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ALLYL-CONTAINING ORGANOMETALLIC GROUPINGS AS SUBSTITUENTS IN PHENYL NUCLEI; RELATIONSHIP BETWEEN ELECTRON EFFECT AND STRUCTURE

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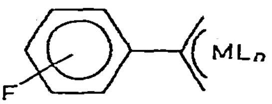
Summary

The authors have synthesized allyl derivatives of mercury, tin, palladium, cobalt, and manganese containing *m*- and *p*-fluorophenyl nuclei in the 1- and 2-positions of the allyl group. They studied the effect of the metal atom and the associated ligands on the shielding of the fluorine nuclei in the phenyl rings. On the basis of the results obtained, they discuss the nature of the electron density distribution within the allyl ligand.

Introduction

In recent years, one of the methods for studying the electron nature of the metal—π-ligand bond has been comparative investigation into the reactivity and physicochemical characteristics of free and coordinated π-ligands. This method has been used most widely and fruitfully to compare free and coordinated arenes in arene $Cr(CO)_3$-complexes. Data on the reactivity of free and coordinated ligands has been demonstrated to be often unsuitable for a rigorous quantitative evaluation of the effect of coordination with respect to the shift of the electron density along the metal—π-ligand bond. In many cases the observed differences in reactivity can be attributed to the differences in the nature of the transient state in reactions of a free and a coordinated ligand. Therefore preference is given to methods which are free from assumptions as to the nature of the transient state in reactions of a coordinated and a non-coordinated π-ligand. In this sense, the most universal method, suitable for any type of π-ligand and π-complex, is introduction of these groups as substituents into *para*- and *meta*-positions of fluorobenzene and measurements of the changes in the chemical shifts of ^{19}F as compared with unsubstituted fluorobenzene; this approach was used to advantage for investigating the electron structure of π-complexes [1] and organometallic compounds [2], as well as other composite multiatomic groupings [3]. It was applied for evaluating the electron effect of such a "difficult" substituent as the cyclopentadienyl anion [4], and also for solving the problem of electron density distribution in a coordinated butadiene π-ligand [5].

As distinct from the cyclical aromatic ligands, in which the electron density is distributed uniformly among all the carbon atoms, in the allyl ligand, as well as in the butadiene one, the charges on the terminal atoms and the central atom are different even in the uncoordinated state. Data of ^{1}H and ^{13}C NMR spectroscopy [6] and quantum-chemical calculations [7] indicate that the nonuniformity of electron density distribution in the allyl ligand persists upon coordination. For a comprehensive description of the electron effect of π-allylmetallic groupings it was necessary to determine the characteristics of the charge distribution both in the 1- and the 2-positions of the allyl group. With this aim in view, the authors studied the electron effect of π-complex substituents bound with the phenyl nucleus via the positions of the 2- and 1-π-allyl ligand (structures I and II, respectively), on the shielding of the fluorine nuclei in the *m*- and *p*-positions of the aromatic rings. To do this, we synthesized *m*- and *p*-fluorophenyl-substituted π-allyl compounds of palladium, cobalt, and manganese and measured the chemical shifts of the fluorine atoms; then we used the data obtained to calculate the inductive (σ_i) and resonance (σ_R°) constants characterizing the electron effect of the substituents under investigation, and also the effect of the solvents on these parameters.



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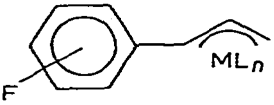

(II)

It is common knowledge that π-allyl compounds of transition metals in solutions, particularly in coordinating solvents, often move to the dynamic state, which possibly includes the σ-form [8]. In this connection it appeared expedient to study by the same method the electron effect of "true" σ-allyl derivatives of nontransition metals capable of taking part in the dynamic processes.

According to data of PMR spectra [9], the allyl compounds of mercury and tin are systems with a localized allyl—metal σ-bond. For the allyl compounds of mercury, the dynamic processes occur only upon addition of mercury salts [10], while for the derivatives of tin no dynamic processes have been detected, even under relatively arduous conditions [11]. There are proofs, however (both kinetic [12] and spectral [13]), of the existence of a special type of interaction between the metal atom and the multiple bond in allyl compounds of mercury and tin; two possible mechanisms of such interaction are suggested namely: (1) interaction of electrons of the metal—carbon σ-bond with the allyl double bond [14], σ,π-conjugation, and (2) direct interaction between the *d*-orbitals of the metal atom and the π-orbitals of the allyl double bond [15]. No final conclusion in favour of either type of interaction has been made so far; therefore, it was interesting to investigate the electron effect of σ-C_3H_4MX-groupings (—Hg, Sn) as substituents in the aromatic nucleus and use the data obtained to make an assumption about the electron density distribution in the allyl compounds of tin and mercury.

For this purpose we investigated NMR spectra of ^{19}F-substituted fluorobenzenes containing $-C_3H_4HgCl$ and $-C_3H_4SnPh_3$ groupings as substituents. The obtained values of chemical shifts of the fluorine were used for calculating the inductive (σ_i) and resonances (σ_R°) constants for the above-indicated substituents by the Taft method [16].

For the sake of comparison, the present authors used the same method to obtain the values of σ_i and σ_R° for the propenyl- and the 1- and 2-methylvinyl-substituents.

Experimental

Substances

The synthesis of the fluorophenyl-substituted allyl compounds of Pd and Hg used in this investigation has been described previously [17]. Fluorophenyl-substituted π-allyl compounds of Mn and Co were obtained from the corresponding substituted π-allylpalladiumhalides:

Interaction of fluorophenyl-substituted bis-π-allylpalladiumchlorides with NaMn(CO)$_5$. General procedure

(a) 50 ml of 0.05 *M* ether solution of $NaMn(CO)_5$, obtained by reduction of $Mn_2(CO)_{10}$ with an excess of 1% sodium amalgam in ether, was added in an argon atmosphere at 0°C to a solution of 0.0025 mol of the corresponding substituted π-allyl complex of palladium in 50 ml of THF [19]. The reaction mixture was stirred for 2 h, then the solvent evaporated in a vacuum, the residue extracted with pentane, and the pentane evaporated to dryness in a vacuum. The dry residue was dissolved in a small amount of pentane and filtered out; the filtrate is slowly evaporated in a vacuum without external heating. Beautiful yellow needles of the complexes formed on the flask bottom. These had crystallized out of the CH_2Cl_2/heptane mixture.

(b) With addition of triphenylphosphine. 0.003 mol triphenylphosphine in 25 ml ether was added to a solution of the fluorophenyl-substituted π-allyl compound of manganese obtained by the above-described procedure, and upon stirring for 1 h the mixture was filtered out; the filtrate was slowly evaporated in a vacuum, and the residue twice recrystallized from the CH_2Cl_2/heptane (1 : 2) mixture.

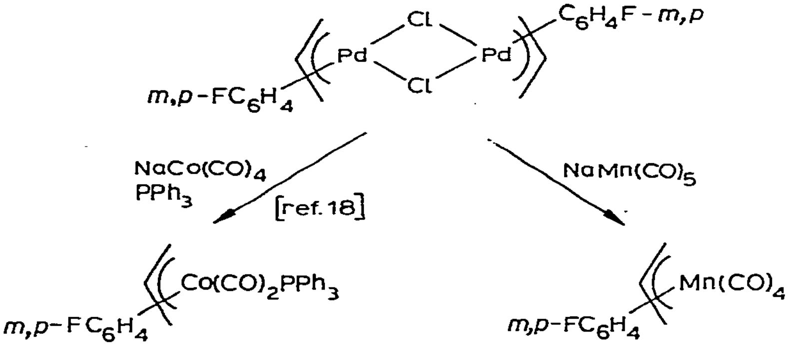

TABLE 1

para- AND *meta*-FLUOROPHENYLALLYL COMPOUNDS OF Co, Mn, AND Sn OBTAINED IN THE PRESENT INVESTIGATION

Compound	Yield (%)	M.p. (°C)	Empirical formula	Analysis (%)			
				Found		Calculated	
				C	H	C	H
π-1-(*p*-fluorophenylallyl)manganese tetracarbonyl	58	65—66	$C_{13}H_8MnFO_4$	51.34	2.86	51.62	2.64
π-1-(*m*-fluorophenylallyl)manganese tetracarbonyl	52	43—44	$C_{13}H_8MnFO_4$	51.87	2.66	51.64	2.64
π-2-(*p*-fluorophenylallyl)manganese tetracarbonyl	62	61—62	$C_{13}H_8MnFO_4$	51.42	2.76	51.64	2.64
π-1-(*m*-fluorophenylallyl)manganese tetracarbonyl	60	48—50	$C_{13}H_8MnFO_4$	51.67	2.66	51.64	2.64
π-1-(*p*-fluorophenylallyl)manganese tricarbonyltriphenylphosphine	40	75—78	$C_{30}H_{23}MnPFO_3$	67.05	4.42	67.16	4.29
π-1-(*m*-fluorophenylallyl)manganese tricarbonyltriphenylphosphine	15	58—60	$C_{30}H_{23}MnPFO_3$	67.00	4.40	67.16	4.29
π-1-(*p*-fluorophenylallyl)cobalt dicarbonyltriphenylphosphine	40	104—106	$C_{29}H_{23}CoFPO_2$	67.91	4.62	67.98	4.51
π-1-(*m*-fluorophenylallyl)cobalt dicarbonyltriphenylphosphine	30	98—100	$C_{29}H_{23}CoFPO_2$	67.60	4.53	67.98	4.51
π-2-(*p*-fluorophenylallyl)cobalt dicarbonyltriphenylphosphine	40	84—86	$C_{29}H_{23}CoFPO_2$	68.43	4.87	67.98	4.51
π-2-(*m*-fluorophenylallyl)cobalt dicarbonyltriphenylphosphine	25	75—78	$C_{29}H_{23}CoFPO_2$	68.39	4.71	67.98	4.51
p-fluorophenylallyltriphenyltin	50	81—83	$C_{27}H_{23}SnPF$	67.18	4.94	66.80	4.74
m-fluorophenylallyltriphenyltin	35	49—51	$C_{27}H_{23}SnPF$	66.70	4.53	66.80	4.74

Interaction of fluorophenyl-substituted π-allyl compounds of palladium with $NaCo(CO)_4$. General procedure

A mixture of 0.0025 mol of the corresponding substituted π-allyl compound of palladium and 36 ml of 0.08 *M* ether solution of $NaCo(CO)_4$ was stirred for 1 h at 25°C in an atmosphere of pure dry argon; then a solution of 0.003 mol triphenylphosphine in 10 ml of ether was added to the reaction mixture; after 1 h stirring the mixture was filtered out and the filtrate evaporated in a vacuum; the residue was twice crystallized from a CH_2Cl_2/heptane (1 : 2) mixture.

Table 1 lists the yields, melting points and the data of elemental analysis of the complexes obtained. Fluorophenyl-substituted π-allylmanganese tetracarbonyls are solid crystalline substances, air- and thermally unstable. All the cobalt complexes obtained are crystalline substances of a brick-red colour stable only in an inert atmosphere. The structure of the compounds obtained has been established on the basis of IR and PMR spectra. In the IR spectra, in the region of stretching vibration of the CO-groups bound with the metal atom, one observes two strong absorption bands of approximately equal intensity at 2005 and 1950 cm^{-1} and one medium intensity band at 2070 cm^{-1}. A similar spectral pattern was observed by Heck [18] for triphenylphosphine derivatives of substituted π-allyl compounds of cobalt. In the case of manganese compounds there are four absorption bands at 2015, 1985, 1967, and 1975 cm^{-1} corresponding to the stretching vibration of the $Mn(CO)_4$ group. The PMR spectra of fluorophenylallylmanganese tetracarbonyls exhibit a spectral pattern characteristic of the complexes 1- and 2-substituted in the π-allyl group. The PMR spectra of fluorophenyl π-allyl compounds of cobalt are qualitatively similar to the spectra of the corresponding manganese derivatives and fully confirm the structure of the compounds obtained.

Obtaining para- and meta-fluorophenylallyltriphenyltin

A small amount of *para-* or *meta*-fluorophenyl-3-bromopropenes-1, obtained by the procedure of [20], was added to 0.02 g-atom of Mg in 10 ml of THF *.

The mixture was stirred rapidly and heated to boiling point. Then a solution of 0.02 mol of *para-* or *meta*-fluorophenyl-3-bromopropenes-1 and 0.013 mol of triphenyltin chloride in 10 ml of THF was slowly added. On adding the whole solution, the reaction mixture was boiled for 24 h, then cooled and hydrolized with an aqueous solution of NH_4Cl. The organic layer was separated, and the solvent vacuum evaporated. The residue was dissolved in ether and shaken with a 5% aqueous solution of KF. The ether was evaporated, the remaining yellow oil being extracted with petroleum ether. The cooling was accompanied by precipitation of a white sediment. Crystallization from the hexane yielded the corresponding fluoro-derivatives of phenylallyltriphenyltin. The yields, melting points and the elemental analysis data of all the compounds obtained are given in Table 1.

The structure of the obtained *para-* and *meta*-fluorophenylallyl compounds of tin and mercury was established on the basis of IR and PMR spectra. In the

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* The reaction proceeds successfully only when Mg is taken in a stoichiometric amount. Purified THF is distilled over $LiAlH_4$ immediately before the reaction.

^{1}H NMR spectrum of the compound m-$FC_6H_4C(=CH_2)CH_2HgCl$, one observes a comparatively simple picture characteristic of two noninteracting A_2 systems of protons; the singlet at 4.29 ppm corresponds to the terminal $=CH_2$ protons, the singlet at 2.30 ppm is referred to protons of the methylene group bound with the mercury atom. In the region of 7.33 ppm, we observed a multiplet characteristic of the protons of the *meta*-disubstituted phenyl nucleus. The spectrum of the compound m-$FC_6H_4CH=CHCH_2HgCl$ is more complex, but it agrees fairly well with the expected pattern for the ABX_2 system in the region of the allyl group protons; at 2.96 ppm one observes a doublet from protons of the CH_2 group ($J_{1,2} = 2.0$ Hz; $J_{2,3} = 5.3$ Hz); the multiplet with a centre at 6.55 ppm corresponds to the protons of the AB system —CH=CH— with a constant $J_{1\text{-}3}$ equal to 15.8 Hz. In the region of phenyl protons, there is a multiplet at 7.17 ppm. Besides, for the signal from CH_2 protons we detected satellites in the form of doublets due to spin-spin coupling with the nucleus of ^{199}Hg ($J(^{199}\text{Hg—}^1\text{H}) =$ 281.1 Hz). A comparison of the value of $J_{1\text{-}3}$ with the corresponding constants of spin-spin coupling of disubstituted propenes of the type $XCH_A=CH_BY$ points to a *trans* position of the substituents relative to the double bond in the mercury compounds studied. The presence of a *trans* isomer is also confirmed by IR spectra: in the range of 970 cm^{-1} one observes intensive bands corresponding to plane deformation vibrations of the *trans*-CH=CH system [21]. A similar *trans* structure is characteristic of the fluorophenyl-substituted allyl compounds of tin ($J_{1,3} = 16.5$ Hz) obtained in the present investigation.

Measuring ^{19}F NMR spectra

^{19}F NMR spectra were taken on an H-60 spectrometer (56.4 MHz) at 34°C. The chemical shifts were measured relative to an external reference sample — fluorobenzene in the same solvent and in approximately the same concentration as the substance investigated. The chemical shifts were reckoned between the centres of the signals from the ^{19}F nuclei. The accuracy of measurement of chemical shifts was ±0.1 ppm. In taking the spectra of poorly soluble substances we used a memory based on the multichannel analyzer LP-4000. The scanning rate in taking the spectra was 10 Hz/sec for highly soluble compounds, and 20 Hz/sec for storing.

The resonance constants were calculated by the generalized Taft equation $\sigma^{\circ}_{R} = \delta_p - \delta_m/29.5$. The values of σ_i were calculated for each solvent. To do this, Taft's results for the important solvents (benzene, $CHCl_3$, pyridine, THF, dimethylsulphoxide, and others) were treated by the least-squares method, and the following formulas were obtained:

$$\sigma_{i(C_6H_6)} = -(\delta_m - 0.939/7.26);\ \sigma_{i(CHCl_3)} = -(\delta_m - 0.600/7.10);$$

$$\sigma_{i(CCl_4)} = -(\delta_m - 0.977/7.50);\ \sigma_{i(THF)} = -(\delta_m - 0.925/7.18);$$

$$\sigma_{i(DMS)} = -(\delta_m - 0.711/6.79);\ \sigma_{i(Py)} = -(\delta_m - 0.711/7.27).$$

Results and discussion

Prior to analyzing the electron effects of metal-containing groupings, we will consider in more detail the electron effect of metal-free tricarbon substitutes with a multiple bond.

TABLE 2

R		δ_p^F	δ_m^F	σ_i	σ_R^o	$\sigma_{i,\ calc.}$ [a]
$-CH_2CH{=}CH_2$	I	4.53	0.90	−0.04	−0.12	−0.08
$-CH{=}CH-CH_3$	II	3.13	1.15	−0.08	−0.07	−0.02
$-CH(CH_3){=}CH_2$	III	2.53	0.85	−0.03	−0.06	
$-CH(OH)CH{=}CH_2$	IV	2.30	0.12	+0.07	−0.07	+0.06
$-CH(OH)CH_2CH_3$	V	2.72	0.53	+0.01	−0.07	+0.05
$-CH{=}CH_2$ [b]	VI	1.43	0.50	+0.01	−0.03	
$-CH_3$ [b]	VII	5.45	1.15	−0.08	−0.15	

[a] The values of $\sigma_{i,\ calc.}$ have been calculated by the following formulas [22]: $\sigma_i(-CH_2X) = \sigma_i(-CH_3) + 1/2.10\ \sigma_i(-X)$; $\sigma_i(-CH{=}CHX) = \sigma_i(-CH{=}CH_2) + 1/2.45\ \sigma_i(-X)$. [b] The data have been borrowed from [22].

Table 2 lists the values of chemical shifts and the constants σ_i and σ_R^o for propenyl, α-hydroxypropenyl, α-hydroxypropyl and 1- and 2-methylvinyl substitutes. The last column contains the values of σ_i calculated according to the additive pattern.

As follows from Table 2, substituents I, II, and III exert an approximately equal electron-donor influence both as to the inductive mechanism and the conjugation effect. The replacement of the α-hydrogen in I by the electron-acceptor OH group leads to a preferential change in the inductive component of the electron effect of this group.

Electron effect of allyl compounds of mercury and tin

Table 3 presents the ^{19}F chemical shifts and the values of σ for the substituents investigated. Besides, it gives, for comparison, the values of σ available in the literature for a number of substituents containing the same metal atoms. The last line lists the values of σ calculated according to the additive formulas.

It can be seen that all the investigated organometallic substituents produce an approximately equal (low) donor effect of conjugation comparable to that of the corresponding hydrocarbon substituents (I—III, Table 2); at the same

TABLE 3

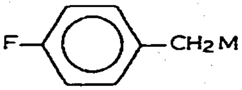
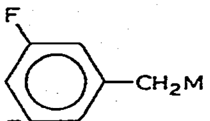
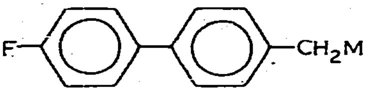
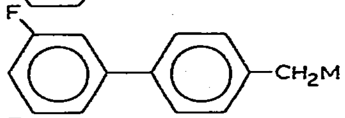
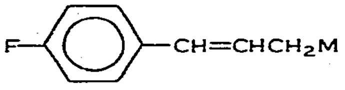
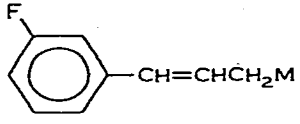
^{19}F CHEMICAL SHIFTS (ppm) IN *m*- AND *p*-FC_6H_4R AND VALUES OF σ FOR SUBSTITUENTS R

R	No.	Solvent	δ_m^F	δ_p^F	σ_i	σ_R^o	$\sigma_{i,\ calc}$ [a]
$-CH{=}CHCH_2HgCl$	VIII	C_6H_6	0.48	1.90	+0.02	−0.05	
$-CH{=}CHCH_2HgCl$		THF	0.49	2.88	+0.02	−0.08	0.00 [b]
$-CH{=}CHCH_2SnPh_3$	IX	$CHCl_3$	0.78	3.30	−0.03	−0.09	0.01
$-CH{=}CHCH_2SnPh_3$		THF	0.58	3.31	0.00	−0.09	
$-C({=}CH_2)CH_2HgCl$	X	C_6H_6	−0.32	0.93	+0.13	−0.04	
$-C({=}CH_2)CH_2HgCl$		THF	−0.05	1.04	+0.09	−0.04	
$-CH_2HgCl$	XI		1.80	6.80	−0.02	−0.14	
$-CH_2SnPh_3$	XII	DMS	0.83	6.91	0.00	−0.21	
$-HgCl$	XIII	$CHCl_3$	−0.60	−0.95	+0.17	+0.01	
$-SnPh_3$	XIV	$CHCl_3$	−0.70	−1.52	+0.18	+0.03	

[a] The values of σ were calculated by the following formulas: $\sigma_i(-CH{=}CHX) = \sigma_i(-CH{=}CH_2) + 1/2.45\ \sigma_i(-X)$. [b] For calculating the values of σ_i($-CH{=}CHCH_2HgCl$ substituent), the values for CH_2HgCl in dioxane were used [23].

TABLE 4

CHANGE IN ^{19}F CHEMICAL SHIFT ($\Delta\delta = \delta(CH_2M) - \delta(CH_3)$) (ppm) AS A RESULT OF REPLACEMENT OF HYDROGEN IN THE CH_3 GROUP BY THE GROUP M (M = $SnPh_3$)

	$\Delta\delta$		$\Delta\delta$
	1.46		−0.30
	0.23		0.11
	0.17		−0.37

time, these substituents differ widely in their inductive effect from their hydrocarbon precursers: on replacement of the hydrogen by a metal they change from electron-donor to electron-acceptor ones, and in the case of group X this results in a rather strong inductive electron-acceptor substituent, comparable in its strength with such groups as COOMe, COOEt, etc.

In using the data presented in [24], it is useful to compare the results of introduction, between the CH_2M substituent and the fluorophenyl nucleus, of various "conducting" groups: a *para*-phenylene nucleus, and a *trans*-ethylene bridge.

The relevant data are given in Table 4 for the case of the CH_2SnPh_3 substituent *.

In the *meta*-series, the introduction of a *trans*-ethylene group between the fluorophenyl nucleus and the CH_2M substituent does not change the inductive effect of the latter; a different picture prevails in the case of *para*-fluorocompounds. Here, on introduction of either a *para*-phenyl nucleus or a *trans*-ethylene bridge, the effect of replacement of the hydrogen in the CH_3 group on the metal decreases drastically, and it is practically an established fact that within the accuracy of measurement the replacement of the hydrogen by a metal does not affect the chemical shifts of the fluorine *para*-atom.

The increase in the electron-donor effect of the methyl group on replacement of the hydrogen by a metal in benzyl systems is attributed to the effect of hyperconjugation of the C—M bond with the π-electron system of the phenyl nucleus [25]. Hyperconjugation is usually regarded as a particular case of a more general effect of polar conjugation [26]. It is well known that polar conjugation is transferred via a system of mutiple bonds, practically without damping [27]. The authors of [24] associate investigation into the hyperconjugation effect of the CH_2M substituent in the case of the 4,4′-biphenylene system with some noncoplanarity of the biphenylene system. At the same time, the double bond and the phenyl nucleus are known to be coplanar in

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* A similar change in chemical shifts is observed for the CH_2HgCl substituent [24].

β-substituted styrenes. However, we observe the same result as in the case of the 4,4′-biphenylene system, i.e. actually the absence of the effect of hyperconjugation of the C—M bond with the phenyl nucleus and the fluorine atom. Indirect physicochemical evidence [28] indicates that the preferred conformation for allyl compounds of mercury and tin is the one in which the M group is removed from the plane of the allyl double bond and conditions are provided for effective interaction of both the electrons of the C—M σ-bond and the valency *d*-orbitals of the metal with the π-orbital of the multiple bond. From the physicochemical studies described in the experimental part one can assume that the fluorophenyl-substituted compounds covered by this investigation have a structure similar to the corresponding unsubstituted allyl compounds, and they have the necessary conditions for effective interaction of the electrons of the M—C bond with the π-system of the double bond. Thus, although the allyl compounds investigated have all the necessary conditions for effective interaction by the hyperconjugation mechanism, this effect is not transferred to the fluorine atom through the multiple bond and the *para*-phenylene nucleus for reasons yet unknown *.

One of the possible explanations is that the two effects — hyperconjugation and *p-d* interaction — will "compensate" ** for each other on the carbon atom, which is directly bound with the fluorophenyl nucleus. As indicated in [30], the pumping of electron density in the double bond by the hyperconjugation mechanism increases the polarization of the π-electron cloud of the multiple bond and hence must enhance *p-d* interaction, which is of an electron-acceptor nature.

The electron effect of the $—C(=CH_2)CH_2HgCl$ group deserves consideration in its own right. If we compare this substituent with $—CH=CH_2$ ($\sigma_i = 0.01$, $\sigma_R^\circ = —0.03$) and $—C(Me)=CH_2$ ($\sigma_i = —0.03$ and $\sigma_R^\circ = —0.06$), we can note that replacement of the hydrogen atom in the α-carbon atom of the vinyl group by such substituents (approximately equal in their electron effect) as $—CH_3$ ($\sigma_i = —0.08$ and $\sigma_R^\circ = —0.15$) and $—CH_2HgCl$ ($\sigma_i = —0.02$ and $\sigma_R^\circ = —0.14$) leads to radically different results. It can be seen that the ability for conjugation remains practically unchanged, while the inductive effect changes in different ways: the CH_3 group, as usual, slightly increases the electron-donor properties of the entire substituent, while the CH_2HgCl group transforms it into a rather strong acceptor. It can be assumed that the increased electron-acceptor inductive effect of the $—C(=CH_2)CH_2HgCl$ substituent is mainly due to the effective positive charge on the carbon atom, which is directly bound with the phenyl nucleus. The literature contains data [28] indicating that this positive charge on the central carbon atom of the allyl systems increases on transition from a plane configuration to a conformation in which the CH_2HgCl group will be located under the plane of the allyl group; it should then be expected that the electron effect of the entire substituent will be similar to that of the π-allylmetallic groupings, whose electron-acceptor effect is discussed in the following sections.

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* For information on the absence of steric hindrances to free rotation of the phenyl nucleus in phenylallyl compounds see [29].

** The results obtained on similar models indicate that the hyperconjugation effect is comparable with *p-d* homoconjugation [30].

TABLE 5

^{19}F CHEMICAL SHIFTS (ppm) FOR 1-*m*- AND -*p*-$FC_6H_4C_3H_4PdX$ AND CONSTANTS σ_i AND σ_R° FOR 1-C_3H_4PdX ($CHCl_3$, 34°C)

X	δ_m	δ_p	σ_i	σ_R°
Cl	−0.44	−1.35	+0.15	+0.03
Br	−0.49	−1.39	+0.15	+0.03
I	−0.56	−1.25	+0.16	+0.02
$C_5H_7O_2$	+0.32	+0.64	+0.04	−0.01
—C_5H_5	+0.29	+1.86	+0.04	−0.05
$\Delta\delta$	0.88	3.21		

Electron effect of π-C_3H_4PdX substituent

Tables 5 and 6 list the ^{19}F chemical shifts and the constants σ_i and σ_R° for 1-*m*, *p*-$FC_6H_4C_3H_4PdX$ and their 2-substituted analogs, as calculated on the basis of these shifts.

As follows from Tables 5 and 6, the π-C_3H_4PdX grouping is an electron-acceptor substituent of medium strength with respect to the phenyl nucleus, and the 2-π-C_3H_4PdX substituent possesses stronger acceptor properties than the same grouping bond via position 1 of the allyl system. The acceptor effect of the substituents investigated is mainly due to their strong negative inductive influence, which is comparable in magnitude with that of such groups as OH (σ_i −0.25) or $OCOCH_3$ (σ_i −0.28). At the same time the ability of π-C_3H_4PdX substituents for conjugation with the phenyl nucleus practically does not differ from the conjugation of the hydrogen. From a comparison of the values obtained with those of σ for the hydrogen-containing precursors (groups I and II of Table 2) it is seen that formal replacement of the hydrogen atom in fluorophelypropenes by a PdX group substantially increases the electronegativity of the carbon atoms both in position 2 and in position 1 of the allyl group and reduces the ability of the allyl group for interacting with the adjacent phenyl nucleus with respect to the conjugation effect.

Comparing the values of chemical shifts and the constants σ_i obtained in the present investigation for π-C_3H_4PdCl substituents bound with the phenyl nucleus via the 1- and 2-positions of the allyl ligand, one can infer that the central carbon atom of the π-allyl ligand has a greater π-accepter ability than the terminal carbon atoms. This may be due to the greater electron-deficiency of the atom.

TABLE 6

^{19}F CHEMICAL SHIFTS (ppm) FOR 2-*m*- AND -*p*-$FC_6H_4C_3H_4PdX$ AND CONSTANTS σ_i AND σ_R° FOR 2-C_3H_4PdX ($CHCl_3$, 34°C)

X	δ_m	δ_p	σ_i	σ_R°
Cl	−1.21	−2.05	+0.25	+0.03
Br	−1.32	−1.93	+0.27	+0.02
I	−1.29	−1.80	+0.26	+0.02
$C_5H_7O_2$	−0.86	−1.55	+0.21	+0.02
π-C_5H_5	+0.18	+0.92	−0.06	−0.02
$\Delta\delta$	1.50	2.97		

Hence, the results obtained indicate that in the π-allyl ligand the electron density on the terminal carbon atoms is about twice that of the central carbon atom

$[\sigma_{i(2\text{-}\pi\text{-}C_3H_4PdCl)}/\sigma_{i(1\text{-}\pi\text{-}C_3H_4PdCl)} = 1.8]$.

Thus, the π-C_3H_4PdX substituent is a sufficiently strong σ-acceptor, and the acceptor properties of the central carbon atom are stronger than those of the terminal atoms. The ability for conjugation with the phenyl nucleus from both positions is the same and practically equal to zero. The nonuniformity of distribution of the electron density within the π-allyl ligand agrees well with the ^{13}C NMR spectroscopy and with the quantum-mechanical calculations for π-allyl complexes of palladium. A comparison of the orbital population of the π-C_3H_5 ligand and the $C_3H_5^-$ anion (Table 7) shows that when the allyl anion is coordinated with the palladium atoms, the prevailing process is donation of electrons from the *s* and p_z orbitals of the ligand and the π-electron density (i.e. the electron density from the p_z orbitals) is taken off mainly from the terminal carbon atoms; electron donation from the central carbon atom occurs predominantly from the *s*, p_x, and p_y orbitals, i.e. from the σ-core. The total electron densities donated by the central atom and each of the terminal atoms are 2.330 and 2.069, respectively, i.e. are approximately equal. Taking into account, however, that in the allyl anion the charge on the central carbon atom is lower than on the terminal ones, one can see the reason for the stronger acceptor ability of the central positions of the π-allyl ligand in palladium complexes. Further, the donation of π-electron density from the p_z orbitals of the ligand is compensated for by the back-donation of electrons from the $4d_{xy}$ orbitals of the palladium atom, while the charge transfer from the *s*, p_x, and p_y orbitals evidently remains entirely uncompensated. Thus, in the coordinated state the allyl system has an electron-deficient σ-core, which explains its σ-acceptor properties.

The weak interaction of the π-allyl substituent with the phenyl nucleus by the conjugation-effect mechanism may be caused by the noncoplanarity of the phenyl ring with the plane of the π-allyl ligand. This interaction, however, differs only slightly from the nonpolar conjugation with the phenyl nucleus of the double bond in styrene (δ = —0.03). Polar conjugation with transition to

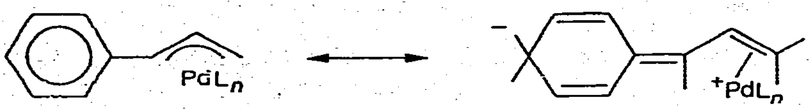
TABLE 7

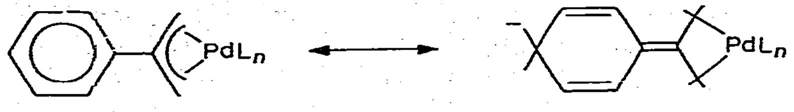
ORBITAL POPULATION DENSITIES FOR C_3H_5 ANION AND π-C_3H_5 LIGAND [a]

	Orbital	Orbital population	
		C_3H_5 anion	π-C_3H_5 ligand
C_2	*s*	2.642	0.998
	p_x	1.208	0.940
	p_y	1.319	0.980
	p_z	0.904	0.825
C_{13}	*s*	2.576	1.048
	p_x	1.074	1.058
	p_y	1.071	1.004
	p_z	1.548	0.990

[a] The *z*-axis is chosen so that the p_z-orbital characterizes the π-electron density.

quinoid structures is evidently difficult since it requires considerable energy expenditures for the reconstruction of the bond system in the molecule:





Effect of solvent on electron properties of π-C_3H_4PdCl substituent

Tables 8 and 9 lists the ^{19}F chemical shifts and the constants δ_i and δ°_R obtained for 1- and 2-*m*- and -*p*-fluorophenylallylpalladium chlorides in various solvents.

As follows from these, the chemical shift of the fluorine in the *m*-position relative to the π-allyl substituent is less sensitive to replacement of the solvent than the chemical shift of the fluorine in the *p*-position. The latter, in turn, is more sensitive to solvation interactions, including those where the π-allyl ligand is bound with the phenyl nucleus via the 1-position. The solvents investigated can be arranged in the following series as regards their effect on the chemical shifts of the fluorine in the *p*-position:

$CHCl_3 <$ benzene $<$ THF $<$ pyridine $\simeq$ DMS

The same sequence was established in studying the solvation sensitivity of the

TABLE 8

EFFECT OF SOLVENT ON ELECTRON PROPERTIES OF 1-π-C_3H_4PdCl GROUP

Solvent	δ_m	δ_p	σ_i [a]	σ°_R
Chloroform	−0.44	−1.38	+0.15	+0.03
Benzene	0.00	−1.50	+0.13	+0.02
Tetrahydrofuran	+0.39	−0.05	+0.07	+0.01
Dimethylsulphoxide	−0.10	+0.44	+0.12	−0.02
Pyridine	0.00	+0.41	+0.10	−0.01

[a] As calculated from Taft's experimental data for this solvent (see experimental section).

TABLE 9

EFFECT OF SOLVENT ON ELECTRON PROPERTIES OF 2-π-C_3H_4PdCl GROUP

Solvent	δ_m	δ_p	σ_i [a]	σ°_R
Chloroform	−1.21	−2.05	+0.25	+0.03
Benzene	−0.78	−2.15	+0.24	+0.04
Tetrahydrofuran	−0.68	−1.20	+0.22	+0.02
Dimethylsulphoxide	−0.73	−1.92	+0.21	+0.04
Pyridine	−0.78	−0.15	+0.20	0.01

[a] See footnote to Table 8.

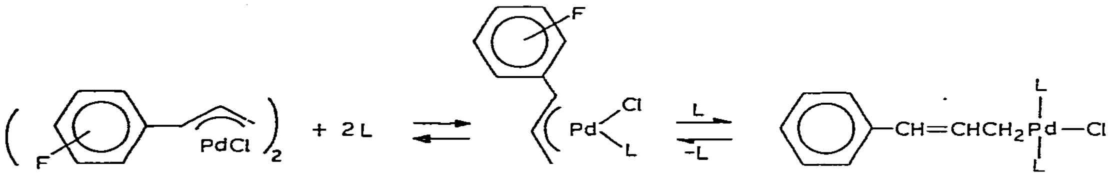
chemical shifts of the fluorine in the *m*- and *p*-fluorophenyl- and benzylmercuric halides [33]. On the whole, however, the solvation interactions for π-allylpalladium chlorides are much weaker than for mercury-containing compounds (the respective values of $\Delta\delta$ ($CHCl_3$/DMS) are 1.82 and 3.16).

Such a marked difference can probably be attributed to the fact that in the case of palladium compounds a change of the charge on the metal atom as a result of solvation interaction is transferred to the phenyl nucleus indirectly through the π-allyl system as distinct from mercury compounds, in which the metal atom is directly bound with the phenyl nucleus.

Indeed, as seen from Table 9, in the case of fluorophenylallyl compounds $\Delta\delta_n$ (THF/benzene) = 0.95 ppm only slightly exceeds the value of $\Delta\delta_n$ (THF/benzene) = 0.45 ppm for the similar palladium compound from Table 8.

Thus, divalent palladium in π-allyl complexes is similar to mercury in organomercuric compounds as to its coordination saturation, which agrees well with the numerous available experimental data on the effect of coordinating solvents on the properties of π-allyl complexes of palladium [34].

The persistence of the strong electron-acceptor effect of $1\text{-}\pi\text{-}C_3H_4PdCl$ in solvents with an increased coordinating ability relative to the atom of Pd^{2+} indicates that the equilibrium



(III)

is hardly displaced towards the formation of the σ-form III to any considerable extent, even with large excesses of the solvent.

Effect of donor-acceptor properties of ligands bound with palladium atom on chemical shifts of fluorine atoms

To evaluate the effect of other ligands bound with the metal atom on the distribution of the electron density in the π-allyl ligand, we investigated the ^{19}F NMR spectra of the 1- and 2-*m*- and -*p*-fluorophenyl-π-allyl complexes of palladium in which the second ligand consisted of the halogens (Cl, Br, and I), a π-cyclopentadienyl- or an acetylacetonate-group. The values obtained of chemical shifts and of the constant σ are given in Tables 5 and 6.

The results obtained suggest that the nature of the halogen affects the chemical shift only slightly and the calculated values of σ coincide within the accuracy of the method. In the sandwich complex containing the $\pi\text{-}C_5H_5$ group as the second ligand, the shielding of both the *m*- and *p*-atoms of fluorine sharply increases. The calculated values of σ for the $\pi\text{-}C_3H_4Pd\text{-}\pi\text{-}C_5H_5$ substituent indicate that it has a weak σ-electron-acceptor and π-electron-donor effect, and there is no substantial difference between the effect of this substituent from the 1- and 2-positions of the π-allyl ligand on the shielding of the fluorine atoms.

A different situation occurs when the halogen is replaced by the acetylacetonate group. The $\pi\text{-}C_3H_4PdC_5H_7O_2$ substituent, bound with the phenyl nucleus via the 1-position of the π-allyl ligand, has a weak electron-acceptor effect, approximately the same as the π-$C_3H_4PdC_5H_5$ substituent. At the same time, the 2-π-$C_3H_4PdC_5H_7O_2$ group exerts a strong electron-acceptor influence similar to that of the 2-π-C_3H_4PdCl grouping.

The sensitivity of *p*-atoms of fluorine to changes in the donor-acceptor properties of ligands is generally higher than that of *m*-atoms. A comparison of the effect of 1- and 2-π-allyl-substituents, however, shows that the *m*-atoms of fluorine in 2-substituted π-allyl-complexes are more sensitive to the replacement of ligands than in 1-substituted complexes. A reverse picture is observed for 1-substituted derivatives.

As follows from a comparison of the electron effect of the π-C_3H_4Pd-π-C_5H_5 and π-C_3H_4Pd-$C_5H_7O_2$ groupings, the electron-donor effect of the π-C_5H_5 ligand is transferred to all the three carbon atoms of the allyl group, while the acetylacetonate ligand increases the electron density only on terminal carbon atoms of the π-allyl ligand. A similar effect of the cyclopentadienyl and acetylacetonate ligands on the chemical shifts of ^{13}C from the central and terminal atoms of the π-allyl ligand is noted in Mann's paper [6]. The observed differences in the effects of the enumerated ligands probably reflect the specific features of transfer of electron effects in plane square and pseudooctahedral sandwich complexes. In π-allyl-π-cyclopentadienylpalladium, the metal atom has the configuration of a distorted octahedron with symmetric-bonded C_5H_5 ligand [35]. The cyclopentadienyl ligand largely compensates for the electron-deficiency of the palladium atom in π-allyl systems owing to its electron-donor effect, and the decrease in the effective positive charge on the palladium atoms affects approximately equally the electronegativity of all the three carbon atoms of the π-allyl ligand.

A quantitatively different picture is observed in the case of the π-allylpalladium acetylacetonate complex, where the palladium atom evidently has the square plane (or almost plane) configuration formed by the terminal carbon atoms of the π-allyl group and the oxygen atoms of the acetylacetonate ligand. The strong *trans* effect of the latter appears to affect only the 1- and 3-positions of π-allyl ligand.

Thus, the charge distribution in the π-allyl ligand depends not only on the donor-acceptor properties of the other groupings bound with the palladium atom, but also on the geometry of the complex as a whole.

Effect of nature of MX group on electron properties of π-C_3H_4MX substituent

In order to study the effect of the nature of the metal atom on the electron properties of π-allylmetallic substituents we investigated the NMR spectra of ^{19}F-substituted fluorobenzenes containing 1- and 2-π-$C_3H_4Mn(CO)_3$ and π-$C_3H_4Co(CO)_2PPh_3$ groupings as *m*- and *p*-substituents. The values of the chemical shifts, δ, and the constants σ_i and σ_R° for these substituents are listed in Table 10.

As seen from the table the 1- and 2-π-$C_3H_4Co(CO)_2PPh_3$ substituents are weak donors both with respect to the inductive and conjugation effects, and their electron effect is approximately equal from the 1- and 2-positions of the π-allyl ligand. In the case of the 1-π-allylmanganese tetracarbonyl substituent a considerable reduction (about two-fold) of the σ-acceptor effect took place, compared with the 1-π-C_3H_4PdCl group, as well as a qualitative change in the ability for interacting with the aromatic nucleus with respect to the conjugation

TABLE 10

^{19}F CHEMICAL SHIFTS (δ (ppm)) OF 1-π-m- AND -p-$FC_6H_4C_3H_4MX$ AND 2-π-m- AND -p-FC_6H_4MX AND VALUES OF σ_i AND σ_R^0 FOR 1-π- AND 2-π-C_3H_4MX SUBSTITUENTS ($CHCl_3$ SOLVENT)

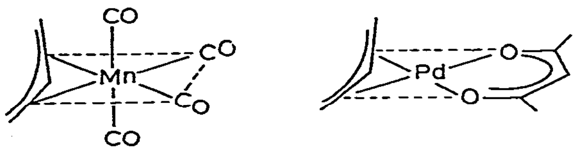
MX	Solvent	δ_m	δ_p	σ_i	σ_R^0
1-π-m- and -p-$FC_6H_4C_3H_4MX$ compounds, 1-π-C_3H_4MX substituent					
$Co(CO)_2PPh_3$	$CHCl_3$	0.96	3.10	−0.05	−0.07
$Mn(CO)_4$	$CHCl_3$	−0.08	2.30	+0.09	−0.09
2-π-m- and -p-FC_6H_4MX compounds, 2-π-C_3H_4MX substituents					
$Co(CO)_2PPh_3$	$CHCl_3$	1.20	3.80	−0.08	−0.08
$Mn(CO)_4$	$CHCl_3$	−0.74	−1.22	+0.19	+0.02

effect; from a weak π-acceptor in the case of palladium, the substitute becomes a π-donor comparable in its strength with such groups as C_6H_5.

The 2-π-$C_3H_4Mn(CO)_4$ grouping is very close in its effect to the 2-π-$C_3H_4PdC_5H_7O_2$ substituent (see Table 10) and, within the accuracy of determination of the constants σ it does not differ from the 2-C_3H_4PdX group (X = halogen). Thus, in this case, as well as for the π-cyclopentadienyl ligand and the acetylacetonate ones, we observed a different effect on the electronegativities of the central and the terminal carbon atoms of the π-allyl ligand.

Comparing the data from Table 10 with the values given in Tables 5, 6 one can infer that the coordination of the allyl with $Mn(CO)_4$ and $PdC_5H_7O_2$ groupings results in approximately the same electron density distribution within the π-allyl ligand despite the different formal degree of oxidation of the metal atoms in the two compounds. Proceeding from the fact that in π-allyl compounds of palladium the degree of oxidation of the metal atom is +1, while in manganese compounds the metal atom is in the zeroth degree of oxidation, it could be expected that in the first case the σ-donor properties of the π-allyl ligand with respect to the metal would be more pronounced than in manganese compounds. However, no such sharp change in the electron effect has occurred for manganese compounds. This may be associated with the differences in the structure of the π-allyl complexes of manganese and cobalt. In the octahedral molecule of π-allylmanganese tetracarbonyl (Scheme 1) the electron density of the allyl ligand is considerably affected only by equatorial carbonyl groups; the axial carbonyls should not exert a substantial effect for reasons of symmetry. The effect of the equatorial carbonyl ligands on the electron density distribution in the π-allyl group is transferred in accordance with the mechanism of *trans* effect in plane square complexes, and from this standpoint the observed formal analogy with plane π-allylacetylacetonate of palladium holds good (Scheme 1).

SCHEME 1



It is seen that the effect of the equatorial CO ligands, as well as that of the oxygen atoms in π-$C_3H_5PdC_5H_7O_2$, is mainly transferred to the terminal carbon atoms of the π-allyl ligand.

The electron-donor effect of the π-$C_3H_4Co(CO)_2PPh_3$ substituent is primarily determined by the strong σ-donor effect of the PPh_3 ligand. Thus, replacement of the CO ligand in $(CO)_3CrC_6H_5COOH$ by PPh_3 is known [36] to reduce considerably the strength of the acid ($\Delta P_{k_a} = 1.38$), so that the coordinated acid becomes weaker than the uncoordinated one.

In the formally tetrahedral complex π-$C_3H_5Co(CO)_2PPh_3$ the effect of the $Co(CO)_2PPh_3$ grouping is transferred to all the three atoms of the π-allyl ligand, most of all (in accordance with the quantum-chemical data) to the terminal carbon atoms, owing to which the electron density in the allyl group levels off, and all the three carbon atoms are characterized by approximately the same π,σ-donor properties.

Therefore, we can conclude from the results obtained that the role of the σ-component in the general allyl—metal bond greatly decreases on going from the π-allyl compounds of palladium and manganese to the π-allyl complexes of cobalt with the PPh_3 ligand. We assume that while the π-allyl-derivatives of palladium are characterized by reactions of nucleophilic addition to the coordinated ligand, such reactions are probably rather uncharacteristic of the cobalt compounds investigated; moreover, the π-allyl ligand will probably be the site of attack of electrophilic reagents.

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