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X-ray Diffraction and ^{19}F and ^{205}Tl NMR Evidence for Electrophile Binding to an Organofluorine Substituent

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Fluorine attached to an sp^3-carbon would not appear to be a very potent Lewis base, due both to its electronegativity and to its lack of ionic charge (cf. fluor*ide* as a ligand[1]). Nevertheless, there are reports of C—F→M "interactions" observed crystallographically in $Ce[CF_3C(O)CHC(O)CF_3]_4$,[2] $Na_2Cu(OCH(CF_3)_2)_4$,[3] and $BaCu_2(OC(CH_3)(CF_3)_2)_6$.[4,5] We report here new results which further clarify the Lewis basicity of organofluorine groups and also identify a remarkable migration process in one such example.

Reaction of Zr(neopentyl)$_4$ with R_fOH ($R_f = C(H)(CF_3)_2$, 1:4 mole ratio) in benzene gives $Zr(OR_f)_4$, which reacts with $TlOR_f$ (1:2 mole ratio) in benzene to give $Tl_2Zr(OR_f)_6$. This compound is poorly soluble in hot benzene and somewhat soluble in hexafluorobenzene. These observations argue for a molecular, rather than a purely salt, constitution. The X-ray diffraction determination[6] of the structure of this compound (Figure 1) reveals a $Tl(\mu\text{-}OR_f)_3Zr(\mu\text{-}OR_f)_3Tl$ connectivity, based on a distorted octahedral $Zr(OR_f)_6^{2-}$ substructure with the thallium ions occupying opposite triangular ZrO_3 faces. The molecule is rigorously centrosymmetric, and thus the Tl/Zr/Tl unit is linear. The alkoxide oxygen coordination environment about thallium is complemented by a planar array of six Tl/F contacts (one from each CF_3 group) in the range 3.068 (8)–3.287 (11) Å.[7] These contacts are similar in magnitude to those observed in TlF.[8]

Since Tl is a spin $^1/_2$ nucleus, it is possible to obtain independent evidence for Tl/F interactions from NMR spectroscopy. However, the accumulated evidence reveals more than just their presence. The ^{19}F NMR spectrum of $Tl_2Zr(OR_f)_6$ in C_6F_6 at 20 °C (Figure 2a) shows one multiplet (the sharp lines are separated by 765 Hz; F-H coupling of less than 5 Hz is not resolved) with an approximate 1:2:1 intensity ratio. This line spacing is independent of field strength, indicating that it represents Tl/F coupling. The spectrum is found to be temperature-dependent (Figure 2a), with the broad central feature sharpening to a central line by +80 °C.[9] The ^{19}F NMR spectrum is thus actually a triplet (splitting of 383 Hz), due to coupling to *two* thallium centers. Moreover, we find that $T_2 \ll T_1$, over the full temperature range, indicating the presence of an efficient dephasing mechanism. The dramatic temperature dependence of the line width and the relaxation data (which show that the line shapes are not dominated by lifetime broadening) indicate that $Tl_2Zr(OR_f)_6$ is a dynamic molecule:[10] in contrast to the situation for the ground-state structure, with chemically-inequivalent fluorines of the trifluoromethyl groups, intramolecular rearrangement causes time-average equivalence of all 36 fluorines and each fluorine is visited by both thallium centers during the fluxional process. We sought to confirm these conclusions by recording the 207.8-MHz ^{205}Tl NMR spectra at various temperatures (Figure 2b). In C_6F_6 at 20 °C, a broad ($\Delta\nu_{1/2}$ = 3700 Hz) resonance is observed, with ~7 lines (spacing 383 ± 14 Hz) resolved at the center of the pattern. At +40, +60, and +80 °C, these lines sharpen (*J*(Tl–F) = 388 ± 12.7 Hz) and at least 19 lines are resolved. The falloff of intensities of these 19 lines fits well that predicted for the centermost lines of a binomial distribution for 36 $I = {}^1/_2$ particles and is inconsistent with the corresponding calculation for 18 I =

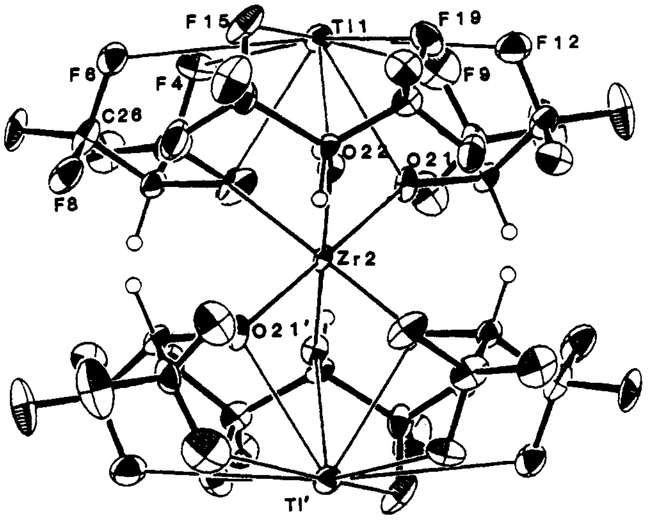
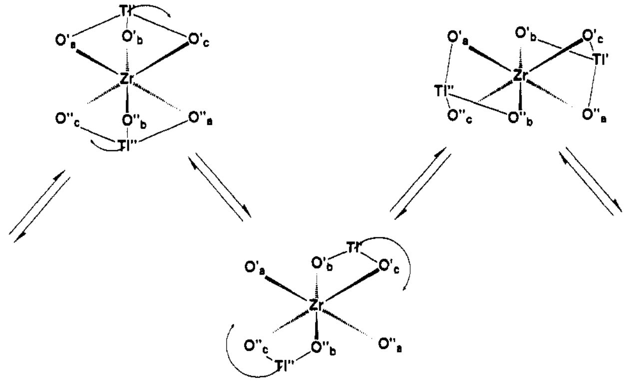


Figure 1. ORTEP drawing of $Tl_2Zr(OCH(CF_3)_2)_6$. Thermal ellipsoids are drawn at the 50% probability level. Primes indicate atoms related by the center of symmetry. Selected structural parameters (distances, Å; angles, deg): Zr(2)–O(21), 2.090 (7); –O(22), 2.035 (8); –O(23), 2.054 (8); Tl(1)–O(21), 2.740 (9); –O(22), 2.814 (10); –O(23), 2.831 (11); Tl(1)–F(4), 3.135 (12); –F(6), 3.215 (11); –F(9), 3.238 (11); –F(12), 3.096 (8); –F(15), 3.068 (8); –F(19), 3.287 (11); C(26)–F(6), 1.356 (16); –F(8), 1.323 (16); O(21)–Zr(2)–O(22), 95.2 (3); O(21)–Zr(2)–O(23′), 94.3 (3); O(21)–Zr(2)–O(23), 85.7 (3); intramolecular Tl–F–C angles, 109.9 (3)–115.4 (3).

Scheme I



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(1) (a) Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553. (b) Edwards, A. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, p 675. (c) Edwards, A. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 83.

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(3) Purdy, A. P.; George, C. F.; Callahan, J. H. *Inorg. Chem.* **1991**, *30*, 2812.

(4) Purdy, A. P.; George, C. F. *Inorg. Chem.* **1991**, *30*, 1970.

(5) A general review of halocarbon–metal interactions: Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89.

(6) Crystal data (–172 °C) for $Tl_2ZrC_{18}H_6O_6F_{36}$: a = 19.879 (2) Å, b = 10.182 (1) Å, c = 20.456 (1) Å, β = 122.97 (0)° with Z = 4 in space group $C2/c$. $R(F)$ = 0.0481, $R_w(F)$ = 0.0497 for 2040 reflections with $F > 3.00\sigma(F)$.

(7) In the unit cell, for each Tl, there are also three contacts to two neighboring Tl/Zr/Tl units in the range 3.289 (11)–3.442 (11) Å.

(8) Interatomic distances for thallium fluoride: 2.58 Å (×4), 3.53 Å (×2, cis). See: Alcock, N. W. *Acta Crystallogr.* **1969**, *A25*, 5101.

(9) Low-temperature spectra are precluded because of the freezing of C_6F_6.

(10) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; Chapter 10.

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$^1/_2$ particles. The difference between the two patterns is striking: for example, in a 19-line multiplet, the peaks removed by five from the central line are 6.3% as intense as the central line, while, in the 37-line pattern, they are 25% as intense, and, in our data, 30% as intense. The Tl NMR results thus provide independent evidence that there is global intramolecular migration of the two Tl centers over all ZrO_3 triangular faces within the molecule $Tl_2Zr(OR_f)_6$.

Scheme I portrays a mechanism of thallium migration passing through a $Zr(\mu\text{-}OR_f)_2Tl$ transition state with the $Zr(OR_f)_6$ octahedron held rigid. This rearrangement, together with Tl/F bond rupture/re-formation and rapid rotation about C–CF_3 bonds, is sufficient to explain the full set of spectral observations.[11,12]

The observation of Tl/F nuclear spin coupling indicates that there is significant interaction between these atoms. Considering the fact that the nuclear spin interactions are distributed among 36 fluorines per thallium, the magnitude[13] of the coupling supports the idea that there is direct bonding involved between the thallium and fluorines and not merely coulombic attractions.[14] We will report later the significance of these contacts on the CVD (thermal decomposition) behavior of this and related molecules.

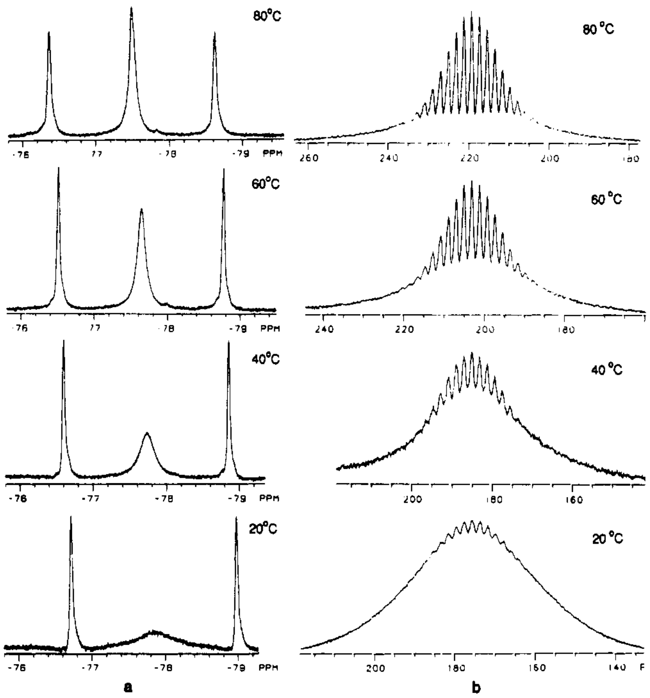

Figure 2. (a) Variable-temperature ^{19}F NMR spectra of $Tl_2Zr(OCH(CF_3)_2)_6$ in C_6F_6 (recorded at 340 MHz with neat F_3CCOOH external standard (−78.45 ppm)). (b) Variable-temperature ^{205}Tl NMR spectra in C_6F_6 (recorded at 207.8 MHz; chemical shift standard 0.3 M aqueous $TlNO_3$).

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Supplementary Material Available: Tables of crystallographic data, fractional coordinates, and isotropic thermal parameters and a plot of the thallium NMR line intensity study (3 pages). Ordering information is given on any current masthead page.

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(11) The retention of two sharp lines even at dynamic exchange rates which broaden other lines of the spectrum is a consequence of $|\beta\beta\rangle$ becoming $|\beta\beta\rangle$ after a thallium "hop" and likewise $|\alpha\alpha\rangle$ becoming $|\alpha\alpha\rangle$, in contrast to the relatively efficient $|\alpha\beta\rangle \leftrightarrow |\beta\alpha\rangle$ interconversion. For another example (in *cis*-$H_2Fe[P(OEt)_3]_4$), see: *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 181–187.

(12) A second fluxional mechanism involving the formation of $[Tl_2Zr]_n$ aggregates was rejected on the basis of retention of Tl–F coupling at elevated temperatures, conditions which should reduce aggregation.

(13) The J observed here is time-averaged over instantaneous structures with six "close" ^1J(Tl–F) and 30 "distant" J'(Tl–F). Taking the latter to be near zero, the ^1J(Tl–F)$'$ for the close contacts can be estimated to be 2298 Hz. This is to be compared to the Tl coupling to an ortho fluorine in $CpMo(SC_6F_5)_4Tl$ of 3630 Hz: Wan Abu Bakar, W. A.; Davidson, J. L.; Lindsell, W. E.; McCullough, K. J.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1989**, 991.

(14) The lack of known J(Tl–F) values in similar systems (cf.: Hinton, J. F.; Metz, K. R.; Briggs, R. W. *Annu. Rep. NMR Spectrosc.* **1982**, *13*, 211) precludes a more quantitative description of the bonding at this time.