from the reaction of the appropriate K$_2$[Fe(CO)$_3$PR$_3$] with Ph$_3$SnCl in THF. Infrared spectra of these species are consistent with trigonal-bipyramidal LL′M(CO)$_3$ structures, where L and L′ occupy the axial positions.

The most interesting characteristic reaction of Fe(CO)$_3$PR$_3^{2-}$ observed so far is their ability to undergo facile ligand-exchange reactions

$$\mathrm{Fe(CO)_3PR_3^{2-} + L \rightleftharpoons Fe(CO)_3L^{2-} + PR_3}$$

For example, bubbling CO at atmospheric pressure through a suspension of K$_2$[Fe(CO)$_3$PPh$_3$] in THF caused the initial orange slurry to change to a white solid within 15 min at room temperature. An 80% yield of bona fide K$_2$Fe(CO)$_4$[10] was isolated from this reaction. Similarly, treatment of K$_2$[Fe(CO)$_3$PPh$_3$] with 10 equiv of P(OMe)$_3$ gave a white slurry within 1 h. On the basis of the close similarity of its mull infrared spectrum[25] to that of bona fide K$_2$[Fe(CO)$_3$PPh$_3$] and its conversion to the triphenyltin derivative [Et$_4$N][Ph$_3$SnFe(CO)$_3$P(OMe)$_3$] (58% yield of colorless, analytically pure crystals),[26] this material is formulated as K$_2$[Fe(CO)$_3$P(OMe)$_3$] (89% isolated yield). By contrast, treatment of K$_2$[Fe(CO)$_3$PPh$_3$] with 20 equiv of PEt$_3$ in THF at room temperature after 24 h gave a deeper orange mixture containing both Fe(CO)$_3$PPh$_3^{2-}$ and what is believed to be Fe(CO)$_3$PEt$_3^{2-}$. Thus, the displacement of PPh$_3$ from Fe(CO)$_3$PPh$_3^{2-}$ by an incoming group L appears to proceed to completion only if L is a better π acceptor than triphenylphosphine.

The mechanism of this ligand-exchange process is unknown, but it may involve an initial dissociation step to generate low concentrations of the highly reactive Fe(CO)$_3^{2-}$ and/or Fe(CO)$_3$THF^{2-}. Indeed, suspensions of K$_2$Fe(CO)$_3$PPh$_3$ in THF appear to slowly react with molecular hydrogen at 1-atm pressure and 25 °C, but the nature of the product is presently unresolved. M. Darensbourg and Hanckel have found related but slower ligand-exchange reactions of V(CO)$_5$PR$_3^-$ to follow a dissociative pathway, perhaps involving V(CO)$_5^-$ and/or V(CO)$_5$THF$^-$.[27]

In conclusion, the two-step process described above which converts Fe(CO)$_4$PR$_3$ to Fe(CO)$_3$PR$_3^{2-}$ may be general route for the conversion of any M(CO)$_x$L$_y$ to the corresponding M(CO)$_{x-1}$L$_y^{2-}$, as long as M(CO)$_x$L$_y$ reacts with OH$^-$ to give reasonably acidic and thermally stable HM(CO)$_{x-1}$L$_y^-$, where L is a poor leaving group[28] and a potential π acceptor. The scope of these reactions is presently under investigation in this laboratory.[29]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE79-12159) for support of this research. J.E.E. is indebted to Professor M. Y. Darensbourg for helpful discussions and receipt of a manuscript (ref 27) prior to publication.

Registry No. Fe(CO)$_4$PPh$_3$, 35679-07-3; [Et$_4$N][HFe(CO)$_3$PPh$_3$], 80312-33-5; K$_2$[Fe(CO)$_3$PPh$_3$], 80612-34-6; Fe(CO)$_4$PMe$_2$Ph, 51743-97-6; [Et$_4$N][HFe(CO)$_3$PMe$_2$Ph], 80612-36-8; K$_2$[Fe(CO)$_3$PMe$_2$Ph], 80612-37-9; [Et$_4$N][Ph$_3$SnFe(CO)$_3$PPh$_3$], 80612-39-1; [Et$_4$N][Ph$_3$SnFe(CO)$_3$PMe$_2$Ph], 80630-28-0; Ph$_3$SnCl, 639-58-7; [Et$_4$N][Ph$_3$SnFe(CO)$_3$P(OMe)$_3$], 80630-30-4; K$_2$[Fe(CO)$_3$P(OMe)$_3$], 80630-31-5.

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(25) IR (Nujol mull) ν_{CO} region (cm^{-1}) 1815 sh, 1800 m, 1710 s, 1660 s.

(26) Anal. Calcd for C$_{32}$H$_{44}$O$_6$FeNPSn: C, 51.65; H, 5.92; N, 1.88. Found: C, 51.85; H, 5.92; N, 1.86. IR (CH$_3$CN) ν_{CO} region (cm^{-1}) 1835 vs. ^{1}H NMR (CD$_3$CN) δ 7.06–7.77 (m, 15H, phenyl), 3.69 (d, 9H, $J_{\mathrm{P-H}}$ = 12.5 Hz, –OMe); Et$_4$N$^+$ signals are omitted.

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(28) Gibson has examined a number of interesting reactions of neutral substituted carbonylmetal halides with hydroxide ion. Usually, halide ion is lost from the intermediate halometallocarboxylic acid anion before decarboxylation occurs: Gibson, D. H.; Hsu, W. L.; Ahmed, F. U. *J. Organomet. Chem.* **1981**, *215*, 379.

(29) **Note Added in Proof:** Cooper et al. have recently described the preparation of thermally unstable solutions of W(CO)$_4$PR$_3^{2-}$ (R = *i*-Pr) by the reduction of W(CO)$_4$(PR$_3$)NMe$_3$: Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1982**, *1*, 215.

Geometries of the Radical Anions of Ethylene, Fluoroethylene, 1,1-Difluoroethylene, and Tetrafluoroethylene

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ESR spectra of radical anions of fluorinated alkenes and aromatics indicate that apparently rather similar species adopt drastically different geometries.[1-5] Because of the importance of these and related species in spectroscopy and as reaction intermediates, we have carried out ab initio calculations which indicate that the geometries of radical anions of ethylene and fluoroethylenes differ significantly from those assigned previously on the basis of hyperfine structure.

Studies of the radical anions of fluorinated ethylenes,[1,2] butadienes,[3] and benzenes[3-5] have focused upon whether these species are formed by electron attachment to σ^* or π^* orbitals and whether the geometries are strongly distorted from planarity. On the basis of ESR results, Yim and Wood[5] argued that the ground-state anions of 1,2,4,5-tetrafluorobenzene, pentafluorobenzene, and hexafluorobenzene have σ symmetry. Symons et al.[3] have argued that the hexafluorobenzene anion is nonplanar, while Wang and Williams have provided new evidence that this anion is planar.[4] Williams has also argued that the ground-state anion of tetrafluoroethylene is planar with the odd electron in a σ^* orbital but that the ground-state anion of 1,1-difluoroethylene has a perpendicular geometry.[1]

These interpretations were based on studies carried out in the condensed phase and should apply to the equilibrium geometries of the anions. Gas-phase electron transmission spectroscopy, which provides vertical electron affinities,[6] easily detects anions arising from occupation of π^* orbitals, but no evidence was seen for states involving occupation of σ^* orbitals. SCF calculations employing DZ basis sets at the equilibrium geometries of the ground states of the fluoroethylenes indicate that the σ^* orbitals lie above the π^* orbitals.[6]

We have used the spin-unrestricted SCF gradient method to optimize the geometries of the ground-state anions of ethylene, fluoroethylene, 1,1-difluoroethylene, and tetrafluoroethylene. The calculations were performed with the GAUSSIAN 80 package of programs[7] and the 3-21G basis set.[8] Although the variational principle is, strictly speaking, not applicable to open-shell anion states lying energetically above the ground state of the neutral molecule, the use of relatively small basis sets provides a means of avoiding the variational collapse that would result from the use of large basis sets. While such calculations will not yield accurate total energies, they should be quite useful for yielding geometries and relative energies.

The energies found for various structures of C$_2$H$_4^-$, C$_2$H$_3$F$^-$, CH$_2$CF$_2^-$, and C$_2$F$_4^-$ are summarized in Table I, and the geometries of the most stable structures are given in Figure 1. For C$_2$H$_4^-$, CH$_2$CF$_2^-$, and C$_2$F$_4^-$, calculations were performed on

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Table I. Energies of Structures of the Radical Anions of Ethylene and Fluoroethylenes

species	geometry	3-21G energy, au	E_{rel}, kcal/mol
ethylene	planar (D_{2h})-neutral geometry[a]	−77.44788	13.0
	planar (D_{2h})-anion geometry	−77.46284	3.7
	perpendicular (D_{2d})[b]	−77.42635	26.5
	syn (C_{2v})	−77.46578	1.8
	anti (C_{2h})	−77.46865	≡0.0
fluoroethylene	planar (C_s)-neutral geometry[a]	−175.77001	22.9
	planar (C_s)-anion geometry	−175.78991	10.4
	syn (C_1)	−175.80624	0.2
	anti (C_1)	−175.80651	≡0.0
1,1-difluoroethylene	planar (C_{2v})-neutral geometry[a]	−274.09644	39.1
	planar (C_{2v})-anion geometry	−274.12149	23.4
	perpendicular (C_{2v})	−274.13710	13.6
	syn (C_{2v})	not a minimum	
	anti (C_s)	−274.15873	≡0.0
tetrafluoroethylene	planar (D_{2h})-neutral geometry[a]	−470.71260	69.1
	planar (D_{2h})-anion geometry	−470.74433	49.2
	syn (C_{2v})	−470.80387	11.8
	anti (C_{2h})	−470.82269	≡0.0

[a] Geometries of neutrals were taken from: Whiteside, R. A.; Binkley, J. S.; Krishman, R.; DeFrees, D. J.; Schlegel, H. B.; Pople, J. A., "Carnegie-Mellon Quantum Chemistry Archive"; Carnegie-Mellon University: Pittsburgh, PA, 1980. Energies of the neutral molecules at the planar neutral geometries are -77.60099, -175.92057, -274.24746, and -470.85535 au for ethylene through tetrafluoroethylene, respectively. Energies of the neutral molecules at the anti radical anion geometries are -77.55417, -175.85805, -274.17361, and -470.75432 au, respectively. Only the *anti*-tetrafluoroethylene radical anion is more stable than the neutral molecules at the same geometry. [b] This D_{2h} structure gave a symmetry broken solution. A D_2 structure optimized with the two H_2C planes maintained at a dihedral angle of 1° is 9.4 kcal/mol higher in energy. [c] Optimization of the C_{2h} structure using the 6-311G basis, which has more diffuse functions in the valence shell, results in a structure only slightly (4°) less pyramidal than that obtained at the 3-21G level.

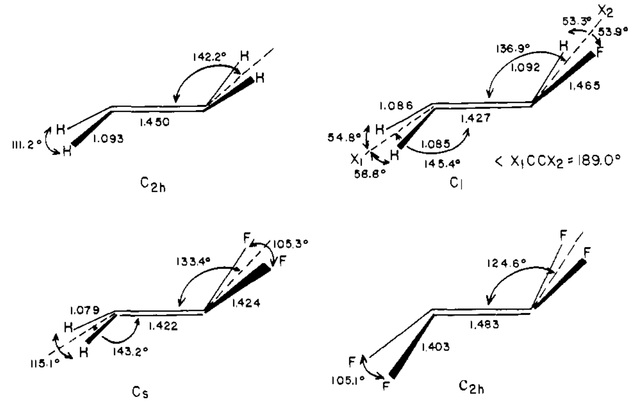
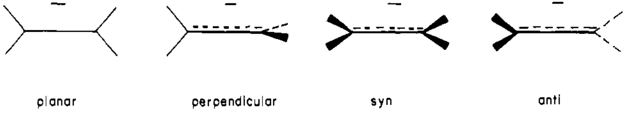


Figure 1. Optimized geometries of the radical anions of ethylene, fluorethylene, 1,1-difluorethylene, and tetrafluoroethylene.

planar, perpendicular, syn (cis bent), and anti (trans bent) structures, defined below:



For all four molecules, the lowest anion states constrained to planarity have π symmetry. However, these planar structures are not stable minima; upon optimization, the planar species relax to the anti structures, which are found to be lowest in energy. The perpendicular structures are saddle points for all four of these species. $C_2H_3F^-$ is found to prefer an "anti" structure which is slightly (9°) rotated. The degree of pyramidalization in the radical anions increases as fluorines are added, in accord with the tendency of both radicals and anions to become more pyramidal upon fluorination.[9]

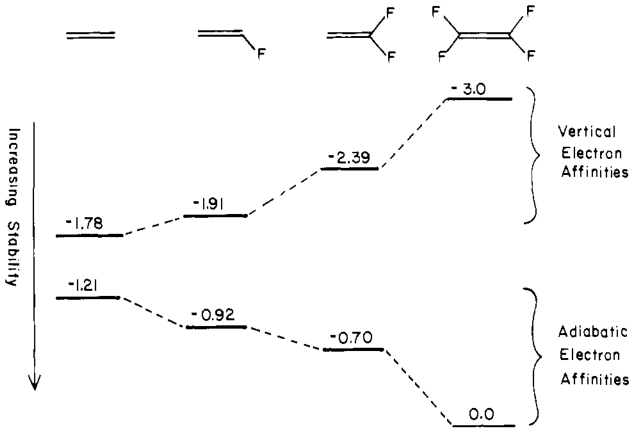


Figure 2. Vertical and adiabatic electron affinities of ethylene and three fluorinated ethylenes, in eV. Vertical EA's are experimental,[6] while adiabatic EA's are calculated as follows: $EA_{ad} = EA_{vert}^{exptl} + [E^{3\text{-}21G}$-(radical anion in 3-21G optimized geometry of neutral) − $E^{3\text{-}21G}$(radical anion in 3-21G optimized geometry of radical anion)].

ETS measurements[6] show that the vertical π^* anions are destabilized by fluorines. On the other hand, $C_2H_4^-$ has never been observed in the condensed phase, while $CH_2CF_2^-$ and $CF_2CF_2^-$ can be isolated in low-temperature matrices.[1,2] This suggests that stabilization due to nonplanar distortions increases upon fluorination. Furthermore, the stabilization of the anti form of the radical anion state upon fluorination must be larger than the destabilization of the planar form with the geometry of the neutral species. This is indeed the case, as illustrated in Figure 2, which compares the experimental vertical (from ETS) and calculated adiabatic electron affinities. The latter are obtained by subtracting the 3-21G vertical → adiabatic relaxation energies from the experimental vertical EA's. This procedure in part corrects for errors, both absolute and relative, in the method employed for the calculating of EA's. The most serious deficiency in our calculations is probably the neglect of d functions, which are needed to predict the correct trend in the vertical EA's with increasing fluorination.[6]

In terms of a molecular orbital picture, the strong distortions in these ions may be interpreted as arising from a mixing of the π^* and the high-lying σ^* orbitals. The situation is similar to that for the acetylene anion which also distorts due to σ^*–π^* mixing.[10,11] Our calculations indicate that the σ^* orbitals of ethylene are 3 eV or more higher in energy than the π^* orbital but that the separation between the σ^* and π^* orbitals decreases with increasing fluorination, which should promote bending upon electron attachment.

Williams has argued that $C_2H_2F_2^-$ has a perpendicular geometry, based on hyperfine coupling constants.[1] However, the evidence provided, namely, that the fluorine hyperfine constant is unusually large and that for the hydrogens is unusually small, is also consistent with the anti structure predicted in the present study.[12] Similarly, the hyperfine data available for the tetrafluoroethylene anion are inconclusive.

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(12) This conclusion is based on spin densities in the various geometries of the radical anions. Details will be described in the full report of this work.

Preliminary calculations for the chloroethylenes indicate that the anions of these species also adopt nonplanar structures but that after the anion distorts, dissociation to R· + Cl$^-$ occurs.[13] Recent electron scattering work confirms this instability of C$_2$H$_3$Cl$^-$.[14,15] For symmetry reasons, a nonplanar distortion must necessarily accompany chloride loss.[15]

The distortion of alkenes upon electron attachment is the same as that which occurs in the transition states of nucleophilic additions to alkenes.[10,16] Indeed, we believe that the origin of these distortions[10] is the same in both cases. The relevance of these results to the mechanisms and stereochemistries of reactions of nucleophiles with alkenes and aromatics will be reported in due course.[16-18]

Acknowledgment. This research was supported by National Science Foundation grants to K.N.H. and K.D.J. We are grateful to Professor J. A. Pople for the use of the GAUSSIAN 80 programs and the CMU VAX 11/780.

Registry No. Ethylene radical anion, 34527-91-8; fluoroethylene radical anion, 80009-98-9; 1,1-difluoroethylene radical anion, 77845-44-4; tetrafluoroethylene radical anion, 65338-13-8.

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(17) After completion of this work, we learned of an independent study of the geometries of ethylene and fluorinated ethylene radical anions: Merry, S.; Thomson, C. *Chem. Phys. Lett.* **1981**, *82*, 373. The geometries and energies of the minima reported by these authors are essentially identical with ours, except for those of the ethylene and fluoroethylene radical anions, which are apparently given for the syn species in the Merry–Thomson work. These authors did not present energies for geometries other than the purported global minima.

(18) **Note Added in Proof**: We wish to note that Professor Symons [Symons, M. C. R. *J. Chem. Res.* **1981**, 286] has also concluded that the tetrafluoroethylene anion is pyramidal with either a syn or anti structure consistent with our conclusions and those of ref 17.

Chirality due to ^{18}O Substitution. Synthesis and Chiroptical Properties of (1*S*)-2,4-Adamantanedione-*4*-^{18}*O*

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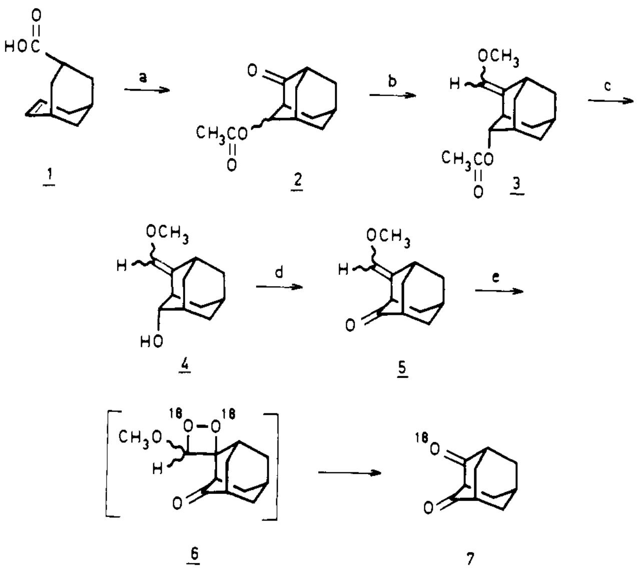
The rigid adamantane skeleton has proved of special value in the interpretation of subtle effects in the circular dichroism spectra of chiral carbonyl compounds.[1] In addition, the adamantane framework has shown its usefulness in the construction of chiral ketones whose chirality is due to isotopic substitution.[2,3] Only one example is known of an optically active cycloalkanone, the 1,2-diketone α-(^{16}O,^{18}O)fenchocamphorone quinone, whose chirality is solely due to oxygen-18 substitution.[4,5]

Two features interfere with studies of oxygen-18 labeled carbonyl compounds. First the available oxygen-18 starting materials are limited and expensive; the incorporation is usually obtained by an exchange or hydrolysis reaction with (^{18}O) water. Secondly, ketones rapidly exchange oxygen in aqueous media.[6] Thus a nonaqueous final step in the preparation of an oxygen-18 compound has obvious advantages. This paper reports the synthesis and circular dichroism data of (1*S*)-2,4-adamantanedione-*4*-^{18}*O* (**7**), a rigid 1,3-diketone, in which the chirality is solely due to the oxygen isotope. The synthetic route to this ketone is new, general, and applicable to a variety of chiral and achiral oxygen-18 labeled ketones. In addition to its novelty and generality this route appears to be more effective than the present methods of introduction of oxygen 18. The critical difference in the route we followed is the *nonaqueous* introduction of oxygen 18, through the intermediacy of an 1,2-(^{18}O)dioxetane.

Scheme I^a



^{a} (a) Boron trifluoride etherate, (CH$_3$CO)$_2$O, C$_6$H$_6$, room temperature, 1 h, 85%; (b) PH$_3$P$^+$–CH$_2$OCH$_3$Cl$^-$, *n*-BuLi, THF, room temperature, 24 h, ~25%; (c) LiOH, C$_2$H$_5$OH, H$_2$O, room temperature, 12 h, ~80%; (d) PDC, CH$_2$Cl$_2$, room temperature, 4 h, 40% (anti) and 60% (syn); (e) ^{18}O$_2$ (99%), methylene blue, CH$_2$Cl$_2$, $h\nu$, room temperature, 3 h, 70%.

The starting material in our synthesis was (+)-*endo*-bicyclo-[3.3.1]non-6-en-3-carboxylic acid (**1**).[7] The optically active 3*R*-acid **1**[8] was cyclized to an epimeric mixture of the 4-acetoxyadamantan-2-one (**2**) in a 2:1 equatorial axial[9] ratio. The equatorial **2** could be transformed into the two isomeric (syn and anti)[10] enol ethers **3** in ~25% yield. Basic hydrolysis afforded the two 4(e)-hydroxy-2-(methoxymethylene)adamantanes (**4**). The isomers could be separated and oxidized under neutral conditions to yield the corresponding (1*S*)-4-(methoxymethylene)-adamantan-2-one isomer (**5**). The optically active diketone (1*S*)-2,4-adamantanedione-*4*-^{18}*O* (**7**) was prepared by a photooxygenation of **5** with ^{18}O$_2$ gas (99%) and methylene blue in CH$_2$Cl$_2$.[11] Although the 1,2-dioxetane **6** could not be isolated, it is reasonable to assume that **6** is the intermediate in the photooxygenation.[12] Purification of **7** was achieved by sublimation. The diketone **7** was found to be very sensitive to water; even when stored as crystals a fast exchange with water in the air occurred.[13]

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(7) (a) Numan, H.; Troostwijk, C. B.; Wieringa, J. H.; Wynberg, H. *Tetrahedron Lett.* **1977**, 1761–1764. (b) The optical purity of **1** was established as 76 ± 3%, $[\alpha]_{578}$ +114 (*c* 1.0, ethanol).

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(9) Axial and equatorial with respect to the cyclohexanone ring.

(10) Syn and anti with respect to the methoxy group and the substituent at the 4-position.

(11) The excess of ^{18}O$_2$ gas could easily be isolated and reused if necessary.

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