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Short communication

A reactivity study of phenyl and ferrocenyl phosphates within the anionic phospho-**F**ries rearrangement^{*}



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ARTICLE INFO	A B S T R A C T				
Article history: Received 13 June 2016 Accepted 22 July 2016 Available online 25 July 2016	Temperature-dependent anionic phospho-Fries rearrangements of ferrocenyl/phenyl phosphates $P(O)(OFc)_n(OPh)_{3-n}$ (Fc = Fe(η^5 -C ₅ H ₅)(η^5 -C ₅ H ₄); n = 0,1,2,3) were investigated. Whereas ferrocenyls solely undergo one rearrangement per reaction step, the number of phenyl-based 1,3-O \rightarrow C shifts depends on the temperature. This results in different types of otherwise hardly accessible mixed ferrocenyl/phenyl organophosphorus compounds. Detailed investigations of the triple-rearrangement of triphenyl phosphate (n = 0) reveals a consecutive formation of its phosphonate and phosphinate prior to the known phosphane oxide.				

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Organophosphorus compounds are common additives in polymers to control, for example, their inflammatory properties [1,2]. They also are of importance in light-emitting diodes [3], due to their easy linking within polymeric networks [2]. Suitable connecting functionalities, e.g. the hydroxy group, can be obtained by the reaction of ortho-metallated species with $PX_3/P(O)X_3$ (X = Cl, Br), followed by deprotection to give the respective triple-ortho-substituted phosphine/-oxide derivatives [4, 5]. More efficiently, the anionic phospho-Fries rearrangement, as a single-step 1,3-O \rightarrow C process, allows the conversion of triaryl phosphates into tris(2-hydroxyaryl)phosphine oxides in high yields [6,7]. These species were used for the colorimetric determination of, for example, Fe³⁺ ions [4,8]. In general, they can act as binding agents for cations [9], e.g. Li⁺ [10] dimethyl tin complexes [11], amino acids [12] and C_{60} [13]. Ortho-hydroxy phosphine oxides bearing a chiral binol backbone are exceptional catalysts for the asymmetric addition of ZnEt₂ to aldehydes, with the alcohols obtained in excellent yield and high ee [14]. The triple ortho-alkoxy-substituted phosphines are widely used for C,C cross-coupling catalysis by applying axially pure biphenyl phosphanes in catalytic Heck reactions [15].

Our recent results on the synthesis of 1,2-*P*,O ferrocenyl phosphanes and their use for *C*,*C* cross-coupling Suzuki-Miyaura reactions [16] and diastereomerically enriched multiple-step anionic phospho-Fries rearrangements [17], prompted us to investigate the rearrangement of triferrocenyl phosphate (**A**), which will be reported herein. The rearrangement to a triple-2-functionalized phosphane oxide (**A-3**) should give access to an electronically-rich phosphane by reduction [17] or as

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a tripodal ligand in transition metal complex chemistry. The anionic phospho-Fries rearrangement provides a novel and straightforward access to 2-hydroxy phosphonates and phosphinates, which will be reported, too.

Triferrocenyl phosphate (**A**) is accessible by the reaction of ferrocenol FcOH (Fc = Fe(η^5 -C₅H₅)(η^5 -C₅H₄)) and phosphoryl chloride in the presence of a base (Scheme 1) [18,19,20]. The yield could be increased from 36 % to 92 % by using BuLi instead of NEt₃ as base [16,17, 20]. The investigations of the anionic phospho-Fries reactions for **A** have been carried out at various temperature regimes (Scheme 1, Table SI1). At -70 °C treatment of **A** with an excess of LDA resulted in the formation of novel phosphonate **A-1** in a yield of 74 %, whereas 17 % of the starting material **A** remained. At -30 °C the yield of **A-1** increased and reached 86 %. However, at higher temperatures **A-1** started to decompose.

Phosphonate **A-1** undergoes a consecutive anionic phospho-Fries rearrangement [1,16,17], resulting in the formation of phosphinate **A-2** in a yield of 86% at 0 °C within 4 h (Scheme 1). The planar chirality of both ferrocenyls resulted in a diastereomeric excess (de) of 77% with a predominantly formed configuration of the pair of the *meso* enantiomers $R_{p,}S_{p,}r^{p}$ and $S_{p,}R_{p,}s^{p}$ as it could be confirmed by using single crystal Xray diffraction analysis (Fig. 1). Compound **A-2** crystallizes in the monoclinic space group $P2_{1}/c$ in a ratio of 0.9:0.1 of their $R_{p,}R_{p}/S_{p,}S_{p}$ diastereomers, which is similar to the diastereomeric ratio obtained by ³¹P{¹H} NMR spectroscopy (0.885:0.115, Experimental section). However, phosphine oxide **A-3** (Scheme 3) could not be obtained, neither by the reaction of **A**, **A-1** nor **A-2** with LDA (Table SI1).

The rearrangement of **B**, in which all ferrocenyls are replaced by phenyls, has been reported to exclusively result in oxide **B-3** within one reaction step at -78 °C and subsequent warming to 0 °C (Scheme 2) [6,21]. Interestingly, neither phosphonate **B-1** nor phosphinate **B-2**

 $^{\,\,\}star\,\,$ Dedicated to a dear friend, Professor Dr. Michael Hietschold on the occasion of his 65th birthday.

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Scheme 1. Consecutive anionic phospho-Fries rearrangement of triferrocenyl phosphate **A** to afford phosphonate **A-1** and phosphinate **A-2**. (*i*) LDA, thf, -30 °C, 3 h, Me₂SO₄, 86% (based on **A**). (*ii*) LDA, thf, 0 °C, 3 h, Me₂SO₄, 86% (based on **A-1**). *a*) Obtained by the reaction of 3 equiv of FcOLi with POCl₃ in diethyl ether.

have been isolated so far. The question is, if they were formed during this reaction or a simultaneous rearrangement from **B** to **B-3** occurs excluding their formation.

To investigate the reactivity of phosphonate **B** at low temperatures, the treatment of this compound with an excess of LDA and the addition of the electrophile HCl_{aq} , were performed at -80 °C (Scheme 2). At this temperature **B** was successfully transferred to phosphonate **B-1** and phosphinate **B-2**, confirming an increased reactivity of **B** as compared to **A** [22]. When the temperature was increased to 0 °C then oxide **B-3** was accessible [6,21]. This reactivity behavior of **B** towards an anionic phospho-Fries rearrangement can be explained by an increased electron density at the remaining *O*-bonded aromatics, requiring higher temperatures for their lithiation.

The increased reactivity of the phenyl-based hydroxyls might affect the number of possible rearrangements of **A** and thus, PhOLi (3 and 12 equiv) were added to the reaction of **A** with LDA at -30 °C (Table SI1). The yield of phosphonate **A-1** decreased from 86% (Scheme 1) to 59% (3 equiv) and 44% (12 equiv), whereas the formation of phosphinate **A-2** was observed with a yield of 16% (3 equiv) and 46% (12 equiv) as a single diastereomer (de 0.99).

To further investigate the difference between the phenyl and ferrocenyl substituents in **A** and **B**, compounds **C** and **D** were prepared bearing both types of aromatics (Schemes 3 and 4).



Fig. 1. ORTEP diagram (50% probability level) of the molecular structure of *meso*-**A**-**2** with the atom-numbering scheme. All hydrogen atoms and the co-crystallized *racem*-**A**-**2** (10%) have been omitted for clarity.



Scheme 2. Anionic phospho-Fries rearrangement of triphenyl phosphate (B) to give B-1– B-3. (*i*) thf, LDA, B, 2 h, Me₂SO₄. *a*) Yield based on B.

For the synthesis of diferrocenylphenyl phosphate **C**, FcOLi was reacted with dichlorophenyl phosphate (Supporting information). However, treatment of **C** with 4 equiv of LDA at -75 °C (Scheme 3) produced only phosphonates **C-1** and **C-2** in minor yield. Increasing the reaction temperature to 0 °C resulted in a complete conversion of **C** giving **C-3**. Although an excess of dimethyl sulfate was present, compounds **C-1** and **C-3** were obtained in form of **C-1a/C-3a** (R = H) and as **C-1b/C-3b** (R = CH₃). As observed for **A** (Scheme 1), the ferrocenyls prevent the formation of any type of phosphine oxides, within the anionic phospho-Fries rearrangement of **C** (Scheme 3).

To examine the influence between one (**C**) and two phenyls (**D**) on the product-mixture within an anionic phospho-Fries rearrangement, the treatment of ferrocenyldiphenyl phosphate (**D**) has been reinvestigated [16]. Replacing NEt₃ by BuLi as the base for the deprotonation of ferrocenol, increased the yield of **D** from 62 [16] to 99%. Unmethylated **D-2** could recently be obtained in a yield of 8% by running the reaction at -40 °C, due to an unsuccessful methylation by using iodomethane [17].

Carrying out the anionic phospho-Fries rearrangement below -75° C reduces the amount of unreacted starting material from 80% for **C** to 25% for **D**. The formation of phosphonate **D-1** and phosphinate **D-3** is observed. This reveals a positive influence of the two phenyls towards the lithiation behavior compared to **C**, where the formation of a phosphinate has not been observed. At -70° C compound **D** was completely converted and the yields of **D-1** and **D-3** increased

$(FcO)_2P$ OPh $(FcO)_2P$ (FcO)								
C 63 % ^{a)}		C- 1	-1a, R = H C-2		2 C	-3a , R = H		
		C- 1	lb, R =	= CH ₃	c	:-3b , R = CH ₃		
Nr.	Temp.	Time	Yield / % ^{b)}					
	/ ° C	/ h	С	C-1	C-2	C-3		
1	-75	2	80	10 b	9 (de 0.45)	_		
2	-60	4	25	27 a , 13 b	29 (de 0.27)	—		
				$\Sigma = 40$				
3	-35	3.5	-	25 a , 10 b	20 (de 0.65)	19 a , 9 b		
				$\Sigma = 35$		$\Sigma = 28$		
4 ^{c)}	0	2	-	-	-	77 a , 13 b		
						$\Sigma = 90$		

Scheme 3. Anionic phospho-Fries rearrangement of diferrocenylphenyl phosphate **C** to afford phosphonates **C-1**, **C-2** and phosphinate **C-3**. (i) thf, LDA (4 equiv); **C**, Me₂SO₄, a) Obtained by the reaction of 2 equiv of FcOLi with $Cl_2P(O)OPh$ in diethyl ether. b) Yield based on **C**. c) 7 equiv of LDA were used.



Scheme 4. Anionic phospho-Fries rearrangement of ferrocenyldiphenyl phosphate D to give phosphonates D-1 and D-2, phosphinate D-3 as well as phosphine oxide D-4. (i) thf, LDA (8 equiv), **D**, 2 h, Me_2SO_4 (12 equiv). a) Obtained by the reaction of 0.5 equiv of FcOLi with $ClP(O)(OPh)_2$ in diethyl ether. b) Yield based on **D**.

accordingly. Additionally, the formation of phosphinate D-2 is observed. Phosphine oxide D-4 could be isolated at 0 °C in a yield of 25% (Scheme 4).

Characterization and differentiation between the different families of organophosphorus compounds is based on ${}^{13}C{}^{1}H$ and ${}^{31}P{}^{1}H$ NMR spectroscopy. The ³¹P{¹H} NMR downfield shift increases by replacing oxygens with carbon atoms [16, 17]. Thus, phosphates (-15.3(**A**) to -17.8 (**B**) ppm) and phosphonates (11.5 to 18.8 ppm) could be distinguished, whereby the electron-rich phosphonates A-1 and C-2 are shifted to lower field (D-1, 18.8 ppm; C-2, 18.3 ppm) as compared with their phenyl derivatives (C-1b, 11.5 ppm to C-1a, 15.8 ppm). Additionally, in phosphinates **D-3b** (26.1 ppm) – **D-3a** (44.1 ppm) and phosphine oxides **D-4b** (38.2 ppm), **D-4a** (49.3 ppm) and **B-3** (51.1 ppm) the presence of an electron-donating hydroxyl groups increases the chemical shift as compared to their methoxy derivatives (Supporting information). Further criteria are the decreasing ${}^{1}J_{C,P}$ coupling constants with significant smaller values for P-C_{Phenyl} (phosphonates B-1, C-1 and D-1: 184–190 Hz; phosphinates B-2, C-3 and D-2,3: 134–147 Hz; oxides **B-3** and **D-4b**: 107 and 110 Hz) as compared to P–C_{FC} (phosphonates A-1 and C-2: 220 and 222 Hz; phosphinates A-2, C-3 and D-3: 162.5-183.9 Hz; oxide **D-4**: 120 ppm).

In conclusion, the synthesis of a series of ferrocenyl/phenyl phosphates of type $P(O)(OFc)_n(OPh)_{3-n}$ (Fc = Fe(η^5 -C₅H₅) (η^5 -C₅H₄); n = 0, 1, 2, 3) was investigated in anionic phospho-Fries rearrangements [1]. Triferrocenyl phosphate (A, n = 3) undergoes step-wise rearrangements to the respective phospho- and phospinate. In contrary, the product mixture derived from the triphenyl derivative **B** (n = 0)solely depends on the reaction temperature. Furthermore, the investigations of **B** reveal that the literature-stated reaction temperature of -78 °C does not result in the formation of the respective phosphine oxide B-3. Moreover, stirring at 0-25 °C is essential. Our investigations provide a new straightforward access to mixed phosphonates and phosphinates, derived from ferrocenyl/phenyl phosphates within one reaction step by applying the anionic phospho-Fries rearrangement. The number of rearrangements could be controlled by varying the reaction temperature, revealing an increased reactivity for phenyl substituents. Thus, adding PhOLi within the reaction of triferrocenyl phosphate enables a second rearrangement.

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Appendix A. Supplementary material

Detailed experimental procedures, Tables SI1-4 and a CIF file giving additional experimental and crystallographic data as well as spectroscopic details for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data of A-2 are also available from the Cambridge Crystallographic Database as file number CCDC 1474108 (A-2). Supplementary data associated with this article can be found in the online version, at http://dx.doi. org/10.1016/j.inoche.2016.07.017.

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