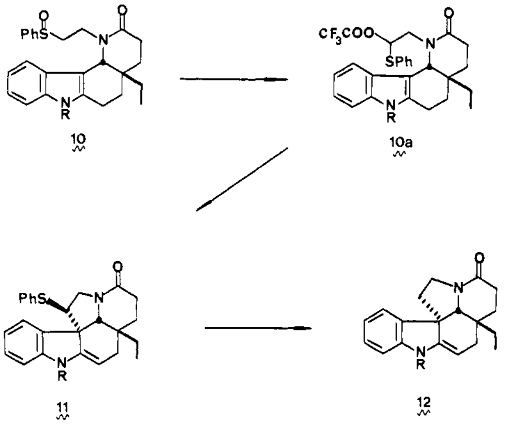
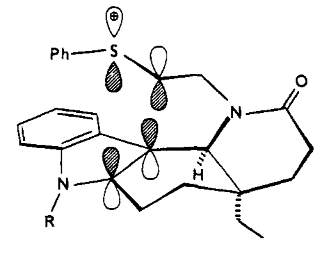
2.75 h gave the tetracyclic system **9**, mp 195–195.5 °C, in 33% yield after chromatography and crystallization from benzene/hexane. The only other product isolated from this reaction was **9a**, which did not convert into **9** on further heating.[6] The relative stereochemistry of **9** was demonstrated by single-crystal X-ray crystallography to be cis.[7] No trace of any other stereoisomers could be detected in the above reaction mixture. A plausible transition state for this reaction is **9b**.[2] The conformation of **9** in the crystalline state is most unusual, in that the $PhSCH_2CH_2$ group is bent back across the indole ring with the C(11) carbon atom in close proximity to C(12).

Oxidation of **9** with $MCPBA/CH_2Cl_2/NaHCO_3$ at 0 °C gave the sulfoxide **10** as a mixture of diastereomers in 97% yield. When the sulfoxides **10** were treated with trifluoroacetic anhydride[8] in dichloromethane at 0 °C for 10 min, the trifluoroacetate **10a** was formed. The mixture was warmed to 20 °C, and chlorobenzene was added and heated at 130 °C for 2.5 h to give the pentacycle **11** in 81% yield after direct crystallization from the reaction mixture, mp 135–137 °C. The structure and stereochemistry of **11** was confirmed by single-crystal X-ray crystallography.[9] The configuration of the PhS group at C(11) was predicted from the conformation of **9**, leading to the sulfonium ion **11a** and its subsequent closure to **11**. Desulfurization of **11** with Raney nickel (W-2, not deactivated) in ethanol at 20 °C for 1 h gave **12** (81%), mp 195–196 °C. Reduction of **12** with $LiAlH_4$/THF at 20 °C for 48 h cleanly gave *dl*-aspidospermidine **5** (54%), mp 99–103 °C (from acetone).[10,11]





11a

This new strategy for indole alkaloid synthesis provides a short, highly convergent route to aspidospermidine **5** (11.7% overall yield from **6**) and illustrates for the first time the use of an indole-2,3-quinodimethane in synthesis. We anticipate that its flexibility in allowing more complex alkaloids to be readily synthesized through intermediates such as **11**, where C(11), C(8), and C(13) are functionalized, will prove to be its most useful asset.

Acknowledgment. The National Institute of Health and Upjohn Co. are gratefully thanked for their support of this work. Professor Martin Kuehne is thanked for the generous gift of (+)-vincadifformine.

Supplementary Material Available: ORTEP structures for **9** and **11** and listings of IR, NMR, and microanalytical data (3 pages). Ordering information is given on any current masthead page.

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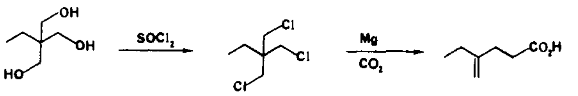
(5) 4-Ethylpent-4-enoic acid was prepared as follows: McCaffery, E. L.;



Shalaby, S. W. *J. Organomet. Chem.* **1967**, *8*, 17.

(6) A variety of mixed anhydrides and different activated esters were examined without any improvement in yield. It should be noted that the cyclization reaction **7** → **9** in the desethyl series proceeds in ca. 70% yield at almost the same rate. A detailed description of this reaction will be presented later.

(7) Compound **9** crystallizes in space group $P\bar{1}$ with cell dimensions (at −160 °C) $a = 20.992$ (13) Å, $b = 15.246$ (8) Å, $c = 10.010$ (5) Å, $\alpha = 118.83$ (2)°, $\beta = 92.29$ (2)°, and $\gamma = 95.22$ (2)°. The calculated density for $Z = 4$ is 1.372 g cm^{-3}. A description of the diffractometer, low-temperature apparatus, and data handling techniques are described in: *Inorg. Chem.* **1980**, *19*, 2755. Final residuals for the full-matrix refinement were $R_F = 0.097$ and $R_{wF} = 0.083$ for 7312 independent reflections. The two independent molecules in the crystal adapt essentially the same conformation. Complete crystallographic data are available in microfiche form from the Chemistry Library, Indiana University; request IUMSC Report No. 81064.

(8) Pummerer reaction applied to indoles: Oikawa, Y.; Yonemitsu, O. *J. Org. Chem.* **1976**, *41*, 1118.

(9) Compound **11** crystallizes in space group $P\bar{1}$ with cell dimensions (at −160 °C) $a = 11.162$ (3) Å, $b = 15.860$ (5) Å, $c = 9.321$ (2) Å, $\alpha = 81.25$ (1)°, $\beta = 103.63$ (1)°, and $\gamma = 107.89$ (1)°. The calculated density for $Z = 2$ plus one molecule of benzene solvent in the cell is 1.336 g cm^{-3}. Final residuals for the 3946 unique data are $R_F = 0.066$ and $R_{wF} = 0.061$. See ref 7 concerning experimental details. Complete crystallographic data are available in microfische form from the Chemistry Library, Indiana University; request IUMSC Report No. 81065.

(10) Djerassi, C.; Budzikiewicz, H.; Wilson, J. M.; Gosset, J.; LeMen, J.; Janot, M.-M. *Tetrahedron Lett.* **1962**, 235. Smith, G. F.; Wahid, M. A. *J. Chem. Soc.* **1963**, 4002. (+)-Vincadifformine was converted into aspidospermidine by decarboxylation to dehydro aspidospermidine followed by reaction with $LiAlH_4$.

(11) The synthetic material was identical [IR (soln), NMR (220 MHz), four TLC systems (20% MeOH/80% EtOAc; 30% CH_2Cl_2/70% Me_2CO; 40% EtOH/60% EtOAc; 5% MeOH/95% MeCN on silica gel 60F-254)] with the natural material. A wide variation in melting points for racemic aspidospermidine has been observed.

Highly Reduced Organometallics. 6.[1] Synthesis and Chemistry of Tricarbonylphosphineferrates(2−), $Fe(CO)_3PR_3^{2-}$

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Received November 23, 1981

Mononuclear carbonylmetallate dianions are well-established species[2] and have been valuable stoichiometric reagents in organic chemistry,[3] metal cluster synthesis,[4] and in the preparation of novel mononuclear organometallic compounds.[2] However, there have been no previous reports on phosphine-substituted metal carbonyl dianions.[5] Since these materials may be as useful in synthetic chemistry as the parent carbonyl dianions, we have recently investigated possible methods for their synthesis. In this paper some of our results are presented, including a potentially general two-step synthesis of carbonylphosphinemetallate dianions.

One-step reductions of $M(CO)_xPR_3$ to $M(CO)_{x-1}PR_3^{2-}$ almost invariably fail since the coordinated phosphine is generally lost in the presence of reducing agents.[6,7] For example, treatment

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(1) Part 5: Ellis, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 6106.

(2) For a review, see: Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1.

(3) Collman, J. P., *Acc. Chem. Res.* **1975**, *8*, 342.

(4) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207.

(5) Excepted are the completely substiuted $M(PF_3)_4^{2-}$ (M = Fe, Ru, and Os) prepared over 10 years ago: Kruck, T. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 679.

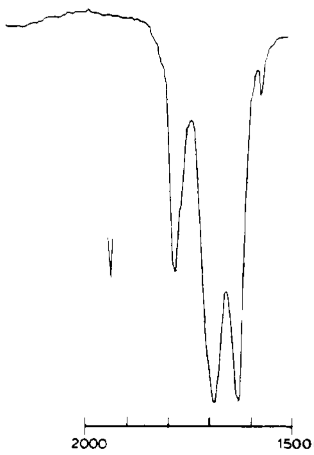

Figure 1. Nujol mull spectrum of $K_2[Fe(CO)_3PPh_3]$ in the carbonyl stretching frequency region. Positions of bands (ν_{CO}) (cm^{-1}): 1785 m, 1690 s, 1640 s. The peak at 1944 cm^{-1} is a polystyrene band. The weak band at 1580 cm^{-1} is due to coordinated PPh_3.

of $Fe(CO)_4PPh_3$ with potassium amalgam or K(*sec*-Bu)$_3$BH in tetrahydrofuran (THF) resulted in the formation of essentially quantitative yields of $K_2Fe(CO)_4$ and free triphenylphosphine.[8-10] Attempts to reduce $I_2Fe(CO)_3P(C_6H_{11})_3$[11] with sodium–benzophenone in ethyl ether also provided only $Fe(CO)_4^{2-}$ in low yields.

Previous reports that neutral and cationic-phosphine-substituted carbonyls react with a variety of nucleophiles without rapid loss of phosphine were extremely important in our development of a strategy to prevent or minimize loss of PR_3 during reduction. In particular, D. Darensbourg and Froelich noted that carbonyl oxygen exchange with water in $Fe(CO)_4PPh_3$ is catalyzed by hydroxide ion under phase-transfer conditions.[12] They proposed that the metallocarboxylic anion $Ph_3PFe(CO)_3CO_2H^-$ is a key intermediate in this exchange process.[13] Also, Pettit et al. isolated $C_5H_5Fe(CO)(CO_2H)PPh_3$ from the reaction of $C_5H_5FeCO)_2PPh_3^+$ with hydroxide ion. Subsequent decarboxylation of the metallocarboxylic acid provided $C_5H_5Fe(CO)PPh_3H$.[14] Since substituted metal carbonyl hydrides can often be deprotonated to form the corresponding carbonyl anions,[2] it was essential to determine whether the previously unknown $HM(CO)_{x-1}PR_3^-$ could be prepared from the reaction of $M(CO)_xPR_3$ and OH^- and, more importantly, whether these hydride monoanions could be deprotonated to give the desired dianions. We began this study with the inexpensive and readily available $Fe(CO)_4PR_3$ (PR_3 = PPh_3 and PMe_2Ph).[15]

Surprisingly, treatment of $Fe(CO)_4PPh_3$ with 15 equiv of $Et_4N^+OH^-$ in methanol did not lead to any apparent reaction after 24 h at room temperature.[16] However, after most of the methanol was removed under vacuum at or slightly below room temperature, the sparingly soluble $Fe(CO)_4PPh_3$ rapidly dissolved with simultaneous gas evolution, and the viscous solution turned to a bright yellow color. From this mixture, air-sensitive, yellow, crystalline, and analytically pure $[Et_4N][HFe(CO)_3PPh_3]$ was isolated in high yield (80–90%).[17]

Treatment of $[Et_4N][HFe(CO)_3PPh_3]$ with one or more equivalents of K(*sec*-Bu)$_3$BH in THF at room temperature caused gas evolution and converted the nearly insoluble tetraethylammonium salt to the much more soluble $K[HFe(CO)_3PPh_3]$.[18] When $[Et_4N][HFe(CO)_3PPh_3]$ was refluxed in the presence of at least 2 equiv of K(*sec*-Bu)$_3$BH, precipitation of a microcrystalline yellow-orange solid occurred. On the basis of elemental analysis, infared spectra (Figure 1), and derivative chemistry, this extremely moisture- and oxygen-sensitive substance is formulated as unsolvated $K_2[Fe(CO)_3PPh_3]$.[19] Yields from 60 to 82% have been obtained for reflux times of 6–16 h when the initial concentration of K(*sec*-Bu)$_3$BH is 0.25 M. Shorter reflux times are required when higher concentrations of K(*sec*-Bu)$_3$BH are employed.

The reaction of $Fe(CO)_4PMe_2Ph$ with $Et_4N^+OH^-$ by the same procedure mentioned above gave a yellow oil. After extraction with hot toluene to remove the excess $Et_4N^+OH^-$, filtration provided a solution of bright yellow and spectroscopically pure $[Et_4N][HFe(CO)_3PMe_2Ph]$. Although this substance could not be crystallized, its spectroscopic[20] and chemical properties are entirely consistent with the proposed formulation. The reaction of this hydride anion with excess 0.62 M K(*sec*-Bu)$_3$BH (10 equiv) in THF provided after only a 2 h reflux period a 75% yield (based on the initial amount of $Fe(CO)_4PMe_2Ph$) of nearly insoluble, yellow, crystalline, and analytically pure product formulated as $K_2[Fe(CO)_3PMe_2Ph]$.[21,22]

These materials are extremely reactive. For example, they rapidly deprotonate acetonitrile (pK_a = 25) at 25 °C to generate essentially quantitative yields of $HFe(CO)_3PR_3^-$ based on infrared solution spectra. Bona fide $[Et_4N][HFe(CO)_3PPh_3]$ was isolated in 90% yield from the reaction of $K_2Fe(CO)_3PPh_3$ with CH_3CN followed by cation exchange with $Et_4N^+Br^-$. In contrast, $K_2Fe(CO)_4$ does not react with CH_3CN at 25 °C. Good to moderate yields of the crystalline and colorless triphenyltin derivatives, $[Et_4N][Ph_3SnFe(CO)_3PPh_3]$ (65% yield)[23] and $[Et_4N][Ph_3SnFe(CO)_3PMe_2Ph]$ (43% yield)[24] have also been obtained

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[6] This is a specific result of an important generalization reported previously:[7] *Reduction of a mononuclear metal complex containing both good and poor π-acceptor ligands usually causes preferential loss of the poor or non-π acceptors.* One indication of the utility of this guideline is in the one-step syntheis of $Na_4M(CO)_4$ (M = Cr, Mo, and W) by the sodium metal reduction of $M(CO)_4$TMEDA (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) in liquid ammonia.[7]

[7] Ellis, J. E.; Parnell, C. P.; Hagen, G. P. *J. Am. Chem. Soc.* **1978**, *100*, 3605.

[8] The reduction of $Fe(CO)_4PPh_3$ by K(MeO)$_3$BH was reported previously to give a product tentatively identified as $K_2Fe(CO)_4$.[9] We find that this product is identical with ours as well as bona fide $K_2Fe(CO)_4$[10] made from $Fe(CO)_5$ and K(*sec*-Bu)$_3$BH in THF.

[9] Winter, S. R.; Cornett, G. W.; Thompson, E. A., *J. Organomet. Chem.* **1977**, *133*, 339.

[10] Gladysz, J. A.; Tam, W. *J. Org. Chem.* **1978**, *43*, 2279.

[11] Cohen, I. A; Basolo, F. *J. Inorg. Nucl. Chem.* **1966**, *28*, 511.

[12] Darensbourg, D. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 338.

[13] We were concerned also about the possibility of phosphine loss via the reaction $M(CO)_xPR_3 + OH^- \rightarrow M(CO)_xH^- + OPR_3$. At least in systems examined thus far, this pathway appears to be unimportant.

[14] Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627.

[15] Butts, S. B.; Shriver, D. F. *J. Organomet. Chem.* **1979**, *169*, 191.

[16] At reflux in alcoholic hydroxide, $Fe(CO)_4PPh_3$ decomposed to give insoluble $Fe(CO)_3(PPh_3)_2$ (yield ~30%) and a red solution that contained no $HFe(CO)_3PPh_3^-$.

[17] Anal. Calcd for $C_{29}H_{36}O_3FeNP$: C, 65.33; H, 6.75; Fe, 10.48; N, 2.63. Found: C, 65.23; H, 6.84; Fe, 10.61; N, 2.51. ^1H NMR (acetone-d_6) δ 7.14–7.90 (m, 15H, phenyl), 3.46 (q, 8H, CH_2 of Et_4N^+), 1.36 (t of t, 12H, CH_3 of Et_4N^+), –9.02 (d, 1H, J_{PH} = 6.4 Hz); IR (CH_3CN) ν_{CO} region (cm^{-1}) 1930 m, 1865 w, 1820 vs.

[18] Treatment of anhydrous tetraethylammonium salts (e.g., $Et_4N^+Br^-$) with a THF solution of K(*sec*-Bu)$_3$BH caused a rapid evolution of gas. The gaseous products of this reaction have not been examined, but it is reasonable to assume that a Hoffman elimination reaction occurred, i.e., (*sec*-Bu)$_3$BH$^-$ + $Et_4N^+ \rightarrow CH_2{=}CH_2 + H_2 + Et_3N$ + (*sec*-Bu)$_3$B. One equivalent of HBR_3^- is required for this reaction. The second equivalent is required for the much less facile deprotonation of $HFe(CO)_3PPh_3^-$.

[19] Anal. Calcd for $C_{21}H_{15}O_3FeK_2P$: C, 52.50; H, 3.12; Fe, 11.63; K, 16.29. Found: C, 52.22; H, 3.22; Fe, 11.61; K, 16.46. IR (Nujol mull) ν_{CO} region (cm^{-1}) 1785 m, 1690 s, 1640 s. IR (HMPA) ν_{CO} region (cm^{-1}) 1775 m, 1695 s br.

[20] ^1H NMR (CD_3CN) δ 7.27–7.66 (m, 5H, phenyl), 1.67 (d, 6H, J_{PH} = 7.3 Hz), –9.40 (d, 1H, J_{PH} = 5.2 Hz). Et_4N^+ positions are nearly the same as those shown in ref 17. IR (CH_3CN) ν_{CO} region (cm^{-1}) 1925 m, 1807 vs.

[21] Anal. Calcd for $C_{11}H_{11}O_3FeK_2P$: C, 37.10; H, 3.09; Fe, 15.68; K, 21.96. Found: C, 36.88; H, 2.99; Fe, 15.58; K, 21.81. IR (Nujol mull) ν_{CO} region (cm^{-1}) 1770 m, 1660 s, 1645 s.

[22] Lithium salts of $Fe(CO)_3PR_3^{2-}$ are prepared by the reaction of corresponding $HFe(CO)_3PR_3^-$ with excess $LiEt_3BH$ or Li(*sec*-Bu)$_3$BH in THF. These materials may be more useful for syntheses since they are soluble in THF. So far, no attempts have been made to isolate $Li_2Fe(CO)_3PR_3$ from solution.

[23] Anal. Calcd for $C_{47}H_{50}O_3FeNPSn$: C, 63.98; H, 5.67; N, 1.59; Fe, 6.34. Found: C, 64.04; H, 5.72; N, 1.71; Fe, 6.39. IR (CH_3CN) ν_{CO} region (cm^{-1}) 1930 vw, 1820 vs. ^1H NMR (CD_3CN) δ 7.18–7.81 (m, 30H, phenyl); Et_4N^+ signals are omitted.

[24] Anal. Calcd for $C_{37}H_{46}O_3FeNPSn$: C, 58.63; H, 6.07; N, 1.85. Found: C, 58.41; H, 5.97; N, 2.03. IR (CH_3CN) ν_{CO} region (cm^{-1}) 1810 vs. ^1H NMR (acetone-d_6) δ 7.03–8.14 (m, 20H, phenyl), 1.88 (d, 6H, J_{PH} = 8.2 Hz); Et_4N^+ signals are omitted.

from the reaction of the appropriate $K_2[Fe(CO)_3PR_3]$ with Ph_3SnCl 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 $Fe(CO)_3PR_3^{2-}$ observed so far is their ability to undergo facile ligand-exchange reactions

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

For example, bubbling CO at atmospheric pressure through a suspension of $K_2[Fe(CO)_3PPh_3]$ 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 $K_2Fe(CO)_4$[10] was isolated from this reaction. Similarly, treatment of $K_2[Fe(CO)_3PPh_3]$ 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 $K_2[Fe(CO)_3PPh_3]$ and its conversion to the triphenyltin derivative $[Et_4N][Ph_3SnFe(CO)_3P(OMe)_3]$ (58% yield of colorless, analytically pure crystals),[26] this material is formulated as $K_2[Fe(CO)_3P(OMe)_3]$ (89% isolated yield). By contrast, treatment of $K_2[Fe(CO)_3PPh_3]$ with 20 equiv of PEt_3 in THF at room temperature after 24 h gave a deeper orange mixture containing both $Fe(CO)_3PPh_3^{2-}$ and what is believed to be $Fe(CO)_3PEt_3^{2-}$. Thus, the displacement of PPh_3 from $Fe(CO)_3PPh_3^{2-}$ 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 $Fe(CO)_3THF^{2-}$. Indeed, suspensions of $K_2Fe(CO)_3PPh_3$ 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 $V(CO)_5PR_3^-$ to follow a dissociative pathway, perhaps involving $V(CO)_5^-$ and/or $V(CO)_5THF^-$.[27]

In conclusion, the two-step process described above which converts $Fe(CO)_4PR_3$ to $Fe(CO)_3PR_3^{2-}$ may be general route for the conversion of any $M(CO)_xL_y$ to the corresponding $M(CO)_{x-1}L_y^{2-}$, as long as $M(CO)_xL_y$ 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. $Fe(CO)_4PPh_3$, 35679-07-3; $[Et_4N][HFe(CO)_3PPh_3]$, 80312-33-5; $K_2[Fe(CO)_3PPh_3]$, 80612-34-6; $Fe(CO)_4PMe_2Ph$, 51743-97-6; $[Et_4N][HFe(CO)_3PMe_2Ph]$, 80612-36-8; $K_2[Fe(CO)_3PMe_2Ph]$, 80612-37-9; $[Et_4N][Ph_3SnFe(CO)_3PPh_3]$, 80612-39-1; $[Et_4N][Ph_3SnFe(CO)_3PMe_2Ph]$, 80630-28-0; Ph_3SnCl, 639-58-7; $[Et_4N][Ph_3SnFe(CO)_3P(OMe)_3]$, 80630-30-4; $K_2[Fe(CO)_3P(OMe)_3]$, 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 $C_{32}H_{44}O_6FeNPSn$: C, 51.65; H, 5.92; N, 1.88. Found: C, 51.85; H, 5.92; N, 1.86. IR (CH_3CN) ν_{CO} region (cm^{-1}) 1835 vs. ^1H NMR (CD_3CN) δ 7.06–7.77 (m, 15H, phenyl), 3.69 (d, 9H, J_{P-H} = 12.5 Hz, $-OMe$); Et_4N^+ signals are omitted.

(27) Darensbourg, M. Y.; Hanckel, J. M. *Organometallics* **1982**, *1*, 82.

(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 $W(CO)_4PR_3^{2-}$ (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 $C_2H_4^-$, $C_2H_3F^-$, $CH_2CF_2^-$, and $C_2F_4^-$ are summarized in Table I, and the geometries of the most stable structures are given in Figure 1. For $C_2H_4^-$, $CH_2CF_2^-$, and $C_2F_4^-$, calculations were performed on

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§ Camille and Henry Dreyfus Teacher–Scholar.

(1) Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1981**, *103*, 2902.

(2) McNeil, R. I.; Shiotani, M.; Williams, F.; Yim, M. B. *Chem. Phys. Lett.* **1977**, *51*, 433.

(3) Symons, M. C. R.; Selbey, R. C.; Smith, I. G.; Bratt, S. W. *Chem. Phys. Lett.* **1977**, *48*, 100.

(4) Wang, J. T.; Williams, F. "^{13}C. Hyperfine Interaction in the Hexafluorobenzene Radical Anion", submitted to *Chem. Phys. Lett.*

(5) Yim, M. B.; Wood, D. E. *J. Am. Chem. Soc.* **1976**, *98*, 2053.

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