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# A FIRST NMR IDENTIFICATION OF A GEM-DIFLUORO MEISENHEIMER COMPLEX.

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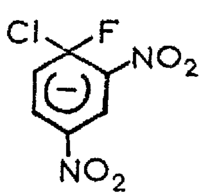
The crown ethers form complexes with alkali and other metal salts which often provide increased salt solubility and enhanced anion reactivity in nonpolar as well as aprotic organic solvents [1]. Liotta et al. have recently shown that fluoride ion, solubilized as the potassium salt in acetonitrile or benzene containing 18-crown-6 is sufficiently nucleophilic to give displacement reactions at sp$^2$ hybridized carbon [2]. Thus, the reaction of this "naked" fluoride[2], with 2,4-dinitrochlorobenzene occurs smoothly at room temperature to yield quantitatively 2,4-dinitrofluorobenzene[2]; As any nucleophilic aromatic substitution[3], such a reaction should involve the formation of the unstable Meisenheimer-type intermediate complex 1. In view of our interest in the field of Meisenheimer complexes [4], this result led us to search for a system where the intermediate would be stable enough to allow direct nmr observation. We found that the system picryl fluoride (2)-fluoride ion which leads to the symmetrical complex 3 was suitable or such a nmr study. Complex 3 is particularly interesting because it is the first stable -complex involving geminal fluorine atoms which has been detected to date.

Complex 3 was formed by adding picryl fluoride 2 to a heterogeneous mixture of 18-crown-6 and potassium fluoride in dry acetonitrile. The concentrations of picryl fluoride and crown ether were approximately 0.2 M. The 100 MHz-proton nmr spectrum exhibits a 1:2:1 triplet at $\delta = 8.70$ ppm (internal reference TMS, $J_{F-H} = 3.9$ Hz), showing the symmetry of the formed adduct. When irradiating fluorine at 94.1 MHz, the 1:2:1 triplet collapses to a singlet, provi-



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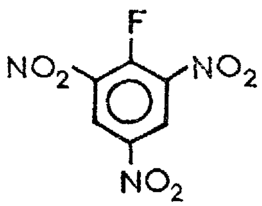

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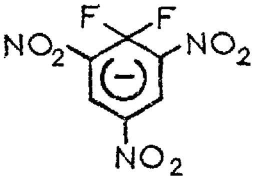

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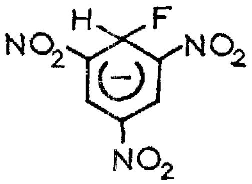

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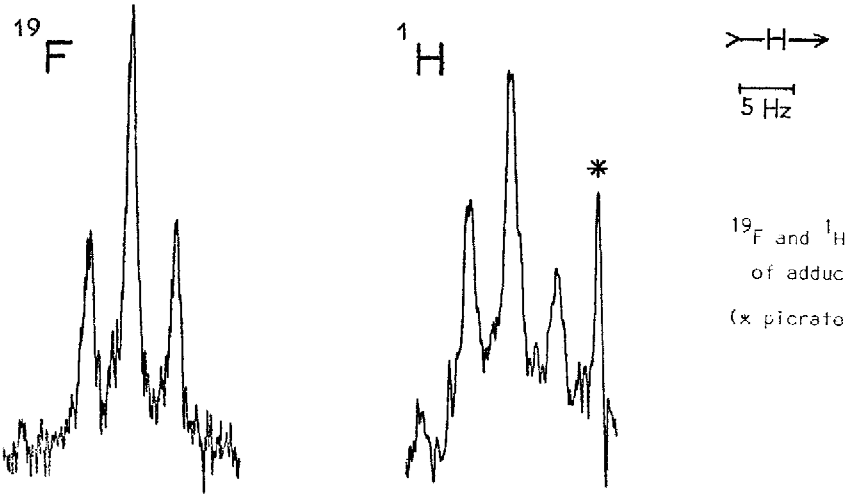

$^{19}F$ and $^{1}H$ nmr Spectrum of adduct 3

(* picrate anion)

ding additionnal evidence that the fine structure comes from coupling with two equivalent fluorine nuclei. In agreement with this result, the fluorine nmr spectrum consists of one 1:2:1 triplet at -61.2 ppm (internal reference $CCl_3F$) . These nmr parameters, compared with those of picryl fluoride ($\delta_H = 9.11_5$ ppm, $\delta_F = -115.2$ ppm, $J_{F-H} = 5.7_5$ Hz), show that the proton signal is shifted upfield ($\Delta\delta$ = 0.41 ppm) which is consistent with previous observations for various σ-complexes [5], whereas the fluorine signal is shifted downfield ($\Delta\delta$ = 54 ppm).

Complex 3 is relatively stable at room temperature. Traces of moisture cause, however, a slow appearance of a singlet at 8.62 ppm which is due to the formation of some picrate anion (figure). Similar results have been observed for 3 in DMSO-d6 ($\delta_H = 8.66$ ppm, $J_{F-H} = 3.9$ Hz). In contrast, although Butler has reported a visible spectrum indicating the formation of the σ-complex 4 formed by attack of $F^-$ on 1,3,5-trinitrobenzene [6], we were not able to obtain nmr evidence for 4. Presumably, the equilibrium does not favor this complex sufficiently.

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