102.0°. In contrast to this, Ta(2) is linked to a η^5-C_5Me_4Et ligand, to two chloride ligands, to a *terminal hydride ligand*, and to the bridging atoms C(1) and O; the coordination environment of Ta(2) is thus best described as a "3,4,1" type. We emphasize that we did not locate directly the terminal hydride ligand on Ta(2). However, there is clearly a hole in the pseudooctahedral arrangement around Ta(2) where it should be; i.e., Cl(3)-Ta(2)-Cl(4), 96.5 (2); Cl(4)-Ta(2)-O, 98.0 (3); but O-Ta(2)-Cl(3), 150.1 (3)°. The observable Cp-Ta(2)-L angles are Cp-Ta(2)-Cl(3), 101.1; Cp-Ta(2)-Cl(4), 104.7; Cp-Ta(2)-O, 100.3; Cp-Ta(2)-C(1), 172.5°.

We propose that the C-O bond in the "η^2-formyl" ligand is disrupted when PMe_3 attacks the carbon. Angles within this system [C(1)-Ta(1)-O, 78.0 (6); Ta(1)-O-Ta(2), 102.1 (5); O-Ta(2)-C(1), 72.7 (5); Ta(1)-C(1)-Ta(2), 82.2 (6)°] and the cross-bridge distances [Ta(1)···Ta(2) = 2.992 (1) and C(1)···O, 2.579 (2) Å] do not allow an unambiguous assessment as to the importance of any direct tantalum-tantalum bonding. The Me_3PCH moiety is best regarded as a phosphonium ylide, the P-C(1) distance being 1.750 (18) Å, compared with P-Me distances of 1.834 (20), 1.840 (21), and 1.847 (25) Å. Similar distances were found in the related species $Fe_2(CO)_6[(CHO)P(Ph_2C_6H_4)]$.[16]

Evidently, the "formyl" ligand in **2** is grossly "overstabilized" as a metallaoxirane complex of d^0 Ta(V). Nevertheless, we feel that there must be some circumstances where such stabilization is great enough to yield a fair concentration of metallaoxirane but not great enough to prevent its reacting further with CO or H_2. We think that these results further provoke the question as to whether intermolecular addition of M-H to M-CO may be more favorable than intramolecular addition of M-H to M-CO (with or without any stabilization in either case)[17] and also raise some intriguing questions concerning nucleophilic attack at an "η^2-formyl" carbon atom.

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(7) Calcd for $Ta_2(\eta^5$-$C_5Me_4Et)_2Cl_5H$: C, 31.50; H, 4.20. Found: C, 31.16; H, 4.44. A similar iridium complex has been prepared: White, C.; Oliver, A. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1901–1907.

(8) This complex can be prepared in ~25% yield from the reaction of a mixture of $Ta(\eta^5$-$C_5Me_4R)(CH_2CMe_3)_2Cl_2$ and $Ta(\eta^5$-$C_5Me_4R)(CH_2CMe_3)Cl_3$ with H_2.

(9) Calcd for $Ta_2(\eta^5$-$C_5Me_4Et)_2Cl_4H_2(CO)$: C, 33.19; H, 4.36. Found: C, 33.62; H, 4.40. Mol wt calcd: 832. Found: 800 ± 50 (benzene).

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EPR Detection of $(CF_3)_3CI^-$. A Test Case Regarding the Stability of RX^- Radical Anions

Sir:

Recent EPR studies have shown that electron attachment to certain halides of saturated carbon, including the perfluorocycloalkanes and trifluoromethyl halides, leads to the formation of stable σ^* radical anions.[1-3] The stability of the CF_3X^- (X = Cl, Br, I) series of radical anions contrasts with the fact that the methyl halides invariably undergo a dissociative reaction immediately after electron capture, only the weakly bound $CH_3\cdot\text{---}X^-$ species being produced even in a rigid crystalline matrix.[4,5] This difference has led Symons to postulate[6] that the tendency for the dissociation of RX^- is determined by the change which occurs in orbital hybridization and configuration at the α-carbon atom in the formation of the potential radical R·, a large change as exemplified by[4,5]

$$CH_3X^- \rightarrow CH_3\cdot\text{---}X^- \qquad (1)$$

bringing about the immediate dissociation of the virtual RX^- species. We report here a test case which invalidates this general proposition.

Although the CF_3 radical is pyramidal,[7] the $C(CF_3)_3$ radical is judged to be nearly planar on the basis of the ^{13}C hyperfine coupling of 44.3 G for the α carbon.[8] Thus, according to the above postulate, the $(CF_3)_3CX^-$ radical anions should be unstable and only the neutral $(CF_3)_3C$ radicals should be produced on electron attachment to the perfluoro-*tert*-butyl halides. We find, however, that the EPR spectrum of a γ-irradiated solution of $(CF_3)_3CI$ in a 2-methyltetrahydrofuran glass (Figure 1) provides clear evidence for the radical anion.

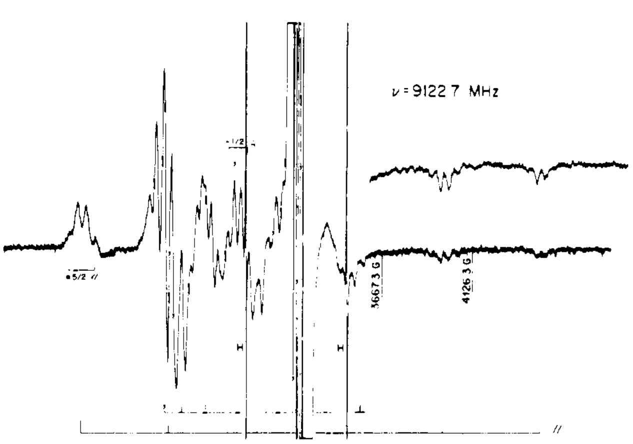
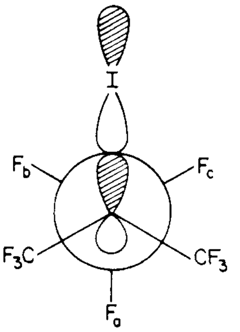


Figure 1. First-derivative EPR spectrum of a 2-methyltetrahydrofuran glass containing 4 mol % perfluoro-*tert*-butyl iodide recorded at 87 K after γ irradiation at 77 K for a dose of 1.5 Mrad. The stick diagrams show the features assigned to the $(CF_3)_3CI^-$ radical anion, and the upper trace at high field was obtained under conditions of larger amplification, modulation, and response time.

As indicated by the stick diagrams, the spectral features are readily analyzed into sets of parallel and perpendicular components resulting from hyperfine interaction with ^{127}I ($I = 5/2$), the substructure of each component consisting of a 1:3:3:1 line group characteristic of coupling to three equivalent ^{19}F's ($I = 1/2$) nuclei. The observation of significant interaction with only three out of the nine fluorines [$^{19}A_{\parallel}(3) = 121$; $^{19}A_{\perp}(3) = 109$ MHz] is accounted for by the preferred conformation **1** in which the C_{β}—F_a bond from each of the three CF_3 groups is aligned parallel to the C_{α}—I bond wherein most of the spin density is concentrated (vide infra). This is quite analogous to the most stable conformation of the perfluoroethyl radical resulting from hindered rotation about the C_{α}—C_{β} bond, the measured couplings for the three axial fluorines being very similar to that (113 MHz) for the unique β-fluorine of C_2F_5,[9] as expected for a largely isotropic interaction.



1

The assignment of the spectrum to the $(CF_3)_3CI^-$ radical anion is established by the marked anisotropy of the **g** and ^{127}I hyperfine tensors which is characteristic of a large spin density in the $5p_{\sigma}$ orbital of the iodine atom.[10] A good least-squares fit of the line positions was obtained by a matrix diagonalization program without the inclusion of an iodine quadrupole interaction, the parameters and their standard deviations[11] being $g_{\parallel} = 1.9631$ (9), $g_{\perp} = 2.1651$ (13); $^{127}A_{\parallel} = 1282.9$ (6.9) and $^{127}A_{\perp} = 489.7$ (8.8) MHz. By including a correction for the orbital contribution to $^{127}A_{\perp}$,[10] values of $^{127}A_{\text{iso}} = 671.1$ and $^{127}B = 305.9$ MHz are derived for the isotropic and anisotropic ^{127}I hyperfine coupling constants. Accordingly, we obtain a ^{127}I (5p) contribution of 0.38 to the semioccupied orbital by taking $^{127}B_0$ for unit spin density to be 812.4 MHz.[12] The existence of such a large spin density on iodine points clearly to the stability of the $(CF_3)_3CI^-$ radical anion despite the near planarity of the $(CF_3)_3C$ radical; so one is forced to look elsewhere for an explanation of the factors governing the stability of RX^- radical anions.[13]

If the R group is considered as a pseudohalogen in a diatomic-like RX^-, it seems reasonable to propose that the stability of RX^- with respect to its dissociation modes ($R\cdot + X^-$ or $R^- + X\cdot$) is governed by the extent to which the spin density is shared between the atomic orbitals of the localized three-electron bond, the maximum stability being attained for homonuclear diatomics such as I_2^- and its congeners. This strongly suggests that relative electronegativity is likely to be an important factor, and this could well be the reason why the ^{127}I (5p) spin density of 0.38 for $(CF_3)_3CI^-$ is larger than the corresponding value (0.23) for CF_3I^-.[3,14,15]

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(15) Our proposal that a higher ^{127}I (5p) spin density promotes the stability of the R_fI^- radical anion to the dissociation path $R_f\cdot + I^-$ is supported by controlled annealing studies on the CF_3I^- and $(CF_3)_3CI^-$ radical anions. Thus, although CF_3I^- has been observed to dissociate into the CF_3 radical in the vicinity of 100 K,[3] the present work showed that the spectrum of the $(CF_3)_3C$ radical did not grow in when the matrix was annealed to 104 K at which temperature the $(CF_3)_3CI^-$ radical anion was observed to disappear gradually.

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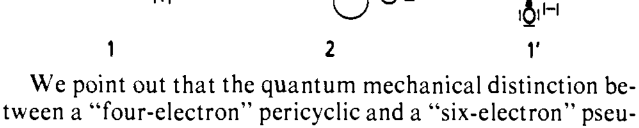
[1,3]-Sigmatropic Shifts for 5-X-Bicyclo[2.1.0]pent-2-enes. An Evaluation of the Pseudopericyclic Model[1]

Sir:

Perfluorotetramethyl (Dewar thiophene) *exo-S*-oxide (**1**) undergoes a remarkably facile degenerate rearrangement ($\Delta H^{\ddagger} = 6.6$ kcal/mol).[2,3] The small barrier has been interpreted by Lemal and co-workers[2,3] to exclude both a four-electron pericyclic [1,3]-sigmatropic shift and a biradical process as the reaction mechanism.[4] A six-electron process was proposed instead in which the endocyclic lone pair on sulfur participates nucleophilicly, with the result that bonding and nonbonding orbitals on sulfur interchange roles. The concept was generalized and the suggestion made that such transformations be designated as *pseudopericyclic.*[2]



1 **2** **1'**

We point out that the quantum mechanical distinction between a "four-electron" pericyclic and a "six-electron" pseudopericyclic transition state is not clear-cut. This conclusion follows from the fact that the pericyclic-shift MO's of Figures