Anions of Transition Metals Carbonyls in Nucleophilic Vinyl Substitution: VII.* Carbonylates Reaction with 1-Chloro-2-(trifluoromethyl)-
and 1-Chloro-2-(perfluoro-tert-butyl)hexafluorocyclopent-1-enes, and with Z and E Isomers of β-Chloro-α,β-difluorostyrenes.
Halophilic and/or Nucleophilic Reaction mechanism**

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Abstract—Reactions were studied between 1-chloro-2-(trifluoromethyl)-hexafluorocyclopent-1-ene with anions \([\text{CpFe(CO)}_2\])\(^{8-}\), \([\text{Re(CO)}_5\] \(^{8-}\), \([\text{Mn(CO)}_5\] \(^{8-}\), \([\text{CpMo(CO)}_3\] \(^{8-}\), and \([\text{CpW(CO)}_3\] \(^{8-}\). The effect of proton donors on the composition of reaction products was established. The reactions with \([\text{Re(CO)}_5\] \(^{8-}\) and \([\text{Mn(CO)}_5\] \(^{8-}\) were shown to proceed quantitatively along nucleophilic route (\(\text{SN}_2\text{Vin}\)) resulting in \(\sigma\)-vinyl complexes of rhenium and manganese. The \([\text{CpMo(CO)}_3\] \(^{8-}\) and \([\text{CpW(CO)}_3\] \(^{8-}\) anions turned out to be \(10^4\) times less nucleophilic than \([\text{Mn(CO)}_5\] \(^{8-}\)). In this case the main course of the reaction is the metal–halogen exchange with concurrent nucleophilic substitution. In reaction of \([\text{CpMo(CO)}_3\] \(^{8-}\) and \([\text{CpW(CO)}_3\] \(^{8-}\) with 1-chloro-2-(trifluoromethyl)-hexafluorocyclopent-1-ene the \(\sigma\)-vinyl complexes arise along an unusual autocatalytic mechanism: the reaction of carbonyl occurs not with the initial substrate but with pentafluoromethylcyclopent-1-ene that forms from the substrate under the action of a fluoride ion. In an extremely fast reaction of the same substrate with \([\text{CpFe(CO)}_2\] the main process is carbonylate oxidation along unestablished mechanism. The reaction between carbonylates and 1-chloro-2-(perfluoro-tert-butyl)hexafluorocyclopent-1-ene proceeds exclusively as metal–halogen exchange that with \([\text{Re(CO)}_5\] \(^{8-}\) furnishes anionic acyl complex cis\([\text{C}_9\text{F}_{15}\text{C(O)}\text{Re(CO)}_4\text{Cl}\])\(^{8-}\). The reaction of \(Z\) and \(E\) isomers of \(\beta\)-chloro-\(\alpha\),\(\beta\)-difluorostyrenes with \([\text{CpFe(CO)}_2\] \(^{8-}\) in the presence of proton donors confirmed the previously assumed (\(\text{SN}_2\text{Vin}\)) mechanism of nucleophilic substitution and also the intermediate formation of alkenyl carbanions in the parallel redox process.

Nucleophilic vinyl substitution effected by metal carbonyls anions *** is known since a fairly long time, and one of the procedures for preparation of \(\sigma\)-alkenyl metal complexes is based thereon [2].

At the same time the real nature of alkenyl halides reactions with carbonylates and their mechanism are still poorly understood. In the most cases the nucleophilic vinyl substitution is only one among many competing directions of the reaction. In our investigations on reactions between carbonylates and perfluoro-
Scheme 1.

\[ \text{BH} = \text{PhCH(Et)CN}, \ t-\text{BuOH}. \]

tert-butanol, the so-called “anion traps,” was the main proof of the reaction mechanism (Scheme 1).

1-Chloro-2-(trifluoromethyl)-hexafluorocyclopent-1-ene (I-Cl) is an agent of high electrophilicity and reacts with the most carbonylates, including also weakly nucleophilic \([\text{Mn(CO)}_5]^-\), \([\text{CpW(CO)}_3]^-\), and \([\text{CpMo(CO)}_3]^-\).

Nucleophilic vinyl substitution by anions of rhenium and manganese pentacarbonyl in alkene (I-Cl) results in quantitative formation of σ-vinyl derivatives (I-Mn, Re, Scheme 2) with no side reactions. The direct monitoring of the reaction by \(^{19}\text{F}\) NMR spectroscopy demonstrated total absence even of traces of the other intermediate or final products beside σ-vinyl complexes (I-Mn, Re). It virtually excludes halophilic reaction mechanism that would have afforded halo(acyl)metalates of rhenium and manganese \([\text{RF(CO)}_2\text{M(CO)}_4\text{Cl}]^-\) (M=Mn, Re) as a result of reaction between alkenyl carbanion with \([\text{M(CO)}_5\text{Cl}]-\).