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2H-HEXAFLUOROISOPROPYLSILVER

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Miller et al.have recently reported[1a,b] a synthesis of polyfluoroaliphatic derivatives of silver.The nucleophilic addition of silver fluoride to the unsaturated compounds proposed by these authors is a special case of the general method of synthesis of organometallic compounds by interaction of a carbanion with a metal ion.A.N.Nesmeyanov et al.[2a,b,c] have synthesized ferrocenylsilvers by way of replacing the boric acid fragment with a metal atom,as it is usually performed in preparation of organomercurials.

We now wish to report a synthesis of an organosilver compound by the decarboxylation reaction.Mercuric salt of α-hydroperfluoroisobutyric acid is known[3] to decarboxylize in pyridine to bis-(2H-hexafluoroisopropyl)mercury. Silver salt of α-hydroperfluoroisobutyric acid (1)obtained by us from the acid and Ag_2CO_3 does not evolve CO_2 when refluxed in dry EtOAc or THF.The addition of pyridine to a THF solution of 1 causes precipitation of 1:1 complex 1·py (2) (m.p.134-5°,with decomposition producing a silver mirror). Calculated for $C_9H_6F_6NO_2Ag$:F 29,84%.Found:F 29,23%.

Salt 1 or complex 2 evolve 100 percent of CO_2 in excess of dry pyridine at room temperature and at 40-50°C in dry MeCN or DMF.The resulting solutions isolate metallic silver while stored.Chemical reactions and the NMR spectra show the presence of 2H-hexafluoroisopropylsilver (3) in the solutions.Thus, action of diluted H_2SO_4 on a solution of 3 in MeCN leads to a 100% formation of a mixture of $CF_3CH{=}CF_2$ and $(CF_3)_2CH_2$ in a ratio of 55:45(GLC,Porapak Q and NMR F^{19} are in agreement with those of the reference compounds).The action of Br_2 on a solution of 3 in MeCN leads to $(CF_3)_2CHBr$ (58% based on the starting bromine),b.p.32°C (lit.b.p.31,5-32,5 °C[4]).The structure was confirmed by the NMR and mass-spectra.A solution of 3 in MeCN reacts with $HgCl_2$ giving bis-(2H-hexafluoroisopropyl)mercury (49% based on $HgCl_2$),m.p. 39-40°C(lit.m.p.38,8-39°C[5]).The structure was confirmed by NMR and mass-spectra.

The NMR* H^1 spectrum of 3 in CH_2Cl_2-py(3:1) is a heptaplet,δ=2,41ppm. The NMR F^{19} spectrum of the compound taken at 24°C is a doublet corresponding to the six equivalent β-fluorines split at α-hydrogen($J_{F-C-C-H}$=13,5c/s). Chemical shifts are weakly dependent on the solvent nature(δ=-12.76ppm in CH_2Cl_2-py 3:1 and -12.66ppm in DMF).The spectrum transforms at lower temperatures,and it becomes possible to observe a spin-spin coupling of F^{19}-C-C-$Ag^{107(109)}$.Thus,the spectrum of 3 in CH_2Cl_2-py(3:1)below -40°C (see Fig.1) is a doublet of doublets ($J_{F-C-C-Ag}$=20c/s,cf.$J_{F-C-C-Ag}$=15c/s in perfluoro-1-methylpropenylsilver at room temperature[1b]).The isotopes Ag^{107} and Ag^{109} do not split separately,apperently due to a small difference of their magnetic moments.Thus,the low-temperature spectrum confirms the covalent nature of the C-Ag bond in the compound under investigation,the form of splitting confirming its monomer structure,in contradistinction to the tetrameric one of MeLi[6].The absence of the F-C-C-Ag spin-spin coupling at 24°C may be attributed to the intramolecular exchange,with the C-Ag bond being involved,while at -70°C such an exchange is rather slow,and the compound under investigation has a sufficiently long life-time,possibly in the form of RAg·py.It is probable,that the absence of such an exchange in perfluoro-1-methylpropenylsilver is associated with the sp^2-character of

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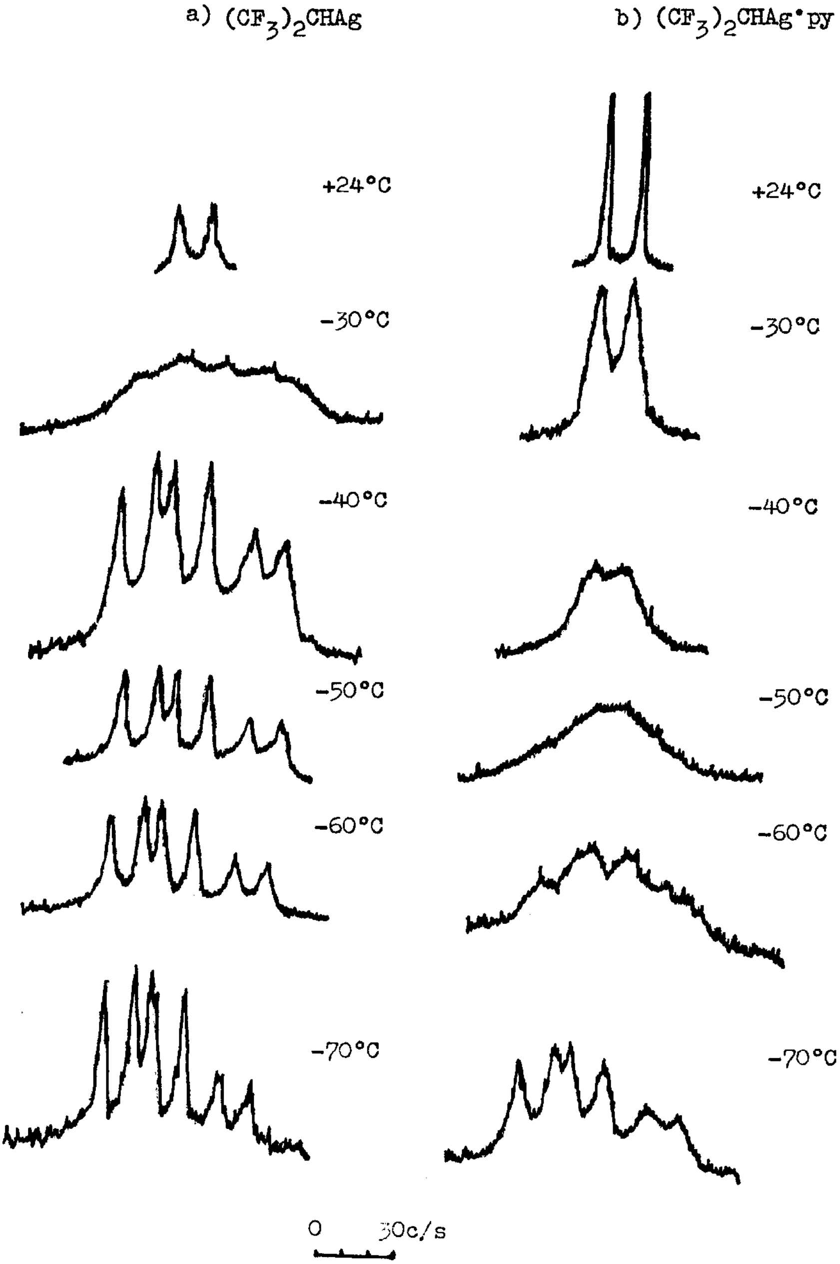
* The NMR spectra were recorded with a NMR-2305 spectrometer.The proton shifts are given in δ scale.The F^{19} chemical shifts are measured with respect to benzotrifluoride as internal standard.Accuracy of measurement: chemical shifts,±0,01ppm spin-spin coupling constants,±0.5c/s.



a) $(CF_3)_2CHAg$

b) $(CF_3)_2CHAg\cdot py$

Fig.1.NMR F^{19} spectra of $(CF_3)_2CHAg$ in: a) CH_2Cl_2 -py 3:1 b) DMF.

carbon bonded with the metal atom. It should be noted, that, by decreasing the pyridine concentration, one may reduce the temperature at which the spectrum of **3** is resolved. In particular, in the absence of pyridine (DMF-THF 3:1), even at -100°C, there is a slow (in the NMR time scale) exchange along the C-Ag bond. The NMR F^{19} show, that at low temperatures **3** may exist in the form of aggregate, other than monomer, a doublet (δ=-12.22ppm $J_{F-C-C-H}$=13.0c/s) corresponding to said aggregate. The intensity of the doublet depends on the composition of the solvent. It can be assumed, that the structure of this aggregate corresponds to the formula nRAg·mpy. The inner (and probably inter) aggregate exchange in such a specia may take place even at -70°C at a sufficiently high rate.

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