SYNTHESIS AND ^{19}F-{^{1}H} NMR SPECTRA OF 4-FLUOROPHENYLACETYLENE AND ITS ORGANOMETALLIC DERIVATIVES

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We have previously studied metal—proton and metal—metal exchange reactions involving several NH, SH, and OH acids and their organometallic derivatives (OMD) containing monovalent organometallic R_nM groups with a heavy nontransition metal as the central atom [1-3]. These exchange reactions were studied in two aspects: kinetic study of the relative lability of the metal—heteroatom and hydrogen—heteroatom bonds and a thermodynamic study to determine the effect of structural factors on the position of the exchange equilibria. It was of interest to clarify whether the previously found behavior extends to exchange reactions involving CH-acids and their OMD.

Convenient model compounds for the study of these questions are substituted acetylenes and their OMD since steric interactions between the R_nM and CH-acid residue are excluded in these derivatives. 4-Fluorophenylacetylene and its OMD containing R_nE groups (E = Hg, C, Ge, Sn, Pb, R = C_6H_5, 4-$CH_3C_6H_4$, CH_3, and cyclo-C_6H_{11}) were used as the model compounds and the study was carried out using ^{19}F-{^{1}H} NMR spectroscopy. The compounds with a 4-tolyl group at the metal atom were used to determine the possibility of studying the kinetics of metal—metal exchange reactions accompanied by the migration of R_nE groups with a monovalent metal in the case of minimal difference in electronic nature of the bound organic groups and the identical nature of their steric requirements, which holds the greatest interest relative to clarification of the relative exchange capacity of metal—carbon bonds.

In the present work, we synthesized model compounds and elucidated the sensitivity of the chemical shift (CS) of fluorine (δF) in the 4-FC_6H_4 group in these compounds to the effect of structural factors, nature of the central metal atom, polar effect of the substituent in the aryl group at the metal atom, and nature of the medium; we also determined the relative polarity of the metal—carbon and hydrogen—carbon bonds in 4-fluorophenylacetylene (FPA) and its OMD.

A sample of FPA was obtained according to Allen and Cook [4]. FPA derivatives not reported in the literature were synthesized by methods proposed by Viene [5] and Esquivel [6] for the synthesis of the corresponding phenylacetylene derivatives.

The δF values measured relative to fluorobenzene as a quasiinternal standard for solutions of the compounds studied in various solvents are given in Table 1. Negative δF values correspond to a downfield fluorine shift relative to fluorobenzene.

The data obtained indicate that the fluorine shielding in 4-$FC_6H_4C{\equiv}CX$ depends significantly on the nature of substituent X at the acetylenic carbon atom and the nature of the medium.

Negative δF values indicate electron-withdrawing properties for all the $C{\equiv}CX$ groups studied. In accord with δF in the most inert solvent (cyclohexane), the electron-withdrawing capacity of these groups increases depending on the nature of X in the series:

$$C_6H_{11}Hg < MeHg < PhHg \approx Ph_3C \approx Ph_3Pb < Ph_3Sn < H < Ph_3Ge \tag{1}$$

In going from cyclohexane to other solvents, this sequence may be altered but in most cases, $C{\equiv}CHgMe$, $C{\equiv}CHgC_6H_{11}$, and $C{\equiv}CHgPh$ are the least electron-withdrawing groups and $C{\equiv}CSnPh_3$ and $C{\equiv}CGePh_3$ are the most electron-withdrawing groups, while the other groups occupy intermediate positions.

In general, the solvent effect on δF in the compounds studied may be the result of a whole series of factors. A change in the nature of the van der Waals interactions with the

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TABLE 1. Fluorine Chemical Shifts for 0.2 M Solutions of $4\text{-}FC_6H_4C \equiv XC$*

X	C_6H_{12} †	$C_6H_5CH_3$	C_6H_5Cl	$C_6H_5NO_2$	$CHCl_3$	THF	C_6H_5N	DMSO
H	−2,72	−2,51	−2,90	−2,83	−3,00	−2,47	−2,80	−2,81
cyclo-$C_6H_{11}Hg$	−0,83	−0,99	−1,08	−1,19	−1,89	−0,57	−0,74	−0,93
MeHg	−1,11	−0,92	−1,19	−1,29	−1,99	−0,60	−0,72	−1,01
PhHg	−1,56	−1,52	−1,52	−1,75	−2,53	−0,89	−0,87	−1,22
$4\text{-}MeC_6H_4Hg$	—	−1,38	−1,48	−1,61	−2,42	−0,86	−0,85	−1,21
Ph_3C	−1,56	−1,47	−2,03	−1,78	−1,72	−1,82	−2,08	−2,27
Ph_3Ge	−2,78	−2,82	−3,50	−3,21	−3,43	−3,13	−3,53	−3,74
$(4\text{-}MeC_6H_4)_3Ge$	—	−2,58	−3,31	−2,94	−2,79	−2,83	−3,30	−3,43
Ph_3Sn	−2,50	−2,59	−3,20	−2,97	−2,78	−2,80	−3,20	−3,10
$(4\text{-}MeC_6H_4)_3Sn$	—	−2,33	−3,02	−2,71	−2,60	−2,58	−3,01	−3,04
Ph_3Pb	−1,55	−1,74	−2,27	−2,03	−2,04	−1,79	−2,23	−2,01
$(4\text{-}MeC_6H_4)_3Pb$	—	−1,47	−2,11	−1,84	−1,78	−1,61	−2,07	−1,95
$4\text{-}FC_6H_4$	−2,17	−2,13	−2,31	−2,31	−2,28	−2,23	−2,48	−2,69

*In ppm from fluorobenzene as quasiinternal standard. A minus sign corresponds to a downfield shift.
†0.01 M solution concentration.

solvent and the effect of the reaction field play a definite role for all the compounds [7]. Chloroform may also have an effect relative to formation of a hydrogen bond with the π-electrons of the acetylene group [8]. In addition, the formation of hydrogen and coordination bonds with coordinating solvents may have a significant effect on δF for FPA itself and its OMD. In contrast, β-triphenylmethyl-4-fluorophenylacetylene is not capable of coordination interactions. Nevertheless, a significant change in δF is seen for this compound in going from cyclohexane to polar and coordinating solvents, which is accompanied by fluorine deshielding.

This effect is unlikely a result of a change in the nature of the van der Waals interaction with the solvent since the geometry of this compound in the region of the $4\text{-}FC_6H_4$ indicator group differs from the molecular geometry of fluorobenzene by not more than the molecular geometry of 4-fluorotoluene, for which δF is shifted by ≤ 0.05 ppm in going from cyclohexane to polar solvents [9]. On the other hand, according to Emsley and Phillips [7], the significant effect of polar solvents for 4-substituted fluorobenzene due to the reaction field on δF measured relative to fluorobenzene should be found only when the difference in the dipole moments (DM) between the substituted and unsubstituted fluorobenzenes exceeds 2 D. In accord with literature data [10], the DM value for phenylacetylene is 0.75 D, while that for fluorobenzene is 1.45 D. This would indicate a DM value of about 0.7 D for FPA for orientation of the negative end of the dipole, as in the case of fluorobenzene, toward the fluorine atom. In accord with the δF data, the DM of FPA derivatives should be either comparable or somewhat higher, approaching the magnitude and direction of the DM of fluorobenzene. Thus, the differences in dipole moment between fluorobenzene and FPA derivatives should not be greater than 0.7 D, which makes a significant effect of the reaction field unlikely.

These considerations indicate that the fluorine deshielding observed for β-triphenylmethyl-4-fluorophenylacetylene in going from cyclohexane to polar solvents may be the result of polarization of the readily polarizable carbon–carbon triple bond [11] by the action of the solvent molecule dipoles in the direction of the already existing polarization of the bonds linking the aromatic carbon and acetylenic carbon. This viewpoint is supported by the increase in the fluorine signal shift for β-triphenylmethyl-4-fluorophenylacetylene with increasing E_T [12] which characterizes the microscopic solvent polarity. The similar changes in going to $CHCl_3$ and chlorobenzene indicate that the potential hydrogen bond of chloroform with the triple bond π-electrons does not have a significant effect.

Another cause for the observed downfield shift in the fluorine signal may be the formation of charge transfer complexes (CTC) in which the acetyleneic compound acts as a donor and the polar solvent acts as an electron density acceptor [13]. The formation of such complexes should be accompanied by partial transfer of triple bond π-electron density to the solvent molecule and lead to an increase in the electron-withdrawing capacity of the acetylenic substituent. Hence, we should note that a decrease in fluorine shielding is also observed for 4-fluorodiphenyl in going from cyclohexane to nitrobenzene and the change in the chemical shift is 0.9 ppm [10].

On the other hand, the same solvent shift for 4,4'-difluorodiphenyltolane gives a decrease in fluorine shielding of only 0.14 ppm while the corresponding shift for $4\text{-}FC_6H_4C{\equiv}CCPh_3$ gives a displacement of 0.47 ppm (see Table 1). This finding indicates an insignificant effect of the formation of CTC on the decrease in fluorine shielding.

In the first approximation, we may assume that the effects of triple bond polarization or the formation of CTC are approximately the same for all the compounds studied and may analyze the difference between the δF shifts upon going from cyclohexane to a given solvent for a given compound and for $4\text{-}FC_6H_4C{\equiv}CCPh_3$

$$\Delta\Delta\delta F = \Delta\delta F\,(XC \equiv CC_6H_4F\text{-}4) - \Delta\delta F\,[Ph_3CC \equiv CC_6H_4F\text{-}4]$$

Analysis of the corresponding values shows that they are negative for all solvents for the Ph_3Ge derivative and, in most cases, are 0.1-0.2 ppm in absolute value. A similar effect is also found for the Ph_3Sn derivative for which ΔΔδF is 0.1 ppm, with the exception of DMSO. The ΔΔδF value for the Ph_3Pb derivative are positive for pyridine and DMSO and approximately zero for THF.

In contrast, positive ΔΔδF values are found for FPA and its mercury derivatives for all solvents with the exception of $CHCl_3$. These values are greatest in THF, pyridine and DMSO (0.5-0.6 ppm for FPA and its $C_6H_{11}Hg$ derivative, 0.8-0.9 ppm for the MeHg derivative, and 1.0-1.2 ppm for the PhHg derivative).

TABLE 2. Melting Points and Elemental Analyses of $4\text{-}FC_6H_4C{\equiv}CER_n$

R_nE	Yield, %	Mp, ℃	Found/Calculated, %		
			C	H	E
PhHg	90	130–131 (EtOH)	42,36/42,38	2,11/2,29	50,84/50,55
$4\text{-}MeC_6H_4Hg$	90	121–122 (EtOH)	44,13/44,07	2,44/2,22	48,98/49,06
Ph_3Sn	55	63–64 (pentane)	65,74/65,57	4,05/4,08	25,73/25,30
$(4\text{-}MeC_6H_4)_3Sn$	50	112 (hexane)	67,95/68,14	4,80/4,93	23,48/23,22
Ph_3Pb	55	72–73 (hexane)	56,02/56,01	3,57/3,41	37,06/37,16
$(4\text{-}MeC_6H_4)_3Pb$	60	107–108 (pentane)	58,76/58,08	4,60/4,20	34,07/34,55
Ph_3Ge	65	71–72 (pentane)	73,30/73,82	4,53/4,53	*
$(4\text{-}MeC_6H_4)_3Ge$	70	108–109 (pentane)	75,01/74,90	5,51/5,38	*
Ph_3C	85	109 (pentane)	89,46/89,47	5,29/5,28	–
MeHg	90	46–47 (MeOH)	32,38/32,28	2,08/2,09	60,04/59,95
cyclo-$C_6H_{11}Hg$	90	88 (EtOH)	41,69/41,74	3,88/3,75	50,10/49,79

*This element was not determined.

These results indicate that, in contrast to the Ph_3Ge derivative, hydrogen bonding and coordination interactions of the organometallic groups with the solvent may give a significant contribution to the change in the fluorine chemical shift and the electronic effect of the $C{\equiv}CX$ groups upon going from cyclohexane to coordinating solvents in the case of FPA and a series of its organometallic derivatives. In this case, the contribution increases depending on the nature of the substituent at the acetylenic carbon atom in the following series: $Ph_3Sn < Ph_3Pb < H \approx C_6H_{11}Hg < MeHg < PhHg$.

These findings permit us to consider FPA and its OMD as convenient model compounds for studying metal—proton and metal—metal exchange reactions involving CH-acids and their OMD, including metal—metal exchange reactions with monovalent metal ions.

We should also note that it follows from the series for the relative electron-withdrawing capacity of $C \equiv CX$ (I) groups obtained in the present work that, in most cases, the bond polarity of the X group with the terminal acetylenic carbon atom increases in the series: $Ph_3Ge < Ph_3Sn < H < Ph_3Pb \approx Ph_3C < PhHg < MeHg < C_6H_{11}Hg$. The relative polarity data for these bonds may be used for interpreting the results of studies on metal—proton and metal—metal exchange reactions involving substituted acetylenes and their organometallic derivatives.

EXPERIMENTAL

The $^{19}F\{^1H\}$ NMR spectra were taken on a Tesla BS-497 spectrometer at 94.075 MHz (for fluorine) for freshly prepared solutions of the compounds studied. The resonance signal was stabilized relative to the signal of a D_2O sample placed between the walls of a 5-mm tube and a 3.5-4.0-mm sealed insert containing the solution studied. The precision in the determination of δF for 0.2 and 0.01 M solutions was ±0.01 and ±0.02 ppm, respectively.

The solvents were purified by standard methods.

The purity of the compounds was controlled by ^1H and ^{19}F NMR spectroscopy and IR spectroscopy relative to the triple bond stretching band at 2155-2135 cm^{-1} ($\nu C{\equiv}C$ for FPA is 2119 cm^{-1}) and the absence of acetylenic hydrogen stretching band at 3292 cm^{-1}. The melting points and elemental analysis of previously unreported compounds are given in Table 2. Typical methods for the synthesis of the compounds studied in this work are given below.

β-4-Tolylmercuri-4-fluorophenylacetylene. A mixture of solutions of 1.75 g (5 mmoles) 4-tolylmercury acetate in methanol and 0.28 g (5 mmoles) KOH in 20 ml aq. methanol was added to a mixture of solutions of 0.6 g (5 mmoles) FPA in methanol and 0.28 g (5 mmoles) KOH in 20 ml aq. methanol. The solvent was evaporated upon standing and the residue was washed with water. Recrystallization from ethanol gave 1.9 g (90%) of the desired product with mp 121-122°C. β-Phenylmercuri-, β-cyclohexylmercuri- and β-methylmercuri-4-fluorophenylacetylenes were similarly obtained.

β-Triphenylstannyl-4-fluorophenylacetylene. A sample of 0.9 g (7.5 mmoles) FPA in 10 ml THF was added in small portions to a solution of EtMgBr obtained from 0.18 g (7.5 mmoles) Mg and 0.82 g (7.5 mmoles) EtBr in 20 ml THF. The reaction mixture was stirred for 30 min and a solution of 2.89 g (7.5 mmoles) triphenylchlorostannane in 10 ml THF was added. Stirring was continued for 3 h at 45-55°C. The mixture was treated with saturated aq. NH_4Cl. The mixture was extracted with ether and the solvent was evaporated in vacuum. Recrystallization of the solid residue from hexane gave 1.75 g (55%) product with mp 53-54°C. Samples of β-tris(4-tolyl)stannyl-, β-triphenylgermyl-, and β-triphenylmethyl-4-fluorophenylacetylenes were prepared similarly.

β-Triphenylplumbyl-4-fluorophenylacetylene. A solution of 2.38 g (5 mmoles) triphenylchloroplumbane in 25 ml benzene was added to a solution of MeONa obtained by the dissolution of 0.138 g (6 mmoles) sodium in 5 ml methanol. Then, 0.6 g (5 mmoles) FPA was added and the mixture was stirred for 15 min. The methanol was distilled off and the solution was centrifuged and the benzene was evaporated in vacuum. Recrystallization of the solid residue from hexane gave 1.55 g (55%) product with mp 72-73°C. A sample of β-tris(4-tolyl)plumbyl-4-fluorophenylacetylene was similarly obtained.

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CONCLUSIONS

1. A ^{19}F NMR spectroscopic study of 4-fluorophenylacetylene and its derivatives showed that the electron-withdrawing capacity of the C≡CX groups increases in the following series for X: $cyclo\text{-}C_6H_{11}Hg < MeHg < PhHg \approx Ph_3C \simeq Ph_3Pb < Ph_3Sn < H < Ph_3Ge$.

2. The formation of a hydrogen bond or coordination bond of coordinating solvents with these compounds makes a significant contribution to the change in the electronic effect of the C≡CX groups and this contribution increases in the following series for X: $Ph_3Sn < Ph_3Pb < H \simeq cyclo\text{-}C_6H_{11}Hg < MeHg < PhHg$.

3. 4-Fluorophenylacetylene and its organometallic derivatives are convenient model compounds for the study of metal—proton and metal—metal exchange reactions.

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