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Coordination chemistry and oxidative addition of trifluorovinylferrocene derivatives

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ABSTRACT

Complexes using trifluorovinylferrocene and 1,1′-bis(trifluorovinyl)ferrocene as ligands can be obtained by the reaction with a series of fragments of transition metal complexes. Formation of $[Pt(\eta^2\text{-trifluorovinylferrocene})(PPh_3)_2]$ (**1**), $[\{Pt(PPh_3)_2\}_2(\eta^2\text{-1,1′-bis(trifluorovinyl)ferrocene})]$ (**2**) and $[Pt(\eta^2\text{-1,1′-bis(trifluorovinyl)ferrocene})(PPh_3)_2]$ (**3**) were achieved by ligand substitution in $[Pt(\eta^2\text{-}CH_2=CH_2)(PPh_3)_2]$. Treatment of eneacarbonyldiiron with trifluorovinylferrocene provided $[Fe(CO)_4(\eta^2\text{-trifluorovinylferrocene})]$ (**4**). Photolytically activated reactions of $[MnCp(CO)_3]$ and $[MnCp'(CO)_3]$ ($Cp' = C_5H_4CH_3$) afforded $[MnCp(CO)_2(\eta^2\text{-trifluorovinylferrocene})]$ (**5a**) and $[MnCp'(CO)_2(\eta^2\text{-trifluorovinylferrocene})]$ (**5b**) respectively. $[Ni(\eta^2\text{-trifluorovinylferrocene})(Cy_2P(CH_2)_2PCy_2)]$ (**6**) could be obtained by reaction with $[Ni(COD)_2]$ and $Cy_2P(CH_2)_2PCy_2$. Furthermore the C—F bond activation by oxidative addition in the presence of lithium iodide yielding two isomers of $[PtI\{\eta^1\text{-difluorovinylferrocene}\}(PPh_3)_2]$ (**7a**/**7b**) is presented. Molecular structures of **1**, **4** and **7a** were elucidated using X-ray single crystal diffraction. The spectroscopic and structural data of these complexes prove the powerful π acceptor abilities of these ligands.

1. Introduction

Although fluorinated alkenes are important monomers for industrial synthesized polymers like PTFE, PCTFE or PVDF [1–3], their transition metal chemistry is rarely investigated compared to their hydrocarbon analogues. The polymerization of organic fluoropolymers via a free-radical mechanism without the use of coordination catalysts [4–7] might be a reason for the less developed organometallic chemistry of fluoroalkenes. Nevertheless the first examples were already published in the 1960s [8–11]. These studies are focused on simple non functionalized monoalkenes like tetrafluoroethene (TFE) [12–29]. However, there exist remarkably detailed studies on special fluorinated alkenes like for example octafluorocyclooctatetraene [30]. Transition metal complexes with perfluorinated and partially fluorinated allene derivatives or fluorinated butadiene and its substituted analogues are rarely studied [31–36]. However, the increasing interest in activation of the unreactive C—F bond refocused the fluoroorganometallic chemistry [37–46].

Recently, we reported on the introduction of trifluorovinyl groups to ferrocene by a Negishi type coupling reaction using iodo precursors and trifluorovinylzinc chloride [47]. Further, we reported on the rich chemistry of trifluorovinylferrocene derivatives, especially on the derivatization at the trifluorovinyl unit by nucleophilic substitution and [2+2]-cycloaddition reactions which could be used for polymerization [47–49]. A nucleophilic substitution with organolithium compounds always takes place in β-position of the C_2F_3 unit.

Herein we report on the coordination chemistry of trifluorovinylferrocene and 1,1′-bis(trifluorovinyl)ferrocene in order to change its reactivity. Activation of the C—F bond in α–position should allow to introduce substituents differently.

2. Results and discussions

2.1. Syntheses

The synthesis of the η^2-trifluorovinylferrocene complexes is outlined in Schemes 1 and 2. Substitution of the labile ethene ligand in $[Pt(\eta^2\text{-}CH_2=CH_2)(PPh_3)_2]$ occurs easily at ambient temperature, yielding complex **1** as a yellow crystalline solid. Trifluorovinylferrocene has C_1 symmetry and there exist two enantiomers which however are easily interconverted by rotation around the C—C bond between the cyclopentadienyl ring and the trifluorovinyl group. Due to the coordination of the bis

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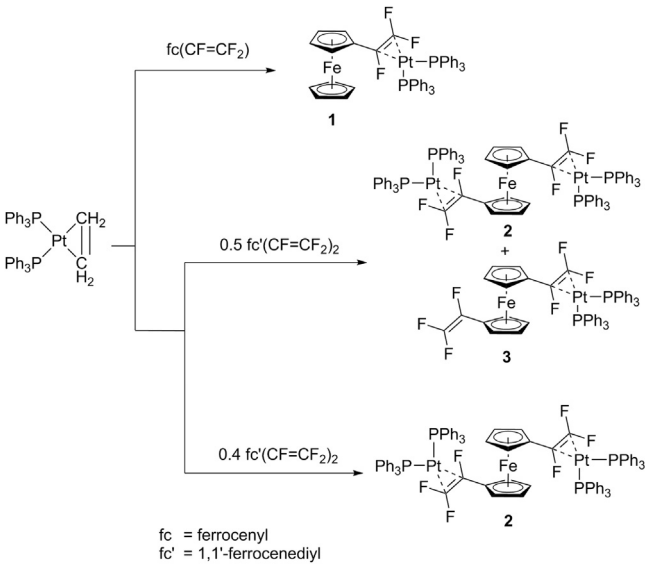


Scheme 1. Reactions of [Pt(η^2-$CH_2=CH_2$)(PPh_3)$_2$] with trifluorovinylferrocene and 1,1′-bis(trifluorovinyl)ferrocene.

(triphenylphenylphospine)platinum fragment the enantiomers can not be interconverted by rotation around a carbon single bond. Nevertheless only a racemic mixture is obtained. Compound **1** rapidly decomposes in the presence of chlorinated hydrocarbons by forming trifluorovinylferrocene and [$PtCl_2(PPh_3)_2$]. **1** resembles complexes of various fluoro alkenes with the bis(triphenylphosphine)platinum moiety which have been prepared by Green et al. [50].

Treatment: of 1,1′-bis(trifluorovinyl)ferrocene with [Pt(η^2-$CH_2=CH_2$)(PPh_3)$_2$] provided a mixture of the dicoordinated **2** and the monocoordinated complex **3**. Both compounds do not show remarkable differences in their polarity and solubility, therefore column chromatographic separation and fractional crystallization are inadequate for purification and failed. Furthermore, **2** and **3** decompose in contact with silica gel and the formation of fluorinated ferrocenophanes can be observed, which are also formed in the case of 1,1′-bis(trifluorovinyl)ferrocene under redox conditions (Scheme 2) [47].

The formation of analytically pure **2** was accomplished by treating 1,1′-bis(trifluorovinyl)ferrocene with an excess of [Pt(η^2-$CH_2=CH_2$)(PPh_3)$_2$] but **3** could only be obtained in mixture with compound **2** even if a deficit of [Pt(η^2-$CH_2=CH_2$)(PPh_3)$_2$] is used. The reaction proceeded almost quantitatively, and complex **2** was isolated as an orange solid in 92% yield. Coordination of a second [$Pt(PPh_3)_2$] fragment results in a mixture of the C_2-symmetric (racemic) and the C_s-symmetric diastereomere, respectively (Fig. 1), as the relative position of the CF and CF_2 groups of the trifluorovinyl substituents can be distinguished due to

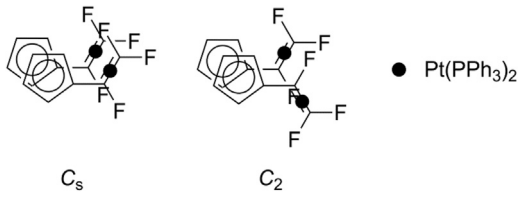


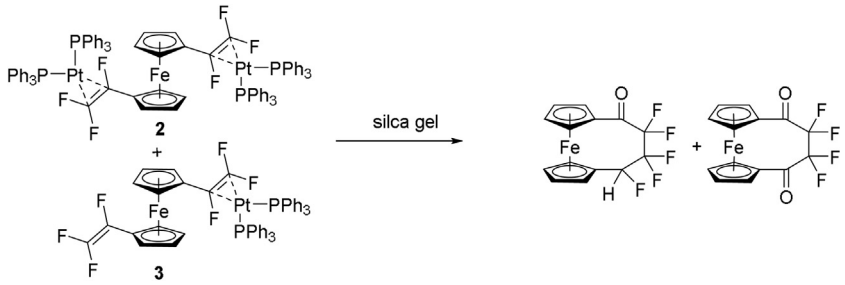
Fig. 1. C_2-symmetric and the C_s-symmetric diastereomers of [{$Pt(PPh_3)_2$}$_2$(η^2-1,1′-bis(trifluorovinyl)-ferrocene)].

coordination of a metal center on one side of the substituents plane (Fig. 1). The two diastereomers (**2a** and **2b**) were formed in a ratio of 1:1.

Eneacarbonyldiiron can be used as a source for a tetracarbonyliron fragment resulting in the complex **4** by forming pentacarbonyliron as a side product, which can be easily removed in vacuum (Scheme 3). Compound **4** was obtained in 72% yield as a red crystalline solid, which decomposes in contact with air after a few days. Reaction of pentacarbonyliron and trifluorovinylferrocene gave no product at room temperature, reaction at higher temperatures leads to dimerization of the starting material by [2+2]-cycloaddition forming the known cyclobutane derivatives [51]. In contrast to the reaction of dodecacarbonyltriiron with tetrafluorethene which results in tetracarbonyl(octafluoro-butan-1,4-diyl)iron [52] no similar C—C coupling could be observed.

In accordance to literature methods [53] the manganese half sandwich complexes **5a** and **5b** were synthesized by reactions of photolytically activated [$MnCp(CO)_3$] or [$MnCp'(CO)_3$] ($Cp' = C_5H_4Me$) with trifluorovinylferrocene in *n*-hexane (Scheme 2). The compounds were obtained as red solids after crystallization from *n*-hexane in 37% (**5a**) or 68% (**5b**) yield, respectively. Usage of the solvent stabilized complexes [$MnCp(CO)_2$(thf)] [54,55] for the reaction with trifluorovinylferrocene do not provide isolable quantities of **5a** and **5b**. Interestingly, treatment of [$MnCp^*(CO)_3$] ($Cp^* = C_5Me_5$) with trifluorovinylferrocene gave no products at all, probably due to the higher bulkiness of the Cp*-ligand.

Complexes of zero valent nickel with unsaturated fluorocarbons are rarely found in literature. First examples of TFE nickel complexes with phosphine ligands were described by Stone et al. starting from [$Ni(COD)_2$] or [Ni(CDT)] and subsequent ligand exchange [56,57]. Reaction of [$Ni(COD)_2$] and PPh_3 in the presence of TFE gave exclusively the octafluoronickelacyclopentane complex as a result of the reaction with a second TFE molecule by oxidative cyclization [58]. Also, the synthesis of the corresponding nickel complex [$Ni(PPh_3)_2$(η^2-trifluorovinylferrocene)] starting from [$Ni(COD)_2$] and triphenylphosphine failed and only precipitation of Ni black was observed. The choice of the ligand seems to be important for the stability of the complex. Usage of the better σ-donor ligand PCy_3 instead of PPh_3 in the presence of [$Ni(COD)_2$] and TFE leads to the formation of η^2-TFE nickel complex [59] but no reaction with trifluorovinylferrocene could be observed.



Scheme 2. Formation of ferrocenophanes by contact with silca gel of **2** and **3**.