single species, $Cp_2W{=}C(H)(CH_3)$ (**5**), which is observed to subsequently rearrange to the ethylene complex **4**.

The mechanism of formation of **3** is not clear. As written, eq 2 leaves two atoms of hydrogen and one atom of oxygen (i.e., the constitutents of H_2O) unaccounted for. While the liberation of free H_2O is implausible in the presence of the oxophiles Zr and W, the production of C_5H_6, CH_4, and hydrolysis-like zirconium complexes suggests the intermediacy of an acidic species. Consistent with this hypothesis is the fact that decomposition of **2** in the presence of added $Cp_2Zr(CH_3)_2$ leads to conversion of the dialkyl complex to oxo species. Heterolytic cleavage of the C–O bond in **2**, followed by proton transfer to yield a complex such as $Cp_2Zr(CH_3)(OH)$, provides one mechanism that accounts for the observed products (see Scheme I).[5] This Zr(IV) hydroxy complex is a plausible source of the CH_4 and C_5H_6 (by bimolecular hydrolysis of Zr–CH_3 and Zr–C_5H_5 bonds) and subsequent coupling with **2** or added $Cp_2Zr(CH_3)_2$ would give **3**.

The 1,2-hydrogen shift in the isomerization **5** → **4** is unusual but not unpredecedented.[6] We have found that it is possible to prevent this rearrangement, however, and thus isolate a Cp_2W-(carbene) complex analogous to that shown in Scheme I.

Reaction of $Cp_2Zr[C(O)Ph]Ph$[7] with Cp_2WH_2 yields the expected bimetallic complex (**7**) in ca. 70% isolated yield (eq 3).[8]



7 (3)

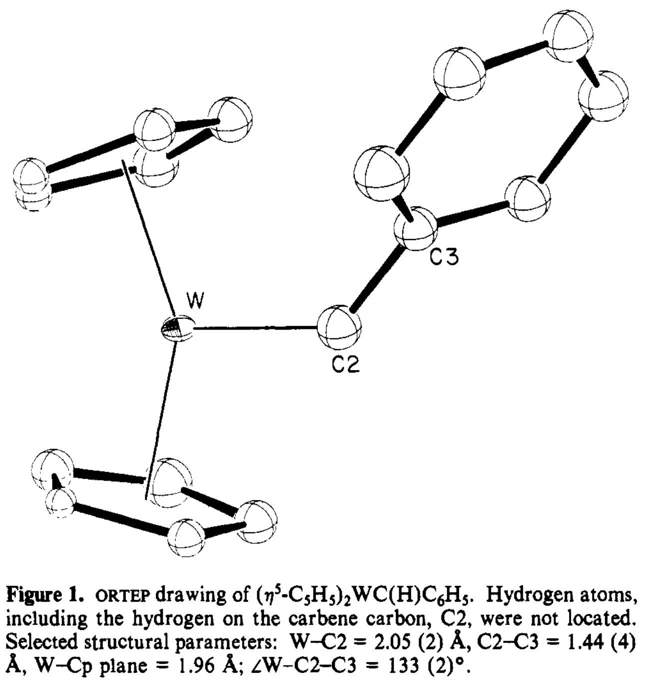


Figure 1. ORTEP drawing of $(\eta^5\text{-}C_5H_5)_2WC(H)C_6H_5$. Hydrogen atoms, including the hydrogen on the carbene carbon, C2, were not located. Selected structural parameters: W–C2 = 2.05 (2) Å, C2–C3 = 1.44 (4) Å, W–Cp plane = 1.96 Å; ∠W–C2–C3 = 133 (2)°.

Thermolysis of **7** in benzene in 70 °C for 3 h (or 100 °C for 15 min) leads to the formation of a green solution and a white solid.[9a] From the green solution, we have obtained crystals suitable for X-ray diffraction.[10] Proton and ^{13}C NMR both suggest that the green complex is $Cp_2W{=}C(H)(Ph)$ (**8**);[9b] an X-ray study confirms this assignment. Figure 1 shows an ORTEP drawing of **8** along with selected bond distances and angles. The orientation of the carbene ligand is such that the cyclopentadienyl rings are inequivalent, consistent with the NMR spectra of both **5** and **8**. This orientation of the carbene plane (within 6.3° of coplanarity with W and the two ring midpoints) is in accord with published molecular orbital calculations[11] and is identical with that found in $Cp_2W{=}C(H)OZr(H)(C_5Me_5)_2$.[12]

Compound **2** is one of a limited number of examples of *cis*-hydrido alkyls.[13,14] We have shown that the molybdenum analogue of **2** rapidly undergoes elimination of "alkane" [$Cp_2Zr(Me)OEt$] to produce Mo(II), scavenged as Cp_2MoCO in the presence of CO.[1] The products derived from **2** and **7** show that this reductive elimination *stoichiometry* is not valid for tungsten. It is possible to argue that "Cp_2W" is sufficiently less stable than Cp_2Mo and that its intermediacy is precluded;[13] yet $Cp_2W(H)Me$ does appear to undergo reduction to "Cp_2W" at 60–80 °C.[14] We therefore prefer to attribute the distinct reaction paths of the Mo and W complexes to a *subtly* diminished stability of Cp_2W relative

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(4) (a) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767. (b) This observation represents a mechanistically significant deviation from the simple collapse of **2** to $^1/_3(Cp_2ZrO)_3$ + CH_4 + Cp_2WCHMe.

(5) Alternatively, the cleavage of the C–O bond in **2** may occur by a homolytic pathway. A closely related complex, $Cp_2Zr(Cl)(CPh_2OCH_3)$, appears to cleave via a free radical process. Erker, G.; Rosenfeldt, F. *Tetrahedron Lett.* **1981**, *22*, 1379. A "1,3-hydrogen shift", taking **2** directly to **5** and $Cp_2Zr(OH)CH_3$, is much preferred by one referee.

(6) (a) Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533. (b) Fischer, E. O.; Held, W. *J. Organomet. Chem.* **1976**, *112*, C59. (c) Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* **1972**, *94*, 4354.

(7) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946.

(8) ^1H NMR (C_6D_6): δ 7.1–7.8 (m, 10 H, Ph), 6.77 (br, s, 1 H, CH), 5.92 (s, 5 H, CpZr), 5.77 (s, 5 H, CpZr), 4.23 (d, $^3J_{H\text{-}H} < 1$ Hz, CpW), 4.07 (d, $^3J_{H\text{-}H} < 1$ Hz, CpW), −11.2 (br, 1 H, W–H, $J_{W\text{-}H}$ = 86 Hz). A ^{13}C enriched sample (from ^{13}CO) shows that the resonances at 6.77 and −11.2 are coupled to the methine carbon, $^1J_{C\text{-}H}$ = 140 Hz, $^2J_{C\text{-}H}$ = 5.3 Hz. ^{13}C NMR: δ 69 (CHO, $^1J_{W\text{-}C}$ = 73 Hz).

(9) (a) A suspension of 200 mg of **7** in 5 mL of toluene was heated to 75 °C for 3 h to form a dark green solution and a gray precipitate. Vacuum removal of toluene left a green oil which was extracted into 75 mL of hexanes. Concentration (by 50%) of this green solution gave first a white precipitate. When further concentration first showed green solid, the solution was filtered. The filtrate was taken to dryness to yield 50 mg (45%) of green solid which is 95% pure by NMR spectroscopy. Additional purification is possible by recrystallization from Et_2O. (b) ^1H NMR (C_6D_6): δ 10.82 (s, 1 H, CH), 7.02 (br, 5 H, Ph), 4.65 (s, 5 H, CpW), 4.58 (s, 5 H, CpW). ^{13}C NMR: δ 224 ($^1J_{W\text{-}C}$ = 141 Hz, $^1J_{C\text{-}H}$ = 131 Hz), carbene carbon.

(10) Crystallographic data (−160 °C): a = 13.967 (4), b = 11.286 (3), c = 16.327 (4), Z = 8, in space group *Pcab*; $R(F)$ = 0.053, $R_W(F)$ = 0.0483 for 987 observed [$F_o > 3\sigma(F_o)$] reflections using isotropic temperature factors for all atoms except tungsten.

(11) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(12) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *101*, 218.

(13) Norton, J. *Acc. Chem. Res.* **1979**, *12*, 139.

(14) Copper, N. J.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Dalton Trans.* **1979**, 1557.

to Cp_2Mo, accentuated by the availability of an alternative mechanism, zirconium-assisted C–O heterolysis. This mechanism (see Scheme I) has the virtue that a 16-electron tungsten complex is never invoked. In any event, the ability to drastically influence product selectivity (alkane vs. alkene) in heterobimolecular CO hydrogenation with elements as similar as Mo and W is revealed in these studies. In addition, this work furnishes an example of one way of accomplishing the poorly understood carbon–oxygen bond scission step in Fischer–Tropsch hydrocarbon synthesis. It also reveals an alternative mechanism (to β-H elimination from a surface-bound alkyl moiety) for the production of olefinic Fischer–Tropsch products,[15] and it thus elaborates the results and proposals of Brady and Pettit concerning the intermediacy of surface-bound alkylidenes.[16]

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 80-06331) and the M. H. Wrubel Computer Center. J. A. Marsella acknowledges a fellowship from the Lubrizol Foundation.

Supplementary Material Available: A table of atomic positional and thermal parameters for $Cp_2WC(H)Ph$ (1 page). Ordering information is given on any current masthead page.

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(15) For a recent review of Fischer-Tropsch mechanisms, see: Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.

(16) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181.

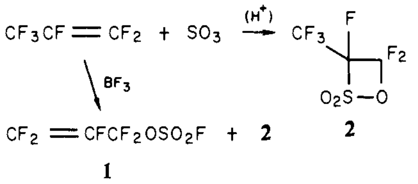
Perfluoroallyl Fluorosulfate, a Reactive New Perfluoroallylating Agent[1]

Carl G. Krespan* and David C. England

E. I. du Pont de Nemours & Co.
Central Research & Development Department
Experimental Station
Wilmington, Delaware 19898

Received May 22, 1981

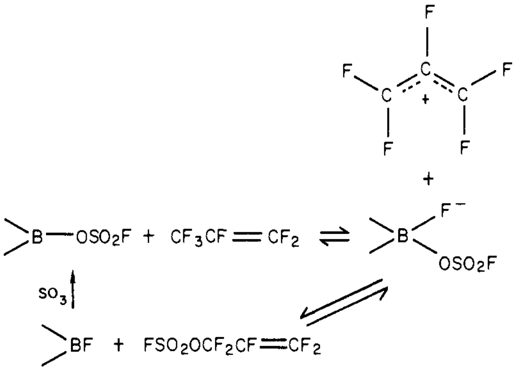
Previous studies[2-4] have shown that the principal reaction path for terminal fluoro olefins with sulfur trioxide is a [2 + 2] cycloaddition to produce β-sultones, although other products may also be isolated depending on reaction conditions and the fluoro olefin structure. We have now found that trivalent boron compounds are capable of catalyzing an unusual net insertion of SO_3 into an allylic C–F bond to give reactive fluorosulfates.[5] The formation of perfluoroallyl fluorosulfate (**1**) from hexafluoropropene and sulfur trioxide is of particular interest.



Pure distilled sulfur trioxide and hexafluoropropene at temperatures up to 100 °C under pressure lead to β-sulfone **2** in high yield as the sole product. The presence of 0.5–2 wt % of BF_3 (or related materials, e.g., $B(OCH_3)_3$ or B_2O_3) in sulfur trioxide at temperatures of 20–60 °C diverts the reaction to one in which moderate yields of fluorosulfate **1** are formed along with **2**. Such reactions carried out at 25 °C or slightly higher over 10–60 h with a 1.5- to 2-fold excess of hexafluoropropene give **1** as the major product (50–60% yield), so that **1** is a reagent readily prepared in quantity.

The catalytic nature of the reaction is implied in the demonstration that fluorosulfate **1** is formed reversibly. A sample of **1** contacted with preformed 3:1 $SO_3/B(OCH_3)_3$ catalyst for 1 week at 25 °C gave ca. 30% of hexafluoropropene along with a small amount of BF_3. Sultone **2** was unaffected by the same catalyst composition.

Although a variety of catalyst compositions derived from BF_3 or $B(OCH_3)_3$ and SO_3 proved to be active, attempts to isolate a simple boron fluorosulfate derivative were unsuccessful. That the compounds present in the catalyst mixture are mainly derivatives of boroxin is indicated by elemental analyses and the formation of pyrosulfuryl fluoride as a byproduct. We believe that such fluorosulfated boroxins are capable of abstracting an allylic fluorine atom from hexafluoropropene to form the perfluoroallyl cation.[6] Transfer of fluorine back to the cation regenerates hexafluoropropene, while transfer of a fluorosulfate group gives **1**. The trivalent B–F species resulting from the latter transfer is rapidly converted to fluorosulfate by the excess sulfur trioxide present, thus driving the reaction in the forward direction.



Fluorosulfate **1**[7,8] is best isolated by preliminary rapid distillation to remove catalyst followed by careful fractionation; bp 63–64 °C; IR (CCl_4) 1785 (C=C), 1485 cm^{-1} (SO_2); NMR[9] (CCl_4) 46.1 (t of d, J_{FF} = 8.5, 1.8 Hz, 1 F, OSO_2F), −74.0 (d of d of d of d, J_{FF} = 28.2, 13.9, 8.5, 7.8 Hz, 2 F, CF_2), −91.2 (d of d of t, J_{FF} = 50.0, 40.5, 7.8 Hz, 1 F, *cis*-$CF_2CF{=}C\mathit{F}F$), −104.7 (d of d of t, J_{FF} = 119.4, 50.0, 28.2 Hz, 1 F, *trans*-$CF_2CF{=}CF\mathit{F}$), and −192.4 ppm (d of d of t of d, J_{FF} = 119.4, 40.5, 13.9, 1.8 Hz, 1 F, $CF_2C\mathit{F}$—). Anal. Calcd for $C_3F_6O_3S$: C, 15.66; F, 49.54. Found: C, 15.31; F, 49.59.

Nucleophilic displacement of fluorosulfate anion from **1** occurs with ease. For example,

$$\mathbf{1} + NaI \xrightarrow[30\ ^\circ C]{acetone} CF_2{=}CFCF_2I\ (68\%) + NaOSO_2F$$

Since attack by nucleophiles such as I^- on sp^3 carbon in highly fluorinated molecules does not occur, the reaction no doubt proceeds by attack at the terminal vinylic carbon in an S_N2' reaction or in a stepwise version of it involving an intermediate carbanion. The fluorosulfate anion produced is unreactive in this system, thereby allowing the use of **1** to introduce a double bond which remains in the terminal position. Perfluoroallyl chloride has previously been shown to undergo similar reactions, but it is difficult to make and purify.[10,11]

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(1) Contribution No. 2924.

(2) England, D. C.; Dietrich, M. A.; Lindsey, R. V. *J. Am. Chem. Soc.* **1960**, *82*, 6181.

(3) Krespan, C. G.; Smart, B. E.; Howard, E. G. *J. Am. Chem. Soc.* **1977**, *99*, 1214.

(4) Knunyants, I. L.; Sokolski, G. A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 583.

(5) Smart (Smart, B. E. *J. Org. Chem.* **1976**, *41*, 2353) reports the only related formation of an allylic fluorosulate of which we are aware. In this case, competitive cycloaddition with the substrate, hexafluorocyclobutene, was not a factor; so the possible involvement of a catalyst was not determined.

(6) Chambers et al. (Chambers, R. D.; Parkin, A.; Matthews, R. S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2107) report evidence for the generation of perfluoroallyl cation from hexafluoropropene and SbF_5. We observed no reaction between hexafluoropropene and BF_3 at moderate temperatures.

(7) U.S. Patent 4235804, 1980.

(8) Dr. G. Hofmann of the Polymer Products Department, Du Pont, first prepared perfluoroallyl fluorosulfate and characterized it as the dibromide.

(9) Downfield from $CFCl_3$ as internal reference.