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PII: S0040-4020(16)30525-7

DOI: 10.1016/j.tet.2016.06.012

Reference: TET 27826

To appear in: *Tetrahedron*

Received Date: 24 April 2016

Revised Date: 23 May 2016

Accepted Date: 3 June 2016

Please cite this article as: Oparina LA, Artem'ev AV, Vysotskaya OV, Tarasova OA, Shagun VA, Bagryanskaya IY, Trofimov BA, Unexpected acid-catalyzed ferrocenylmethylation of diverse nucleophiles with vinyloxymethylferrocene, *Tetrahedron* (2016), doi: 10.1016/j.tet.2016.06.012.

Graphical Abstract

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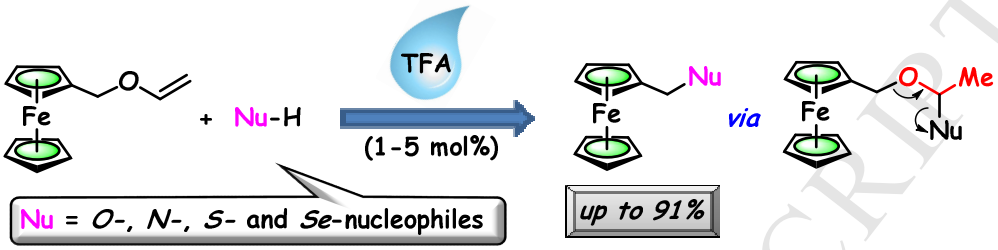

Tetrahedron
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Unexpected acid-catalyzed ferrocenylmethylation of diverse nucleophiles with vinyloxymethylferrocene

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Electrophilic Addition
Enol Ethers
Ferrocene
Regioselectivity
Nucleophiles

ABSTRACT

A new efficient approach for the ferrocenylmethylation of various alcohols, OH-, SH- and SeH-acids (carboxylic, thio- and selenophosphinic) as well as 1*H*-triazoles is elaborated based on the acid-catalyzed reaction with available vinyloxymethylferrocene. The reaction readily occurs under mild conditions to afford product of *O*-, *N*-, *S*- and *Se*-ferrocenylmethylation of the corresponding nucleophiles in good to high yields.

1. Introduction

Ferrocene derivatives have attracted ever-growing attention over the last few decades because of their numerous valuable characteristics.[1] A plethora of ferrocenes nowadays finds a wide application in medicine,[2] materials science,[3] catalysis,[3,4] organometallic[5] and polymer chemistry,[6] molecular recognition[7] and organic synthesis.[1,3,4]

Among a variety of ferrocene derivatives, functionalized molecules bearing the methylferrocene moiety are of special interest owing to their useful properties. These compounds have been shown to serve as potential drugs (anticancer,[8] antitumor,[9] antimalarial,[10] antiplasmodial,[11] antimycobacterial,[12] antimicrobial,[13] anticandidal[14] and antiproliferative[15] agents), efficient ligands for catalysis,[3,4] monomers for functional polymers,[16] ionic liquids[17] and molecular sensors.[18] Today, one of the most efficient and straightforward approaches to access methylferrocene derivatives is the reaction of various nucleophiles with ferrocenylmethylating reagents,[19] among which $[FcCH_2NMe_3]I$, $FcCH_2NMe_2$ and $FcCH_2OH$ are the most available. Although the methods for ferrocenylmethylation with the first two reagents are quite well developed, they have some principal limitations.[19] In this regard, hydroxymethylferrocene is a more versatile reagent, however for its activation, stoichiometric amounts of Brønsted acids (HSO_3F, HBr, HBF_4, $HClO_4$, CH_3CO_2H, etc.)[19,20] are usually required (with a few exceptions[21]), that impose some restrictions on the substrate scope. In recent years, much attention has been paid to nucleophilic substitution of the OH group in hydroxymethyl ferrocene using various metal-based catalysts. For instance, cerium ammonium nitrate was exploited for ferrocenylmethylation of diverse *N*-, *O*- and *S*-nucleophiles containing an active hydrogen atom with $FcCH_2OH$.[22] Later, $Yb(OTf)_3$[23] and $Al(OTf)_3$[24] were used for this purpose. The complex $[RuCl(CO)(PPh_3)(PNS\text{-}Me)]$ was found to be an active catalyst for ferrocenylmethylation of amines.[25] Then iron complex [Fp][OTf] ($Fp^+ = [Fe(CO)_2(Cp)]^+$) was employed for coupling of *C*-, *N*-, *P*- and *S*-nucleophiles with $FcCH_2OH$.[26] More recently, *N*-ferrocenylmethylation of sulfonamides with this alcohol catalyzed by $\{Cp^*Ir\text{-}[6,6'\text{-}OH)_2bpy](H_2O)\}[OTf]_2$[27] and $[Cp^*IrCl_2]_2$[28] was accomplished. It is relevant to note, however, that the above metal catalysts are expensive and/or moisture sensitive therefore requiring dry reaction conditions and special apparatus. In this context, development of new metal-catalyst-free ferrocenylmethylation methods is a challenging task in organic chemistry.

As a contribution to this field, herein we report on the unexpected ferrocenylmethylation of diverse *O*-, *N*-, *S*- and *Se*-nucleophiles (alcohols, phenol, 1,2,4-triazole, 1,2,3-benzotriazole, methacrylic, dithio- and diselenophosphinic acids) in an acid-catalyzed (CF_3CO_2H as catalyst) reaction with available[29] vinyloxymethylferrocene. This novel reaction was

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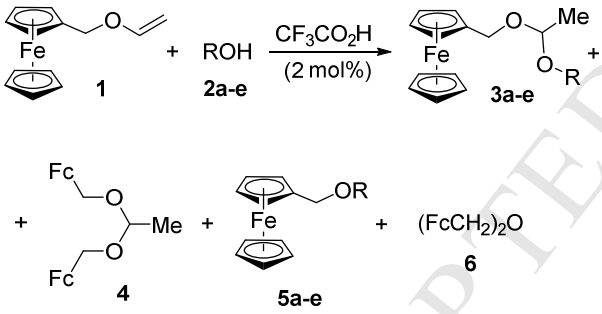
accidently found by us during the study of acid-catalized addition of NuH species to vinyloxymethylferrocene that, according to enol ether chemistry,[30] should chemo- and regioselectively allow the corresponding non-symmetric acetals. Essentially, we describe a first example of formation of such products as R–Nu in the reaction between vinyl ethers R–O–CH=CH_2 (exemplified by vinyloxymethylferrocene) and various nucleophiles (NuH).

2. Results and Discussion

Reaction with alcohols and phenol

Our experiments have shown that vinyloxymethylferrocene (**1**) in the presence of catalytic amounts of CF_3CO_2H (2 mol%) easily reacts with diverse alcohols **2a-e**. The reaction conditions, structures and ratios of isolated products are summarized in Table 1. As seen from these data, the reaction of **1** with methanol (**2a**) selectively occurs at ambient temperature to afford the Markovnikov adduct, isolated in 86% yield (entry 1). Under similar conditions, alcohols with donating and bulkier substituents, e.g. *s*-BuOH (**2b**) and *t*-BuOH (**2c**), add to **1** slower (4 and 6 h, correspondingly *vs.* 2 h for MeOH), giving adducts **3b**,**c** in 67 и 72% isolated yields (entries 2, 3). Also, in both cases, 1,1-bis(ferrocenylmethoxy)ethane (**4**) as by-product was isolated in 17 and 19% yield (entries 2, 3). Note that under the harsher conditions (45 °C), the reaction with *t*-BuOH delivers bis(ferrocenylmethyl) ether (**6**) as almost the only product (75% yield), while the expected adduct **3c** is formed just in traces (entry 4).

Table 1 CF_3CO_2H-catalyzed reaction of vinyloxymethylferrocene with alcohols[a]

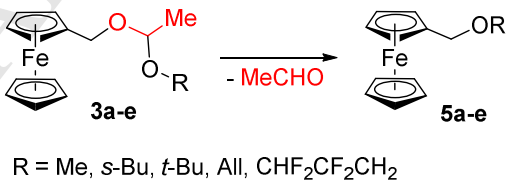


Entry	R	T, °C	Time, h	Products (yield, %)[b]			
				3	**4**	**5**	**6**
1	Me (**2a**)	rt	2	**3a** (86)	none	**5a** (none)	traces
2	*s*-Bu (**2b**)	rt	4	**3b** (67)	17	**5b** (none)	traces
3	*t*-Bu (**2c**)	rt	6	**3c** (72)	19	**5c** (none)	traces
4	*t*-Bu (**2c**)	45	3	**3c** (traces)	traces	**5c** (none)	75
5	All (**2d**)	rt	1.5	**3d** (61)	15	**5d** (trace)	traces
6	All (**2d**)	45	5	**3d** (traces)	none	**5d** (55)	32
7	All (**2d**)	rt	72	**3d** (traces)	traces	**5d** (58)	31
8	$CHF_2CF_2CH_2$ (**2e**)	rt	1.5	**3e** (traces)	traces	**5e** (38)	39

[a]Reaction conditions: vinyl ether **1** (1 mmol), alcohol **2a-e** (1 mmol), CF_3CO_2H (2 mol%, as 0.025 M solution in DME), stirring.
[b]Isolated yields (after chromatographic purification).

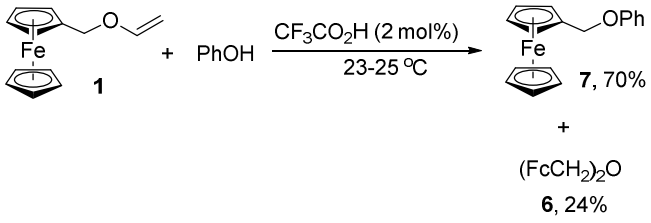
Unlike aliphatic alcohols, allyl alcohol (**2d**) and 2,2,3,3-tetrafluoropropanol (**2e**) add to vinyl ether **1** more easily, however the resulting adducts **3d**,**e** are less stable under the reaction conditions and tend to extrude acetaldehyde furnishing the products of *O*-ferrocenylmethylation of the alcohols, *viz*. **5d,e**. Thus, allyl alcohol (**2d**) at room temperature quantitatively adds to vinyl ether **1** in 1.5 h (*vs.* 2 h for MeOH) to furnish adduct **3d** and side acetal **4** in 61 and 15% yields (entry 5). ^{1}H NMR spectroscopic analysis of the reaction mixture shows signals (broad singlets at 2.10 and 9.75 ppm) relative to the protons of acetaldehyde. Further study has shown that conducting the reaction at 45 °C leads to quantitative conversion of the intermediate Markovnikov adduct **3d** into allyloxymethylferrocene (**5d**), the yield of which being 55% (entry 6). A similar result was obtained when the reaction was performed at ambient temperature for 3 days. Noteworthy, 2,2,3,3-tetrafluoropropanol (**2e**) interacts with vinyl ether **1** under mild conditions (r.t., 1.5 h) giving directly ether **5e** along with diferrocenylmethyl ether **6** (entry 8), the expected adduct **3e** being formed only in trace amounts (by ^{1}H NMR spectroscopy).

We believe that the products of *O*-ferrocenylmethylation of alcohols (**5d**,**e**) and other nucleophiles (*vide infra*) are formed due to the elimination of acetaldehyde from the primary Markovnikov adducts according to Scheme 1. The enhanced stability of the initial Markovnikov adducts in the cases of MeOH, *s*-BuOH and *t*-BuOH follows from DFT computation of the fragmentation of **3a** (model compound) to $FcCH_2OMe$ and acetaldehyde (*vide infra*).



Scheme 1. The formation of *O*-ferrocenylmethylation products with alcohols.

In the reaction of **1** with phenol, the corresponding Markovnikov adduct is so unstable that it cannot be detected by NMR spectroscopy even when the reaction occurs at room temperature. In this case, the fast elimination of acetaldehyde from the initial adduct leads to the formation of phenyloxymethylferrocene (**7**) in 70% isolated yield (Scheme 2). As in the above cases, bis(ferrocenylmethyl) ether (**6**) was also isolated in 24% yield.

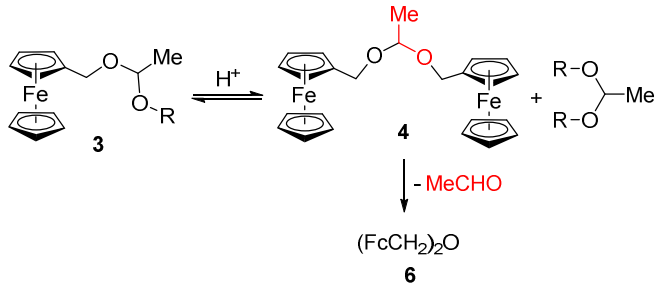


Scheme 2. CF_3CO_2H-catalyzed reaction of vinyloxymethylferrocene with phenol.

All of the above products were purified by column chromatography on basic alumina. It should be mentioned that the isolation of acetals **3a-d** and **4** was accompanied by their partial hydrolysis with release of ferrocenylmethanol. Compounds **3a-d** are orange oils, soluble in common organic solvents. In their ^{1}H NMR spectra, each methyne proton, C*H*Me, resonates as a quartet at 4.71-4.95 ppm, whereas Me protons

appear as doublets at 1.29-1.31 ppm. The FT-IR spectra of **3a-d** contain four or five C–O acetal bands (1040-1155 cm^{-1}) along with bands of the ferrocene moiety (3090, 1450, 1100, 1010, 820, 480 cm^{-1}).

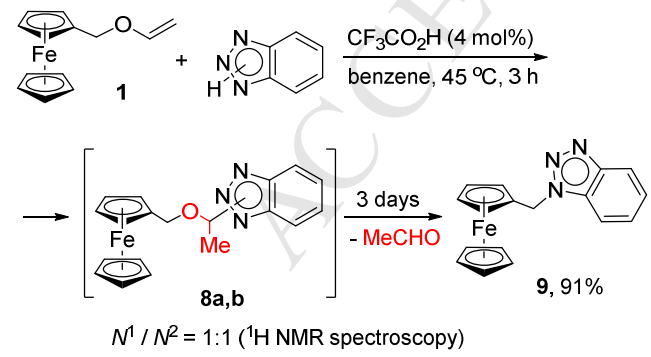
The formation of bis(ferrocenylmethyl) ether (**6**) in the reactions studied (Table 1, Scheme 2) most likely starts with symmetrization of acetal **3** by the action of acid catalyst (CF_3CO_2H) followed by elimination of acetaldehyde from the resulting acetal **4** (Scheme 3).



Scheme 3. Tentative pathway for the formation of ether **6**.

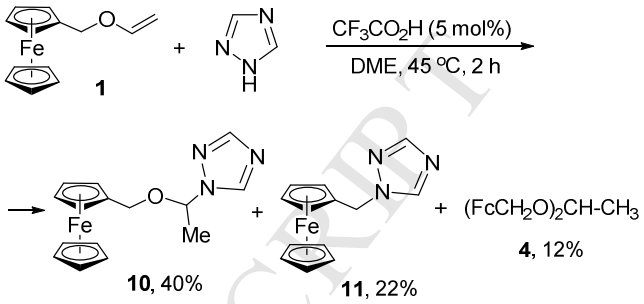
Reactions with 1H-triazoles

Taking into account the data of the easy non-catalyzed addition of benzotriazole to ethyl vinyl ether under reflux in CCl_4 (1.5 h),[31] we have carried out the reaction of vinyloxymethylferrocene (**1**) with benzotriazole under similar conditions. However, no expected adduct was detected (not even in traces) in the reaction mixture, although the reagents were refluxed for as long as 3 h. Eventually, we have found that in the presence of 4 mol% CF_3CO_2H, vinyl ether **1** adds benzotriazole at ambient temperature (3 h) to afford a mixture of N^1- and N^2-isomeric Markovnikov adducts **8a**,**b** in the ratio of about 2:1 (^{1}H NMR spectroscopy) along with 1-ferrocenylmethyl-1*H*-1,2,3-benzotriazole (**9**) (10% content in the reaction mixture). The adducts **8a**,**b** were not isolated in pure form due to their partial decomposition on chromatography (Al_2O_3) to **9** and acetaldehyde. Upon heating (45 °C, benzene, 3 h), the reaction resulted in Markovnikov adducts **8a**,**b** (in about equimolar amounts) and compound **9** (Scheme 4). This mixture, upon storage for several days, was quantitatively (^{1}H NMR spectroscopy) converted to benzotriazole **9**, the isolated yield being 91%.



Scheme 4. CF_3CO_2H-catalyzed reaction of vinyl ether **1** with 1,2,3-benzotriazole.

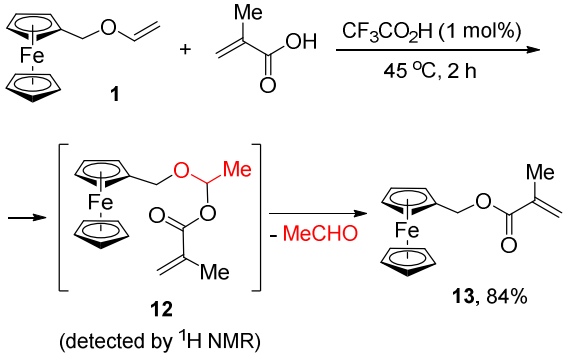
Unlike benzotriazole, 1,2,4-triazole regioselectively reacts with vinyl ether **1** (5 mol% CF_3CO_2H, 40-45 °C, 2-3 h) to give the Markovnikov adduct **10** and 1-ferrocenylmethyl-1*H*-1,2,4-triazole (**11**) along with a minor amount of **4** (Scheme 5). The solvent nature does not significantly affect the reaction outcome: approximately the same ratio (2.5:1) of **10** and **11** was obtained in benzene, dichloromethane and DME. In contrast to all the previous products, in this case the initial Markovnikov adduct appeared to be stable. The product ratio remained unchanged upon storing the reaction mixture for about 1 month at room temperature. During the chromatographic isolation of these products on basic alumina, compounds **10**, **11** and **4** as well as ferrocenylmethanol were isolated in 40, 22, 12 and 10% yield, correspondingly. The latter being resulted from the hydrolysis of the adducts **4**, **10** by trace water present in alumina.



Scheme 5. CF_3CO_2H-catalyzed reaction of vinyl ether **1** with 1,2,4-triazole.

Reaction with methacrylic acid

The addition of carboxylic acids to vinyloxymethylferrocene (**1**) was studied on an example of the reaction with methacrylic acid in the presence of catalytic amounts of CF_3CO_2H (1 mol%). As the ^{1}H NMR spectroscopic monitoring has shown, the reaction occurs *via* the formation of an unstable Markovnikov adduct **12**, which slowly eliminates acetaldehyde (Scheme 6) to give ester **13**. At ambient temperature this process is complete within 10-15 h (^{1}H NMR spectroscopic data), while upon heating (45 °C), the reaction takes for 2 h to afford only ester **13** and acetaldehyde (detected by ^{1}H NMR spectroscopy). The compound **13** was isolated in 84% yield and its structure was proved by ^{1}H and ^{13}C NMR spectroscopy.

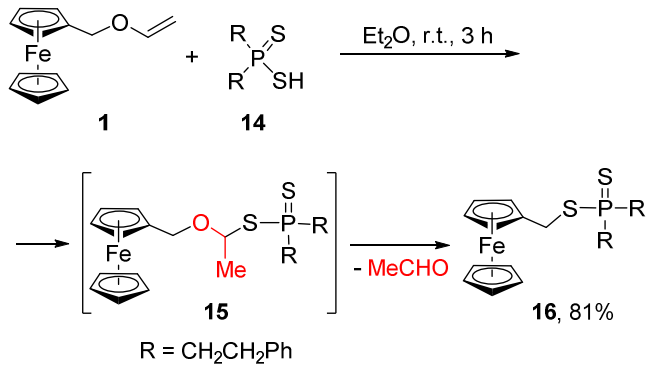


Scheme 6. CF_3CO_2H-catalyzed reaction of vinyl ether **1** with methacrylic acid.

Reaction with S-H and Se-H acids

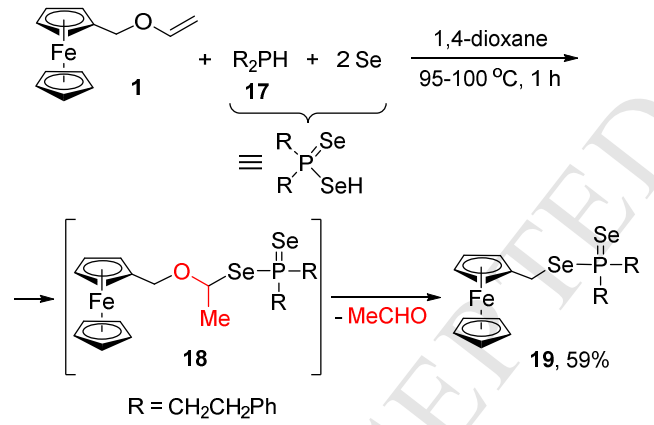
We have observed that the dithiophosphinic acid **14** under mild conditions (r.t., 3 h, Et_2O as solvent) chemo- and regioselectively interacts with vinyloxymethylferrocene (**1**) to give only the Markovnikov adduct **15**, the structure of which was established by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. However, the adduct **15**, owing to its instability, readily eliminates acetaldehyde to form dithiophosphinate **16** (Scheme 7). Furthermore, as a parallel reaction, this process takes place along with the formation of primary Markovnikov adduct **15** (^{31}P NMR spectroscopic data). The complete conversion of the latter to

dithiophosphinate **15** was achieved by recrystallization of the crude reaction product from hexane (upon boiling). Thus, compound **16** was isolated in 81% yield as yellow crystals, the structure of which was determined by X-ray diffractometry.



Scheme 7. Reaction of vinyl ether **1** with dithiophosphinic acid **14**.

Likewise, the diselenophosphinic acid, generated *in situ* from secondary phosphine **17** and elemental selenium (1:2 molar ratio, 95 °C), also without specially added catalyst reacts with vinyloxymethylferrocene (Scheme 8). The ^{31}P NMR spectrum of the reaction mixture shows two major peaks, 50.1 and 48.3 ppm in a ratio of 9:1, assigned to Markovnikov adduct **18** and *Se*-ester **19**, respectively. Upon the storage at room temperature, the product ratio changes for reciprocal one (1:9). The *Se*-ferrocenylmethyl diselenophosphinate **19** was isolated in 59% yield and its structure was also determined by X-ray analysis.



Scheme 8. Reaction of vinyl ether **1** with diselenophosphinic acid.

The structures of esters **16** and **19** are shown in Figures 1 and 2. Despite their similar structures, these compounds crystallized in P-1 and P2$_1$/c space groups, correspondingly. Within both molecules, the ferrocene unit has a nearly eclipsed conformation with the bond lengths and angles typical for monosubstituted ferrocenes. The phosphorus atoms, as expected, exhibit a distorted tetrahedral geometry. The lengths of the P–S [2.0937(5) Å] and P=S [1.9508(5) Å] bonds in **16** as well as the P–Se [2.2415(19) Å] and P=Se [2.0816(18) Å] bonds in **19** are consistent with literature values.[32, 33]

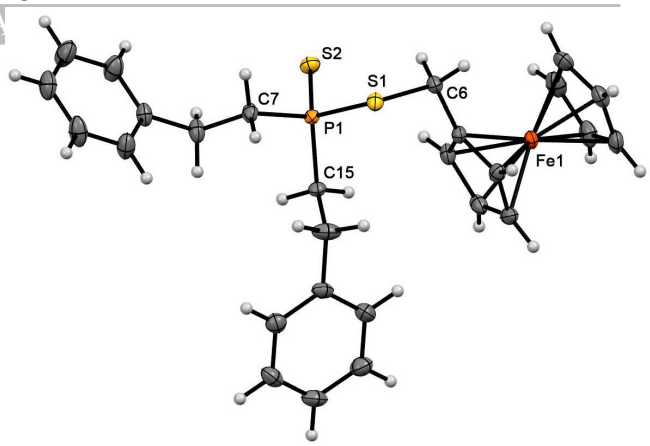


Fig. 1. Molecular structure of **16** (40% thermal ellipsoid). Selected bond distances (Å) and angles (°): Cg(1)···Fe(1) 1.638, Cg(2)···Fe(1)1.648, S(1)–P(1) 2.0937(5), S(2)–P(1) 1.9508(5), S(1)–C(6) 1.8467(15), P(1)–C(7) 1.8174(14), P(1)–C(15) 1.8219(13), S(2)–P(1)–S(1) 114.99(2), C(6)–S(1)–P(1) 101.26(5), Cg(1)···Fe(1)···Cg(2) 178.95.

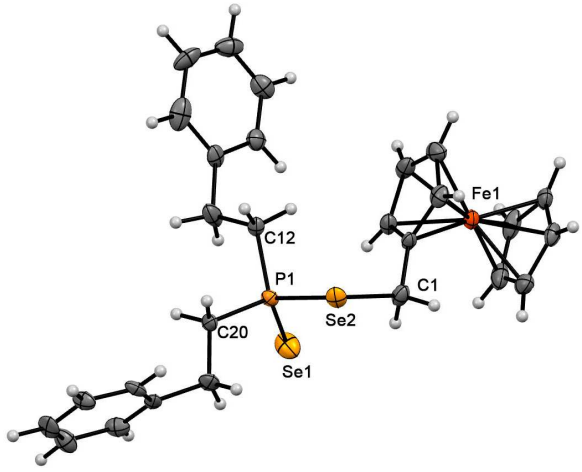


Fig. 2. Molecular structure of **19** (30% thermal ellipsoid). Selected bond distances (Å) and angles (°): Cg(1)···Fe(1) 1.640, Cg(2)···Fe(1) 1.652, Se(1)–P(1) 2.0816(18), Se(2)–P(1) 2.2415(19), Se(2)–C(1) 1.997(6), P(1)–C(12) 1.800(7), P(1)–C(20) 1.826(6), Se(1)–P(1)–Se(2) 114.31(8), C(1)–Se(2)–P(1) 98.0(2), Cg(1)···Fe(1)···Cg(2) 179.26.

Theoretical study

With the aim to interpret the different chemoselectivity in the reaction of vinyloxymethylferrocene (**1**) with the above nucleophiles (formation of ferrocenylmethylation products *versus* stable Markovnikov adducts), we have carried out preliminary DFT [B3LYP/6-311+G(d,p), gas] computations for fragmentation of Markovnikov adducts, key reaction intermediates, to the corresponding ferrocenylmethylation products (FcCH$_2$Nu) and acetaldehyde. As model compounds, adducts with methanol **3a** and 1,2,4-triazole **10** having enhanced stability, as well as the unstable adduct with methacrylic acid **12** have been chosen.

The computations reveal that elimination of acetaldehyde from adduct **3a** occurs through high-energy transition state **TS1** leading to methoxymethylferrocene (**5a**). The corresponding free energy profile is shown in Figure 3. The activation barrier of this stage, being essentially an intramolecular 1,3-shift of the [FcCH$_2$] group to another oxygen atom, is 57.0 kcal/mol. Although taking into account that solvent effect should decrease this value, the barrier of such order is insuperable under common reaction

conditions. Similarly, extrusion of acetaldehyde from the adduct **10** leading to 1-ferrocenylmethyl-1*H*-1,2,4-triazole (**11**) is associated with overcoming a high activation barrier, 54.6 kcal/mol (**TS2**, **Figure S1**).

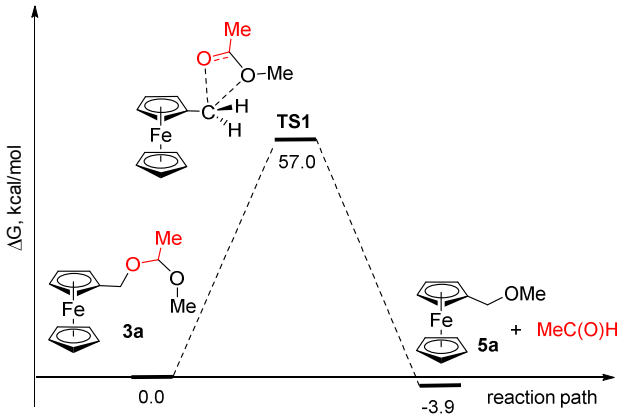
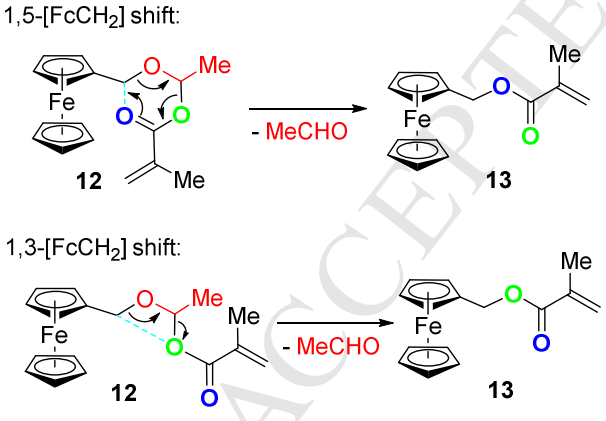


Fig. 3. Free energy profile for fragmentation of **3a** to **5a** and acetaldehyde.

The fragmentation of the Markovnikov adduct with methacrylic acid **12** to ester **13** and acetaldehyde may principally occur either through a 1,5-intramolecular shift of the [$FcCH_2$] group to carbonyl oxygen (C=O) or through a 1,3-shift of this group to another oxygen atom (Scheme 9). While the first pathway is less favorable (activation barrier being 37.9 kcal/mol, **Figure S2**), the second one is quite plausible (Figure 4). This is a thermodynamically preferable one-step process including transition state (**TS3**) with activation barrier of 32.9 kcal/mol. The further transformation of **TS3** leads to the weakly bonded complex of *O*-ferrocenylmethyl methacrylate (**13**) with acetaldehyde. The overall change in the Gibbs free energy of reaction being –12.6 kcal/mol.



Scheme 9. Two possible mechanisms for fragmentation of adduct **12**.

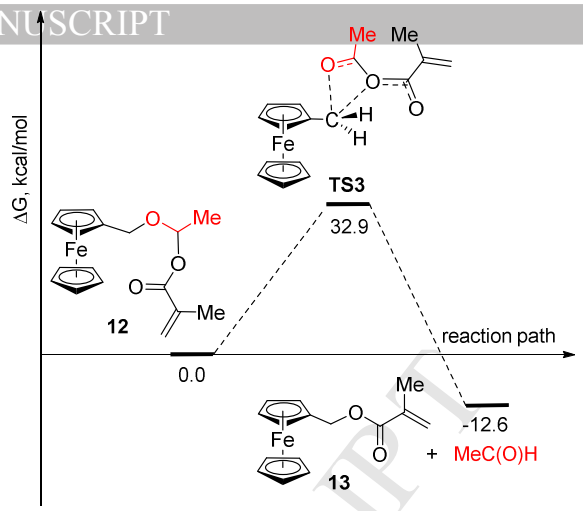


Fig. 4. Free energy profile for fragmentation of adduct **12** to **13** and acetaldehyde.

Thus, the significantly lower activation barrier of fragmentation of adduct **12** (32.9 kcal/mol) in comparison with that of adducts **3a** and **10** (57.0 and 54.6 kcal/mol), explains why the reaction of vinyloxymethylferrocene (**1**) with acids proceeds directly to ferrocenylmethylation products, whereas interaction of **1** with MeOH, *s*-BuOH, *t*-BuOH and 1,2,4-triazole gives stable Markovnikov adducts.

3. Conclusion

In summary, we have found and the elaborated ferrocenylmethylation of diverse *O*-, *N*-, *S*- and *Se*-nucleophiles (alcohols, carbonic acids, triazoles, thio- and selenophosphinic acids) based on the reaction with available vinyloxymethylferrocene. The latter under mild acid-catalyzed (1-5 mol% CF_3CO_2H as catalyst) conditions easily adds these nucleophiles to afford initial Markovnikov adducts, which then readily eliminate acetaldehyde to give the corresponding ferrocenylmethylation products in good to high yields. Exceptions are methanol, butyl alcohols as well as 1,2,4-triazole, which form stable Markovnikov adducts with vinyloxymethylferrocene. The study establishes for the first time a novel type of reactivity of vinyl ethers R–O–Vin, i.e., when the latter reacting with Nu–H species produced products of R–Nu type. Furthermore, the results obtained contribute to the basic chemistry of ferrocene providing a synthetically valuable approach to ferrocenylmethylation of various nucleophiles (including biologically important molecules).

4. Experimental section

4.1. General

^{1}H NMR spectra were recorded with Bruker DPX 400 and Bruker AV-400 spectrometers (400.13 MHz); chemical shifts are expressed with respect to residual protonated solvent (δ = 7.27 ppm for $CHCl_3$), which served as an internal standard. ^{13}C NMR spectra were recorded with a Bruker DPX 400 (100.62 MHz) instrument; chemical shifts are expressed with respect to the deuterated solvent (δ = 77.0 ppm for $CDCl_3$). The ^{31}P NMR spectra were recorded on a Bruker DPX 400 spectrometer (161.98 MHz, respectively) and referenced to H_3PO_4 (^{31}P NMR). Coupling constants (*J*) are reported in Hz. FT-IR Spectra were recorded on a Bruker Vertex 70 spectrometer. The C, H, N microanalyses were performed on a Flash EA 1112 elemental analyzer, while the P and Fe contents were determined by

combustion methods. Melting points (uncorrected) were determined on a Kofler micro hot stage.

Vinyloxymethylferrocene (**1**) was synthesized by KOH/DMSO-catalyzed vinylation of ferrocenylmethanol with acetylene according to reported procedure.[34] Alcohols **2a-e** were dried over 4.0 Å molecular sieves prior to use. Dithiophosphinic acid **14**[35] and secondary phosphine **17**[36] were prepared as described in the literature. All the solvents used were purified and dried by standard methods. Basic Al_2O_3 and *n*-hexane/Et_2O as eluent were used for column chromatography. All reactions were monitored by TLC on silica gel plates 60 F254 (50% *n*-hexane/Et_2O). Visualization was done with iodine vapor.

4.2. Crystallography

Single crystals of **16** and **19** were obtained by slow evaporation of their hexane solutions at ambient temperature. The data were collected on a Bruker Kappa Apex II CCD diffractometer using φ,ω-scans of narrow (0.5°) frames with MoK_α radiation (λ = 0.71073 Å) and a graphite monochromator. The structures were solved by direct methods and refined by full-matrix least-squares method against all F^2 in anisotropic approximation using the *SHELX-97* programs set.[37] The hydrogen atoms positions were calculated with the riding model. Absorption corrections were applied using the empirical multiscan method with the *SADABS* program.[38]

CCDC 994803 (**16**), 1450492 (**19**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

4.3. Synthesis

*4.3.1. General procedure for synthesis of [1-(alkoxy)ethoxy]methylferrocene **3a-d***

To a mixture of vinyloxymethylferrocene (**1**) (242 mg, 1 mmol) and alcohol **2a-d** (1 mmol), a solution of CF_3COOH [2% in 1,2-dimethoxyethane (DME), 0.1 mL, ~ 2 mol%] was added. The resulting mixture was stirred at ambient temperature for 1.5-6 h (Table 1). After complete conversion of starting vinyl ether **1** (TLC control), K_2CO_3 (14 mg, 0.1 mmol) and diethyl ether (2 mL) were added and the mixture was stirred for ~0.5 h. After removal of volatiles, the crude residue was separated by column chromatography (basic Al_2O_3, 1.5 × 10 cm): Markovnikov adduct **3a-d** was washed off first with hexane, and then acetal **4** and ferrocenylmethanol were washed off with hexane/diethyl ether (1:1) and diethyl ether, respectively.

*4.3.2. Synthesis of (2-propenyloxy)methylferrocene (**5d**)*

To a mixture of vinyloxymethylferrocene (242 mg, 1 mmol) and allyl alcohol (**2d**) (58 mg, 1 mmol), a solution of CF_3COOH (2% in DME, 0.1 mL, 2 mol%) was added. The resulting mixture was stirred for 5 h at 45 °C and then quenched with 1% aqueous solution $NaHCO_3$ (10 mL), and extracted with diethyl ether (5 × 5 mL). The extract was dried over Na_2SO_4. The residue after removing of the volatiles was passed through a chromatographic column (basic Al_2O_3, 1.5 × 10 cm): the first product **5d** was washed off with hexane, and then ferrocenylmethyl ether (**6**) was washed with hexane/diethyl ether, 3:1.

*4.3.3. Synthesis of (2,2,3,3-tetrafluoropropoxy)methylferrocene (**5e**)*

Following the typical procedure for **3a**, vinyloxymethylferrocene (242 mg, 1 mmol), 2,2,3,3-tetrafluoropropanol (**2e**) (132 mg, 1 mmol) and a catalytic amount of CF_3CO_2H (2 mol%) were stirred at ambient temperature for 1.5 h until the complete consumption of the starting vinyl ether **1**. Then, the reaction mixture was stirred at rt for additional 3 h. Further treatment was performed in the same way as described for compound **5d**.

*4.3.4. Synthesis of phenyloxymethylferrocene (**7**)*

Following the typical procedure for **5d**, vinyloxymethylferrocene (242 mg, 1 mmol), phenol (94 mg, 1 mmol) and a catalytic amount of CF_3CO_2H (2 mol%) were stirred at ambient temperature for 1.5 h until the complete consumption of the starting vinyl ether **1**. Then, the reaction mixture was stirred at rt for additional 3 h. Further treatment was performed as described for compound **5d**.

*4.3.5. Procedure for the preparation of 1-[1-(ferrocenylmethoxy)ethyl]-1H- and 2-[1-(ferrocenylmethoxy)ethyl]-2H-1,2,3-benzotriazole (**8a,b**)*

To a solution of vinyloxymethylferrocene (242 mg, 1 mmol) in DME (2 mL), 1,2,3-benzotriazole (119 mg, 1 mmol) and CF_3CO_2H (5 mg, 4 mol%) were added. The reaction mixture was stirred at ambient temperature for 3 h until the vinyl ether **1** had disappeared. The mixture was quenched with $NaHCO_3$ (1 % solution, 10 mL) and extracted with diethyl ether (4×5 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue (303 mg), a mixture of α-adducts **8a,b** and 1-ferrocenylmethyl-1*H*-1,2,3-benzotriazole (**9**) (molar ratio 9:1 by ^{1}H NMR spectroscopy), was purified by column chromatography on Al_2O_3 using hexane, then hexane/Et_2O (1:1, v/v) as the eluent to afford an inseparable mixture of **8a** and **8b** (68:32, purity ~95% by ^{1}H NMR spectroscopy).

*4.3.6. Procedure for the preparation of 1-ferrocenylmethyl-1H-1,2,3-benzotriazole (**9**)*

To a stirred solution of vinyloxymethylferrocene (**1**) (242 mg, 1 mmol) in benzene (2 mL), 1,2,3-benzotriazole (119 mg, 1 mmol) and CF_3CO_2H (5 mg, 4 mol%) were added. The reaction mixture was stirred at 45 °C for 3 h and then the solvent was removed under reduced pressure. The crude product, *ca*. equimolar mixture of products **8a,b** and **9** (by ^{1}H NMR spectroscopy), was allowed to stay 3 days until the complete consumption of the Markovnikov adducts **8a,b**. The mixture was quenched with $NaHCO_3$ (1 % solution, 10 mL) and extracted with diethyl ether (4×5 mL). The organic layer was dried over Na_2SO_4. Column chromatography (basic Al_2O_3, eluent hexane/Et_2O 1:1) of the crude residue after removal of the solvent gave **9**.

4.3.7. Reaction of vinyloxymethylferrocene with 1,2,4-triazole

A mixture of vinyloxymethylferrocene (242 mg, 1 mmol), 1,2,4-triazole (69 mg, 1 mmol) and CF_3CO_2H (6 mg, 5 mol%) in dry DME (2 mL) was stirred at 45 °C for 2 h. After removal of the volatiles, the residue was separated by column chromatography (Al_2O_3, 1.5×10 cm) using hexane/Et_2O (1:1, v/v), then Et_2O as the eluent to afford acetal **4** (27 mg, yield 12%), products **10** and **11**, and ferrocenylmethanol (21 mg, 10%).

*4.3.8. Reaction of vinyloxymethylferrocene with dithiophosphinic acid **14***

To a solution of vinyloxymethylferrocene (242 mg, 1 mmol) in diethyl ether (5 mL), acid **14** (306 mg, 1 mmol) was added and the solution was stirred at ambient temperature for 3 h. Then the reaction mixture was passed through a layer of Al_2O_3 (0.5 cm), the latter was additionally washed with diethyl ether (5 mL). The volatiles were removed in *vacuo* to give product, consisting of compound **15** with an admixture of **16** (molar ratio ≈ 7 : 1 by ^{31}P

NMR spectroscopy). The subsequent recrystallization of ester **15** (refluxing in hexane) gave compound **16** as yellow solid.

*4.3.9. Reaction of vinyloxymethylferrocene with diselenophosphinic acid (generated in situ from phosphine **17** and selenium)*

Bis(2-phenethyl)phosphine (**17**) (242 mg, 1 mmol) and powdered grey selenium (158 mg, 2.0 mmol) were added consecutively to a solution of **1** (242 mg, 1 mmol) in 1,4-dioxane (8 mL) at ambient temperature. The suspension was stirred at 95-100 °C until dissolution of the selenium powder (*ca.* 1 h) to give an orange transparent solution consisting of corresponding Markovnikov adduct **18** in an admixture with *Se*-ester **19** in the molar ratio of 9:1 (by ^{31}P NMR spectroscopy, δ_P 50.1 and 48.3 ppm). After vacuum treatment of the reaction mixture at 50–60 °C (1–2 mm Hg) adduct **18** was converted to *Se*-ester **19**. The latter was purified by column chromatography (basic Al_2O_3, 1.5 × 10 cm, hexane as eluent).

4.4. Characterization data for synthesized compounds

*4.4.1. [1-(Methoxy)ethoxy]methylferrocene (**3a**)*

Orange oil. Yield: 236 mg (86%). R_f = 0.51 (hexane/Et_2O, 1:1). FT-IR (film): $\tilde{\nu}$ = 3094, 1449, 1013, 819, 483 (Fc), 1140, 1125, 1106, 1091, 1040 (OCHO) cm^{-1}.^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.29 (d, ^3J = 5.4 Hz, 3 H, Me), 3.31 (s, 3 H, OMe), 4.14 (br s, 7 H, C_5H_5, H_β in Fc), 4.23 (s, 2 H, H_α in Fc), 4.27, 4.38 (2d, ^2J = 11.1 Hz, each 1 H, OCH_2Fc), 4.71 (q, ^3J = 5.4 Hz, 1 H, *H*CMe). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 18.9 (Me), 51.5 (OMe), 68.2 (C_β in Fc), 68.4 (C_5H_5), 69.1 (C_α in Fc), 71.6 (*C*H_2Fc), 83.6 (C_i in Fc), 99.1 (CH). Anal. Calcd. for $C_{14}H_{18}FeO_2$ (274.14): C, 61.34; H, 6.62; Fe, 20.37. Found: C, 61.66; H, 6.44; Fe, 20.81.

*4.4.2. [1-(1-Methylpropoxy)ethoxy]methylferrocene (**3b**)*

Orange oil. Yield: 213 mg (67%). An inseparable 1:1 mixture of two diastereoisomers. R_f = 0.65 (hexane/Et_2O, 1:1). FT-IR (film): $\tilde{\nu}$ = 3096, 1456, 1021, 819, 484 (Fc), 1155, 1106, 1087, 1040 (OCHO) cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.90, 0.98 (2t, ^3J = 7.3 Hz, each 1.5 H, *Me*CH_2), 1.13, 1.22 (2d, ^3J = 6.1 Hz, each 1.5 H, *Me*CHCH_2), 1.33 (d, ^3J = 5.4 Hz, 3 H, *Me*CHO), 1.43-1.66 (m, 2 H, *C*H_2Me), 3.60-3.69 (m, 1 H, Me*CH*Et), 4.14 (br s, 7 H, C_5H_5, H_β in Fc), 4.22, 4.24 (2br s, each 1 H, H_α in Fc), 4.30, 4.40 (2d, ^2J = 11.0 Hz, each 1 H, OCH_2Fc), 4.80, 4.83 (2q, ^3J = 5.4 Hz, 1 H, *H*CMe). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 9.6, 10.2 (*Me*CH_2), 19.6, 20.7 (*Me*CHCH_2), 20.5 (*Me*CHO), 29.3, 30.2 (*C*H_2Me), 62.4 (*C*H_2Fc), 68.2 (C_5H_5), 68.3, 69.1 (C_5H_4), 72.5, 73.6 (CHO), 83.8 (C_i in Fc), 97.0, 98.2 (H*C*Me). Anal. Calcd. for $C_{17}H_{24}FeO_2$ (316.22): C, 64.57; H, 7.65; Fe, 17.66. Found: C, 64.69; H, 7.97; Fe, 17.59.

*4.4.3. [1-(tert-Butoxy)ethoxy]methylferrocene (**3c**)*

Orange oil. Yield: 229 mg (72%). R_f = 0.64 (hexane/Et_2O, 1:1). FT-IR (film): $\tilde{\nu}$ = 3095, 1473, 1001, 818, 484 (Fc), 1144, 1120, 1106, 1091, 1040 (OCHO) cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.25 (s, 9 H, *Me*$_3$C), 1.30 (d, ^3J = 5.4 Hz, 3 H, Me), 4.11-4.12 (nr m, 7 H, C_5H_5, H_β in Fc), 4.20, 4.21 (2br s, 2 H, H_α in Fc), 4.25, 4.31 (2d, ^2J = 11.0 Hz, each 1 H, OCH_2Fc), 4.95 (q, ^3J = 5.4 Hz, 1 H, *H*CMe). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 21.9 (*Me*CHO), 28.8 (3 Me in *t*-Bu), 61.3 (*C*H_2Fc), 68.1, 68.2 (C_α in Fc), 68.4 (C_5H_5), 69.0 (C_β in Fc), 73.7 (C in *t*-Bu), 84.2 (C_i in Fc), 93.5 (H*C*Me). Anal. Calcd. for $C_{17}H_{24}FeO_2$ (316.22): C, 64.57; H, 7.65; Fe, 17.66. Found: C, 64.66; H, 7.44; Fe, 17.81.

*4.4.4. [1-(2-Propenyloxy)ethoxy]methylferrocene (**3d**)*

Orange oil. Yield: 179 mg (60%). R_f = 0.62 (hexane/Et_2O, 1:1). FT-IR (film): $\tilde{\nu}$ = 3088, 1455, 1012, 822, 482 (Fc), 1142, 1123, 1105, 1097, 1040 (OCHO), 1618 (C=C) cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.32 (d, ^3J = 5.4 Hz, 3 H, Me), 3.98-4.14 (m, 9 H, OCH_2CH=, C_5H_5, H_β in Fc), 4.21 (br s, 2 H, H_α in Fc), 4.30, 4.38 (2d, ^2J = 11.3 Hz, each 1 H, OCH_2Fc), 4.81 (q, ^3J = 5.4 Hz, 1 H, *H*CMe), 5.18 (dd, ^3J = 10.4 Hz, ^4J = 1.7 Hz, 1 H, =CH_{cis}), 5.29 (dd, ^3J = 17.2 Hz, ^4J = 1.7 Hz, 1 H, =CH_{trans}), 5. 94 (ddt, ^3J = 17.2 Hz, ^3J = 10.4 Hz, ^3J = 5.4 Hz, 1 H, C*H*=CH_2). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 19.6 (*Me*CH), 63.2 (*C*H_2Fc), 65.5 (OCH_2), 68.3 (C_β in Fc), 68.4 (C_5H_5), 69.1, 69.2 (C_α in Fc), 83.5 (C_i in Fc), 98.2 (Me*CH*), 116.5 (CH_2=), 134.8 (C*H*=CH_2). Anal. Calcd. for $C_{16}H_{20}FeO_2$ (300.17): C, 64.02; H, 6.72; Fe, 18.60. Found: C, 64.06; H, 6.44; Fe, 18.90.

*4.4.5. 1,1-Bis(ferrocenylmethoxy)ethane (**4**)*

Yellow solid, mp 80-82 °C. R_f = 0.56 (hexane/Et_2O, 1:1). FT-IR (film): ν = 3093, 1105, 1002, 819, 493, 482 (Fc), 1123, 1105, 1097, 1040 (OCHO) cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.33 (d, ^3J = 4.8 Hz, 3 H, Me), 4.15 (s, 10 H, 2C_5H_5), 4.18 (s, 4 H, H_β in Fc), 4.26 (br s, 4 H, H_α in Fc), 4.31, 4.39 (2d, ^2J = 11.0 Hz, each 2 H, OCH_2Fc), 4.83 (q, ^3J = 4.8 Hz, 1 H, *H*CMe). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 19.8 (Me), 63.0 (*C*H_2Fc), 68.4 (C_5H_5), 69.3 (C_β in Fc), 69.4 (C_α in Fc), 83.7 (C_i in Fc), 98.0 (CH). Anal. Calcd. for $C_{24}H_{26}Fe_2O_2$ (458.15): C, 62.92; H, 5.72; Fe, 24.38. Found: C, 63.02; H, 5.78; Fe, 24.09.

*4.4.6. (2-Propenyloxy)methylferrocene (**5d**)*

Yellow wax-like solid. Yield: 141 mg (55%). R_f = 0.76 (hexane/Et_2O, 1:1). FT-IR (film): $\tilde{\nu}$ = 3090, 1001, 822, 483 (Fc), 1618 (C=C) cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.99 (d, ^3J = 5.1 Hz, 2 H, OCH_2CH=), 4.14 (s, 5 H, C_5H_5), 4.16 (br s, 2 H, H_β in Fc), 4.25 (br s, 2 H, H_α in Fc), 4.30 (s, 2 H, OCH_2Fc), 5.19 (d, ^3J = 10.3 Hz, 1 H, =CH_{cis}), 5.28 (d, ^3J = 17.4 Hz, 1 H, =CH_{trans}), 5.91 (ddt, ^3J = 17.4 Hz, ^3J = 10.3 Hz, ^3J = 5.1 Hz, 1 H, C*H*=CH_2). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 68.3 (*C*H_2Fc), 68.4 (C_5H_5, C_β in Fc), 69.4 (C_α in Fc), 70.7 (*C*H_2CH=), 83.3 (C_i in Fc), 116.8 (CH_2=), 134.9 (C*H*=CH_2). Anal. Calcd. for $C_{14}H_{16}FeO$ (256.12): C, 65.65; H, 6.30; Fe, 21.80. Found: C, 65.76; H, 6.44; Fe, 21.90. Spectroscopic data are in full agreement with those previously reported.[39]

*4.4.7. (2,2,3,3-Tetrafluoropropoxy)methylferrocene (**5e**)*

Orange solid, mp 54-55 °C (hexane). Yield: 130 mg (39%). R_f = 0.70 (hexane/Et_2O, 1:1). FT-IR (KBr): $\tilde{\nu}$ = 3100, 1405, 1106, 1001, 834, 483 (Fc) cm^{-1}.^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.78 (t, ^3J = 12.4 Hz, 2 H, OCH_2), 4.16 (br s, 7 H, C_5H_5, H_β in Fc), 4.20, 4.24 (2 br s, 2 H, H_α in Fc), 4.41 (s, 2 H, OCH_2Fc), 5.93 (tt, ^2J = 53.3 Hz, ^3J = 5.1 Hz, 1 H, HCF_2). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 66.4 (t, ^2J = 28.9 Hz, CH_2O), 68.5 (C_5H_5), 68.8 (C_α in Fc), 69.4, (C_β in Fc), 70.5 (CH_2O), 81.6 (C_i in Fc), 109.1 (tt, ^1J = 248.8 Hz, ^2J = 33.9 Hz, CF_2), 115.2 (tt, ^1J = 250.0 Hz, ^2J = 26.4 Hz, CF_2). Anal. Calcd. for $C_{14}H_{14}F_4FeO$ (330.10): C, 50.94; H, 4.27; Fe, 16.92. Found: C, 50.69; H, 4.42; Fe, 16.80.

*4.4.8. Bis(ferrocenylmethyl)ether (**6**)*

Orange solid, mp 129-131 °C {ref.[40] 126-128 °C}. R_f = 0.55 (hexane/Et_2O, 1:1). FT-IR (KBr): $\tilde{\nu}$ =3103, 3092, 1103, 1000, 819, 497, 483 (Fc) cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.13 (s, 10 H, C_5H_5), 4.15 (t, ^3J = 1.7 Hz, 4 H, H_β in Fc), 4.24 (t, ^3J = 1.7 Hz, 4 H, H_α in Fc), 4.28 (s, 4 H, OCH_2Fc). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 67.9 (*C*H_2Fc), 68.3 (C_β in Fc), 68.4 (C_5H_5), 69.3 (C_α in Fc), 83.7 (C_i in Fc). Anal. Calcd. for $C_{22}H_{22}Fe_2O$ (414.10): C, 63.81; H, 5.35; Fe, 26.97. Found: C,

63.96; H, 5.48; Fe, 26.49. Spectroscopic data are in full agreement with those previously reported.[41]

*4.4.9. Phenyloxymethylferrocene (**7**)*

Yellow crystals, mp 135-136 °C (hexane). Yield: 204 mg (70%). R_f = 0.71 (hexane/Et_2O, 1:1). FT-IR (KBr): $\tilde{\nu}$ = 3038, 1430, 1104, 1000, 814, 504, 485 (Fc) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 4.20 (s, 7 H, C_5H_5, H_β in Fc), 4.34 (br s, 2 H, H_α in Fc), 4.81 (s, 2 H, O*C*H_2Fc), 6.95-6.99 (m, 3 H, *o*,*p*-H in Ph), 7.28-7.32 (m, 2 H, *m*-H in Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 66.4 (CH_2O), 68.5 (C_5H_5, C_α in Fc), 69.0 (C_β in Fc), 82.7 (C_i in Fc), 114.7 (*o*-C in Ph), 120.7 (*p*-C in Ph), 129.3 (*m*-C in Ph), 158.7 (*i*-C in Ph). Anal. Calcd. for $C_{17}H_{16}FeO$ (292.15): C, 69.89; H, 5.52; Fe, 19.11. Found: C, 69.62; H, 5.46; Fe, 18.94. Spectroscopic data are in full agreement with those previously reported.[41]

*4.4.10. Mixture of 1-[1-(ferrocenylmethoxy)ethyl]-1H- (**8a**) and 2-[1-(ferrocenylmethoxy)ethyl]-2H-1,2,3-benzotriazole (**8b**)*

Orange wax-like solid. Ratio of **8a**/**8b** is 68:32 (^1H NMR). Combined yield: 224 mg (62%). R_f = 0.36 (hexane/Et_2O, 1:1). FT-IR (film): $\tilde{\nu}$ = 3093, 1411, 1105, 1001, 816, 482 (Fc), 1150, 1120, 1076, 1040 (OCHN) cm^{-1}. H NMR (400.13 MHz, $CDCl_3$): δ = 1.82 (d, ^3J = 6.1 Hz, 3 H, Me, major), 1.87 (d, ^3J = 6.0 Hz, 3 H, Me, minor), 4.03-4.31 (m, 11 H, OCH_2, C_5H_5, H_α, H_β in Fc, major + minor), 6.16 (q, ^3J = 6.0 Hz, 1 H, NCHO, minor), 6.35 (q, ^3J = 6.1 Hz, 1 H, NCHO, major), 7.38-7.51 (m, 4 H, BTA, major + minor), 7.80 (d, ^3J = 8.3 Hz, 1 H, BTA, major), 7.94-7.95 (m, 2 H, Btz, minor), 8.12 (d, ^3J = 8.3 Hz, 1 H, BTA, major). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 21.0 (Me, major), 21.5 (Me, minor), 66.7 (CH_2O, major), 67.1 (CH_2O, minor), 68.3 (C_5H_5, major + minor), 68.6, 69.7 (C_α, C_β in Fc, minor), 68.8, 69.1 (C_α, C_β in Fc, major), 81.2 (C_i in Fc, major + minor), 85.6 (NCHO, major), 89.6 (NCHO, minor), 111.3 (2C, BTA, minor), 118.5 (2C, BTA, minor), 120.0, 124.2, 126.6, 127.3 (BTA, major), 131.0 (BTA, major), 144.0 (2C, BTA, minor), 146.8 (BTA, major). Anal. Calcd. for $C_{19}H_{19}FeN_3O$ (361.22): C, 63.18; H, 5.30; N, 11.63. Found: C, 63.03; H, 5.35; N, 11.98.

*4.4.11. 1-Ferrocenylmethyl-1H-1,2,3-benzotriazole (**9**)*

Orange solid, mp 134-136 °C (hexane) {ref.[43] 134-135 °C}. Yield: 288 mg (91%). R_f = 0.25 (hexane/Et_2O, 1:1). FT-IR (KBr): $\tilde{\nu}$ = 3091, 1103, 1000, 813, 482 (Fc) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 4.17 (br s, 2 H, C_5H_4), 4.19 (s, 5 H, C_5H_5), 4.32 (br s, 2 H, C_5H_4), 5.61 (s, 2 H, C*H*$_2$Fc), 7.35, 7.45 (2t, ^3J = 7.6 Hz, each 1 H, $CH^{5,6}$), 7.52 (d, ^3J = 8.3 Hz, 1 H, CH^4), 8.05 (d, ^3J = 8.3 Hz, 1H, CH^7). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 47.6 (*C*H_2Fc), 68.2, 68.3 (C_5H_4), 68.4 (C_5H_5), 81.3 (C_i in Fc), 109.2 (C^7), 119.4 (C^4), 123.2 (C^6), 126.6 (C^5), 132.0 (C^9), 145.5 (C^8). Anal. Calcd. for $C_{17}H_{15}FeN_3$ (317.17): C, 64.38; H, 4.77; N, 13.25. Found: C, 63.97; H, 4.36; N, 13.02. Spectroscopic data are in full agreement with those previously reported.[9a]

*4.4.12. 1-(Ferrocenylmethoxy)ethyl]-1H-1,2,4-triazole (**10**)*

Yellow solid, mp 65 °C (hexane). Yield: 125 mg (40%). R_f = 0.17 (Et_2O). FT-IR (KBr): $\tilde{\nu}$ = 3096, 1102, 1003, 822, 483 (Fc), 1142, 1116, 1049 (OCHN) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.67 (d, ^3J = 6.1 Hz, 3 H, Me), 4.10 (s, 5 H, C_5H_5), 4.16-4.18 (m, 4 H, C_5H_4), 4.22, 4.31 (2d, ^2J = 11.4 Hz, each 1 H, CH_2O), 5.68 (q, ^3J = 6.1 Hz, 1 H, C*H*Me), 8.00, 8.27 (2s, each 1 H, $CH^{3,5}$). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 21.6 (Me), 66.7 (CH_2O), 68.5 (C_5H_5), 68.7, 69.0, 69.2, 69.6 (C_5H_4), 80.8 (C_i in Fc), 84.3 (NCH), 140.7 (C^5H), 150.9 (C^3H). Anal. Calcd. for $C_{15}H_{17}FeN_3O$ (311.16): C, 57.90; H, 5.51; N, 13.50. Found: C, 57.68; H, 5.36; N, 13.39.

*4.4.13. Ferrocenylmethyl-1H-1,2,4-triazole (**11**)*

Yellow solid, mp 82 °C (hexane) {ref.[42] 81.2 °C). Yield: 59 mg (22%). R_f = 0.10 (Et_2O). ^1H NMR (400.13 MHz, $CDCl_3$): δ = 4.18 (s, 5 H, C_5H_5), 4.23 (t, ^3J = 1.7 Hz, 2 H, H_β in Fc), 4.29 (t, ^3J = 1.7 Hz, 2 H, H_α in Fc), 5.12 (s, 2 H, CH_2), 7.93, 7.98 (2s, each 1 H, $CH^{3,5}$). Anal. Calcd. for $C_{13}H_{13}FeN_3$ (267.11): C, 58.46; H, 4.91; N, 15.73. Found: C, 58.32; H, 4.86; N, 15.89. Spectroscopic data are in full agreement with those previously reported.[42]

*4.4.14. O-Ferrocenylmethyl 2-methacrylate (**13**)*

Yellow crystals, mp 76-77 °C (hexane) {ref.[42] 76.5 °C). Yield: 238 mg (84%). R_f = 0.65 (hexane/Et_2O, 1:1). FT-IR (KBr): $\tilde{\nu}$ = 1408, 1104, 1002, 813, 483 (Fc), 1632 (C=C), 1710 (C=O) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.96 (s, 3 H, Me), 4.18 (br s, 7 H, C_5H_5, H_β in Fc), 4.30 (s, 2 H, H_α in Fc), 4.97 (s, 2 H, O*C*H_2Fc), 5.56 (s, 1 H, =CH_{cis}), 6.11 (s, 1 H, =CH_{trans}). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 18.3 (Me), 62.9 (OCH_2), 68.5 (C_5H_5), 68.6 (C_α in Fc), 69.3 (C_β in Fc), 81.6 (C_i in Fc), 125.5 (CH=), 136.3 (C=), 167.2 (C=O). Anal. Calcd. for $C_{15}H_{16}FeO_2$ (284.13): C, 63.41; H, 5.68; Fe, 19.65. Found: C, 63.76; H, 5.68; Fe, 19.88. Spectroscopic data are in full agreement with those previously reported.[42]

*4.4.15. S-[1-(Ferrocenylmethoxy)ethyl]diphenethyldithio-phosphinate (**15**)*

This compound was not isolated in pure state. Its structure was determined from a mixture of **15** and **16** (molar ratio of *ca*. 7 : 1) obtained after flash-chromatography. Yellow wax-like solid. Yield: 472 mg (77%). FT-IR (film): $\tilde{\nu}$ = 3085, 1105, 1000, 820 (Fc), 1156, 1100 sh, 1040 (OCHS), 750 (P-C), 698 (P=S), 494 (P-S) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.79 (d, 3 H, ^3J = 5.9 Hz, Me), 2.28-2.54 (m, 4 H, PCH_2), 2.97-3.16 (m, 4 H, $PhCH_2$), 4.15-4.16 (nr m, 7 H, C_5H_5, H_β in Fc), 4.27, 4.33 (2br s, each 1 H, H_α in Fc), 4.45, 4.60 (2d, ^2J = 11.0 Hz, each 1 H, OCH_2), 5.48-5.56 (dq, ^3J = 10.8 Hz, ^3J = 5.9 Hz, 1 H, OCHS), 7.27-7.36 (m, 10 H, Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 25.6 (Me), 29.0, 29.3 ($PhCH_2$), 39.6, 39.8 (2d, ^1J = 50.0 and 48.7 Hz, PCH_2), 67.4 (OCH_2), 68.6 (C_5H_5), 68.7, 69.1, 69.5, 69.6 (C_5H_4), 82.5 (C_i in Fc), 86.9 (OCHS), 126.6 (*p*-C in Ph), 128.4 (*o*-C in Ph), 128.8 (*m*-C in Ph), 140.4 (d, ^3J = 16.4 Hz, *i*-C in Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 72.03.

*4.4.16. S-Ferrocenylmethyldiphenethyldithiophosphinate (**16**)*

Yellow solid, mp 77-78 °C (hexane). Yield: 408 mg (81%). R_f = 0.67 (hexane/Et_2O, 1:1). FT-IR (KBr): $\tilde{\nu}$ =3085, 1105, 1000, 821, 482 (Fc), 749 (P-C), 698 (P=S), 498 (P-S) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.26-2.33 (m, 4 H, PCH_2), 2.84-3.04 (m, 4 H, $PhCH_2$), 4.02, 4.05 (2s, each 1 H, H_α in Fc), 4.16 (s, 2 H, H_β in Fc), 4.19 (s, 5 H, C_5H_5), 4.33 (s, 2 H, SCH_2), 7.14-7.31 (m, 10 H, Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 29.1 (CH_2Ph), 31.8 (SCH_2), 38.7 (d, ^1J = 49.1 Hz, PCH_2), 68.4 (C_5H_4), 68.9 (C_5H_5), 69.1 (C_5H_4), 82.2 (C_i in Fc), 126.4 (*p*-C in Ph), 128.2 (*o*-C in Ph), 128.6 (*m*-C in Ph), 140.4 (d, ^3J = 16.4 Hz, *i*-C in Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 73.70. Anal. Calcd. for $C_{27}H_{29}FePS_2$ (504.52): C, 64.28; H, 5.79; Fe, 11.07; P, 6.14. Found: C, 64.10; H, 5.46; Fe, 10.70; P, 5.70.

*4.4.17. Se-[1-(Ferrocenylmethoxy)ethyl]diphenethyldiseleno-phosphinoate (**18**)*

was identified by ^{31}P NMR spectroscopy. ^{31}P NMR (161.98 MHz, 1,4-dioxane): δ = 50.15 (satellites: $^1J_{P=Se}$ = 755 Hz, $^1J_{P\text{-}Se}$ = 351 Hz).

*4.4.18. Se-Ferrocenylmethyldiphenethyldiselenophosphinate (**19**)*

Orange solid, mp 80-82 °C (hexane). Yield: 353 mg (59%). R_f = 0.60 (hexane/Et_2O, 1:1). FT-IR (KBr): $\tilde{\nu}$ = 3083, 1103, 1000, 810, 481 (Fc), 734 (P-C), 493 (P=Se), 471 (P-Se) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.47 (dt, ^2J = 8.8 Hz, ^3J = 8.6 Hz, 4 H, PCH_2), 2.80-3.02 (m, 4 H, $PhCH_2$), 4.03, 4.07 (2s, each 1 H, H_α in Fc), 4.11 (s, 2 H, H_β in Fc), 4.15 (s, 5 H, C_5H_5), 4.29 (s, 2 H, $SeCH_2$), 7.10-7.26 (m, 10 H, Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 30.2 (d, ^2J = 2.6 Hz, CH_2Ph), 31.7 ($SeCH_2$), 39.1 (d, ^1J = 36.0 Hz, PCH_2), 68.5 (C_α in Fc), 69.0 (C_5H_5), 69.2 (C_β in Fc), 85.1 (C_i in Fc), 126.5 (*p*-C in Ph), 128.3 (*o*-C in Ph), 128.6 (*m*-C in Ph), 140.2 (d, ^3J = 17.3 Hz, *i*-C in Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 48.58 (satellites: $^1J_{P=Se}$ = 742 Hz, $^1J_{P-Se}$ = 358 Hz). Anal. Calcd. for $C_{27}H_{29}FePSe_2$ (598.26): C, 54.21; H, 4.89; Fe, 9.33; P, 5.18. Found: C, 54.50; H, 4.62; Fe, 9.44; P, 5.23.

Acknowledgments

Authors would like to acknowledge the Multi-Access Chemical Service Center SB RAS for XRD measurements. The authors are also grateful to the Baikal Analytical Center for spectral measurements.

Supplementary Material

Supplementary data for this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.... .

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