IMIDAZOLIUM-TAGGED FERROCENE LIGANDS

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Dedicated to Professor Štefan Toma on the occasion of his 70th birthday.

New chiral imidazolium-tagged ferrocene ligands were prepared. Diastereoselective *ortho*-lithiation of the Ugi amine was employed in the synthesis of planar chiral P/P, P/N and Se/N ligands. These compounds were attached through six-carbon spacers to an imidazolium moiety. Pd-complexes of these ligands were successfully used as catalysts for asymmetric allylic substitution in ionic liquids.

Keywords: Ferrocenyl phosphines; Immobilized catalysts;, Ionic liquids; Allylic substitutions; Chiral ligands.

Asymmetric catalysis is a dynamically developing field of modern chemistry. A variety of stereoselective transformations can be performed using transition metal complexes with chiral organic ligands[1]. Majority of these chiral complexes are used as homogeneous catalysts and their utilization often leads to highly effective and enantioselective reactions[2]. However, it is difficult or even impossible to reuse such, often very expensive, catalysts. Immobilization of the catalytic system appears as a possibility to circumvent this issue. Heterogeneous catalysts can have several advantages, such as easy separation of products and possibility of catalyst recycling[3]. On the other hand, heterogeneous systems often suffer from lower activities in comparison with homogeneous complexes. A possible solution to this problem could be utilization of homogeneous but supported catalyst. In this way catalysts can be immobilized in ionic liquids, soluble polymers or in fluorous phases[4].

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Numerous works describing application of transition metal complexes in ionic liquids are known in the literature. The area of asymmetric catalysis in ionic liquids has been reviewed recently[5]. Much less attention has been devoted to catalysts with covalently bound ionic moiety. Recently, several achiral imidazolium-tagged catalysts were described in the literature. Such catalysts were used in the Baylis–Hillman reaction[6], olefin metathesis[7–9], epoxidation[10], oxidation of alcohols[11], and Pd-catalyzed cross-couplings[12]. However, only a limited number of reports on chiral catalysts covalently immobilized to ionic liquids are known in the literature. Lee and coworkers attached chiral bisphosphane/Rh complex to imidazolium moieties and used the resulting catalyst in asymmetric hydrogenation in ionic liquid [bmim]SbF_6^+. The catalyst was successfully recycled up to four times with only a slight decrease in enantioselectivity and conversion[13]. Chiral vanadyl salen complex was anchored to imidazolium ion and used for enantioselective cyanosilylation of aldehydes[14]. Geldbach and Dyson described immobilized chiral ruthenium catalyst for transfer hydrogenation[15]. A proline-containing imidazolium moiety was shown to be an efficient organocatalyst for Michael addition of ketones to nitrostyrenes[16]. Recently, Doherty and co-workers published utilization of imidazolium-tagged bis(oxazolines) in copper-catalyzed Diels–Alder reaction[17].

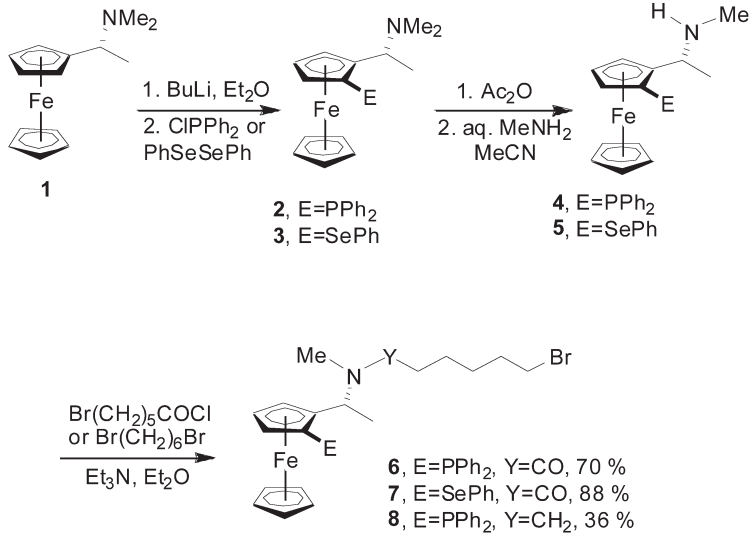
Nonracemic ferrocene derivatives have interesting stereochemical properties and many methods are established for their stereoselective synthesis. For these reasons ferrocenes represent an important class of chiral ligands for asymmetric catalysis[18,19]. Especially ferrocenyl phosphanes were proved to be valuable ligands for many transition metal catalyzed enantioselective reactions[20,21]. Several homogeneous ferrocene ligands were also used in ionic liquids. Toma and co-workers demonstrated that ferrocenyloxazolines are good catalysts for Pd-catalyzed allylic alkylation in ionic liquids[22,23]. Enantioselective hydroamination of activated olefins was catalyzed by the Ni-complex with ferrocene phosphane Pigiphos in various ionic liquids[24].

Herein we present preparation of new imidazolium-tagged ferrocene ligands and their application in Pd-catalyzed allylation reaction in ionic liquids.

+ *Abbreviations used*: bmim, 3-butyl-1-methyl-1*H*-imidazol-3-ium ligand; emim, 3-ethyl-1-methyl-1*H*-imidazol-3-ium ligand; BSA, *N*,*O*-bis(trimethylsilyl)acetamide; dba, dibenzylidene acetone ligand; DMM, dimethyl malonate; TMEDA, *N*,*N*,*N*′*N*′-tetramethylethylenediamine.

RESULTS AND DISCUSSION

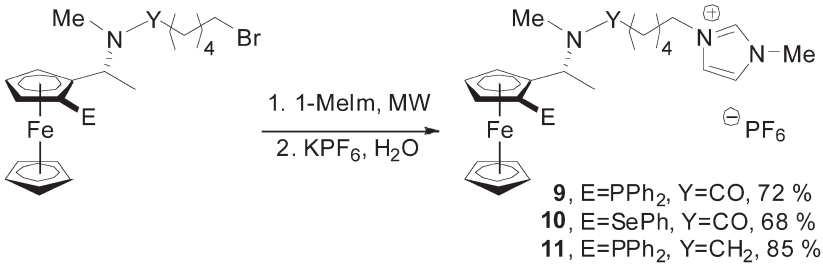
The synthesis of imidazolium-tagged ferrocenes starts with well-known diastereoselective *ortho*-lithiation of the Ugi amine **1** [25]. To introduce suitable donor atoms, $ClPPh_2$ and PhSeSePh were used as electrophiles affording derivatives **2** and **3** [26]. Using the fact that the nucleophilic substitution on α-carbon next to the ferrocene moiety proceeds with retention of configuration[27], we synthesized desired amines **4** [28] and **5** [29]. Subsequently, a six-carbon spacer was introduced via the reaction of corresponding amines with 6-bromohexanoyl chloride or 1,6-dibromohexane (Scheme 1).



SCHEME 1

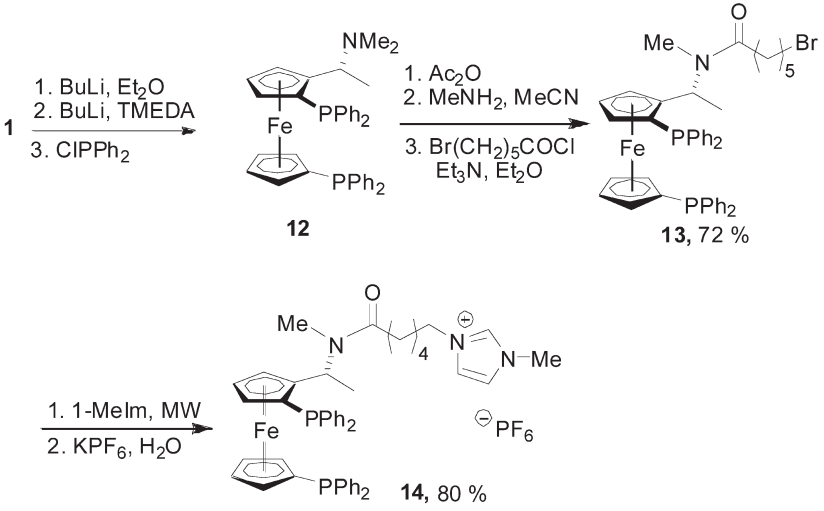
The bromo derivatives **6**–**8** were immobilized on an ionic liquid via alkylation of 1-methylimidazole under microwave irradiation. This reaction resulted in the formation of imidazolium salts with bromide anion, which, as we anticipated, could be detrimental to the catalytic reactions. Therefore, bromide anion was exchanged for a non-complexing hexafluorophosphate. Thus we prepared three new P/N and Se/N ferrocene ligands **9**–**11** with imidazolium moiety (Scheme 2).

The use of more than two equivalents of BuLi and addition of TMEDA to Ugi amine leads to functionalization of the second cyclopentadienyl ring. In this way we prepared diphosphane **12** [25], which was transformed by the above mentioned methods to bromide **13** and then into imidazolium-tagged diphosphane **14** (Scheme 3).



9, E=PPh_2, Y=CO, 72 %
10, E=SePh, Y=CO, 68 %
11, E=PPh_2, Y=CH_2, 85 %

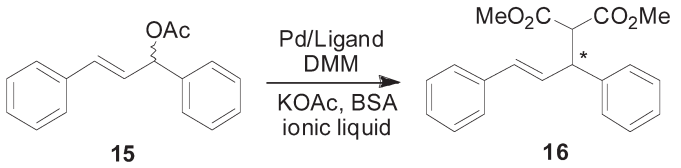
SCHEME 2



SCHEME 3

Catalytic nucleophilic substitution involving Pd-allyl intermediates is a powerful strategy for C–C bond formation[30]. Although palladium-catalyzed allylic substitution have been studied extensively, it is a useful benchmark reaction in ligand design[31]. We decided to evaluate utility of our new ligands in this asymmetric reaction. We used 1,3-diphenyl-1-acetoxypropene (**15**) as substrate and a nucleophile generated in situ from DMM with KOAc/BSA (Scheme 4).

The catalysts were prepared by mixing the Pd-precursor, $[Pd_2(dba)_3]\cdot CHCl_3$ or $[Pd(allyl)Cl]_2$ (2 mole % of Pd), with appropriate ligand in ionic liquid. The reaction was performed using standard conditions[32]. For initial study, we chose $[bmim]PF_6$ as reaction medium. Chart 1 depicts all the ionic liquids used in this study.



SCHEME 4

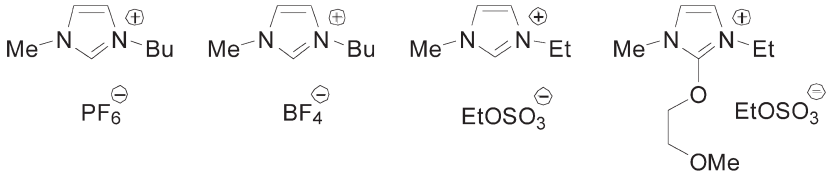


CHART 1

We started our investigation with ligand **9** and $[Pd_2(dba)_3]\cdot CHCl_3$ as Pd source. Even after 48 h at room temperature or at 75 °C, we did not isolate compound **16** from the reaction (Table I, entries 1 and 2). Exchange of Pd source for $[Pd(allyl)Cl]_2$ was more successful reaction, but the enantioselectivity of product **16** was only moderate (47% ee) (Table I, entry 3). The reaction with ligand **10**, which bears the PhSe group instead of diphenylphosphanyl group did not afford the desired product (Table I, entry 4).

Amino-phosphane ligand **11** proved to be more useful in this reaction. We obtained product **16** in 84% yield and with good enantioselectivity (60% ee) (Table I, entry 5). Using $[Pd_2(dba)_3]\cdot CHCl_3$ as Pd source led again to a considerable decrease in yield (6%) and enantioselectivity (15% ee). Interestingly, ligand **11** in combination with $[Pd(allyl)Cl]_2$ led preferentially to allylation product **16** of opposite configuration compared with the situation when ligand **11** was used with $[Pd_2(dba)_3]\cdot CHCl_3$ as a source of palladium (cf. Table I, entries 5 and 6). The necessity to use 2 mol of ligand **9** per 1 mol of Pd led us to the synthesis of diphosphane **14**. We found out that the Pd-complex of ligand **14** catalyzed formation of diester **16** in high yield (97%) and enantioselectivity (92% ee) (Table I, entry 8). To evaluate an effect of imidazolium moiety on the ligand performance in the reaction, we performed one catalytic experiment also with compound **13**. Allylation product **16** was also in this case obtained in good yield (85%) and the same

enantioselectivity (92% ee) as with ligand **14** (Table I, entry 7). Interestingly, enantioselectivity obtained with ligand **14** is higher than that of parent compound **12**. Hayashi[33] reported allylic substitution reaction of acetylacetone with substrate **15** and obtained enantioselectivity of 62% ee using ligand **12** in THF. Toma[22] used compound **12** in $[bmim]PF_6$ and observed similar 68% ee in the reaction of substrate **15** with DMM.

TABLE I
Alkylation of dimethyl malonate catalyzed by Pd-complexes in 3-butyl-1-methyl-1*H*-imidazol-3-ium hexafluorophosphate

Entry	Ligand	Pd-complex	Ligand/Pd	Time h	Yield of **16**[a] %	ee[b,c]
1	**9**	$[Pd_2(dba)_3]\cdot CHCl_3$	2:1	48	0	–
2	**9**	$[Pd_2(dba)_3]\cdot CHCl_3$	2:1	24	0[d]	–
3	**9**	$[Pd(allyl)Cl]_2$	2:1	48	24	47 (*R*)
4	**10**	$[Pd_2(dba)_3]\cdot CHCl_3$	1:1	48	0	–
5	**11**	$[Pd(allyl)Cl]_2$	1:1	48	84	60 (*S*)
6	**11**	$[Pd_2(dba)_3]\cdot CHCl_3$	1:1	48	6	15 (*R*)
7	**13**	$[Pd(allyl)Cl]_2$	1:1	22	85	92 (*S*)
8	**14**	$[Pd(allyl)Cl]_2$	1:1	22	97	92 (*S*)

All reactions were run at 1 mmol scale. [a] Purified product. [b] Determined by HPLC on Chiralpak AD-H. [c] Absolute configuration was assigned by comparison of optical rotation data with literature[35]. [d] Reaction performed at 75 °C.

We wondered whether our catalysts could be used also in other ionic liquids. An attempt to use ligand **9** with $[Pd_2(dba)_3]\cdot CHCl_3$ in $[bmim]BF_4$ was not successful. On the other hand, in $[emim]SO_4Et$ we isolated small amount of product **16** (24% yield) with moderate enantioselectivity (40% ee). When we reused ionic liquid with catalyst ($[bmim]PF_6$ + $[Pd(allyl)Cl]_2$ + ligand **14**) we observed considerable decrease in reactivity of the allylic substitution reaction. Only small amount of product **16** (32% yield, 77% ee) was obtained after 4 days. Therefore, we questioned the effect of ionic liquid structure on the reaction. Hydrogen in the position 2 on the imidazolium moiety is rather acid, and formation of Pd-carbene complexes were documented in the literature[34]. For this reason we performed allylation with ligand **14** in an ionic liquid with substituted position 2 ($[2\text{-R-emim}]SO_4Et$). With freshly prepared catalyst Pd/**14**, the allylation product **16** was obtained in excellent

yield (96%) but with only moderate enantioselectivity (64% ee) (Table II, entry 1). The reused catalytic system was less active, but product **16** was still obtained in a fair yield of 52% and with only a small decrease in enantioselectivity (58% ee). The third run with this system, however, afforded only traces of allylation product **16** (Table II, entries 2 and 3). Surprisingly, the allylation reaction in similar [emim]SO_4Et led to better results, both in terms of yield and enantioselectivity (Table II, entries 4–6). Therefore, it is likely that there is another reason for decrease in activity of the catalyst after the first run, than the originally suspected Pd-carbene formation. This could be palladium leaching from the reaction media during the work-up. The test results with ligand **14** in different ionic liquids are summarized in Table II.

TABLE II
Alkylation of dimethyl malonate catalyzed by **14**/Pd-complex in ionic liquids

Entry	Run	Ionic liquid	Time h	Yield of **16**[a] %	ee[b]
1	1st	[2-R-emim]SO_4Et	24	96	64 (*S*)
2	2nd	[2-R-emim]SO_4Et	24	52	58 (*S*)
3	3rd	[2-R-emim]SO_4Et	48	0	–
4	1st	[emim]SO_4Et	24	94	89 (*S*)
5	2nd	[emim]SO_4Et	24	57	77 (*S*)
6	3rd	[emim]SO_4Et	24	16	69 (*S*)

All reactions were run at 1 mmol scale. [a] Purified product. [b] Determined by HPLC on Chiralpak AD-H.

To summarize, we have prepared several new ferrocenylphosphane ligands tagged with imidazolium moiety. The Pd-complex of diphosphane **14** proved to be useful catalyst for asymmetric allylic substitution in ionic liquids. Further development of ligand structure and investigation of applications of other ionic liquids to improve recycling of the catalytic system are under way in our laboratory.

EXPERIMENTAL

All reactions were carried out in inert atmosphere of N_2 or Ar. The solvents were purified by standard methods. Reactions with BuLi were carried out using standard Schlenk techniques. NMR spectra were recorded on a Varian Mercury plus instrument (300 MHz for ^{1}H, 75 MHz for ^{13}C and 121.5 MHz for ^{31}P). Chemical shifts (δ) are given in ppm relative to tetra-

methylsilane for ^{1}H NMR, relative to residual solvent peak for ^{13}C NMR and relative to H_3PO_4 as external standard for ^{31}P NMR. Coupling constants (*J*) are given in Hz. Specific optical rotations were measured on Perkin–Elmer instrument and are given in deg cm^3 g^{-1} dm^{-1}. Column chromatography was performed on Merck silica gel 60. Thin layer chromatography was performed on Merck TLC-plates silica gel 60, F254. Enantiomeric excesses were determined by HPLC on Chiralpak AD-H (Daicel Chemical Industries) column using hexane/i-PrOH 9:1 as a mobile phase and detection with UV-detector at 254 nm. IR spectra are given in cm^{-1}. Mass spectra were recorded on Waters Premium QTOF instrument. Compounds **2**–**5** and **12** were synthesized according to literature procedures[25,26,28,29].

Preparation of Amines **6**–**8**. General Procedure 1

The amine **5** (927 mg, 2.33 mmol) and Et_3N (0.49 ml, 354 mg, 3.50 mmol) were dissolved in anhydrous Et_2O (30 ml). Into this solution $Br(CH_2)_5COCl$ (747 mg, 3.50 mmol) was added dropwise with syringe and the resulting mixture was stirred at room temperature for 1 h. White precipitate was formed after addition. Aqueous 1 M NaOH (25 ml) was added and phases were separated. The aqueous phase was extracted with Et_2O. The organic extract was dried (anhydrous Na_2SO_4) and concentrated. The crude product was purified by column chromatography.

(R,S$_p$)-6-Bromo-N-{1-[2-(diphenylphosphanyl)ferrocen-1-yl]ethyl}-N-methylhexanamide (**6**). The crude material obtained by general procedure 1 was purified by column chromatography (SiO_2, hexane/EtOAc 9:1). Pure compound **6** (986 mg, 70%) was isolated as an orange oil. $[\alpha]_D$ –239 (*c* 0.50, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$), peaks of minor rotamer are in italics: 7.16–7.58 m, 10 H (Ph); 6.16 dq, *J* = 6.6, 1.7, 1 H (CH); *5.31 q*; 4.48–4.49 m, 1 H (CH_{Fc}); *4.36 t*; 4.32 t, *J* = 2.5, 1 H (CH_{Fc}); *4.07 s*, 4.05 s, 5 H (Cp); *3.83 t*, 3.79 t, *J* = 2.2, 1 H (CH_{Fc}); *3.43 m*, 3.35 t, *J* = 6.9, 2 H (CH_2); *2.23 s*, 2.17 s, 3 H (N-CH_3); *1.54 d*, 1.43 d, *J* = 6.7, 3 H (CH_3); 1.90–0.82 m, 8 H. ^{13}C NMR (75 MHz, $CDCl_3$): 170.6; 139.7 d, *J* = 12.3; 137.1 d, *J* = 10.3; 135.0 d, *J* = 21.2; 132.6 d, *J* = 19.5; 129.2–127.9; 93.4 d, *J* = 25.8; 72.3 d, *J* = 4.9; 70.3 d, *J* = 4.3; 70.0; 68.9; 47.2 d, *J* = 8.3; 33.7; 32.8; 31.9; 28.6; 23.1; 16.0. ^{31}P NMR (121.5 MHz, $CDCl_3$): *–24.6*, –26.7. HR-MS (ESI), *m/z*: calculated for $C_{31}H_{36}BrFeNOP$ (MH^+) 604.1094, found 604.0618.

(R,S$_p$)-6-Bromo-N-{1-[2-(phenylselanyl)ferrocen-1-yl]ethyl}-N-methylhexanamide (**7**). Column chromatography of the crude product obtained by general procedure 1 (SiO_2, hexane/EtOAc 9:1) afforded pure bromide **7** (1.18 g, 88%) as a yellow oil. $[\alpha]_D$ –53.9 (*c* 0.54, $CHCl_3$). IR (neat): ν(CO) 1641. ^{1}H NMR (300 MHz, $CDCl_3$), peaks of minor rotamer are in italics: 7.07 m, 5 H (Ph); 5.93 q, *J* = 6.9, 1 H (CH); *5.20 q*, *J* = *6.79*; 4.53 m, 1 H (CH_{Fc}); 4.41 m, 2 H (CH_{Fc}); *4.23*, 4.22 s, 5 H (Cp); 3.38 t, *J* = 6.88, 2 H (CH_2); *2.34*, 2.18 s, 3 H (N-CH_3); *1.52*, 1.39 d, *J* = 6.9, 3 H (CH_3); 1.88–1.62 m, 3 H; 1.44–1.36 m, 1 H; 1.28–1.06 m, 4 H. ^{13}C NMR ($CDCl_3$, 75 MHz): 171.0; 135.3, *133.7*; *128.9*, 128.5; *128.1*, 128.0; *126.0*, 125.3; 92.2, *91.8*; 77.9, *77.7*, *70.3*, 70.2, 70.1, *69.9*, *69.6*, 69.4, *69.3*, 69.2, *50.9*, 47.5, *34.0*, 33.9, 32.9, *32.8*, 32.7, *32.6*, 28.7, *28.1*, 27.8, *26.5*, *24.0*, 23.6, *17.9*, 16.0. HR-MS (ESI), *m/z*: calculated for $C_{25}H_{31}BrFeNOSe$ (MH^+) 576. 0078, found 575.9714.

(R,S$_p$)-1-{1-[(6-Bromohexyl)methylamino]ethyl}-2-(diphenylphosphanyl)ferrocene (**8**). Amine **4** (250 mg, 0.585 mmol) was dissolved in CH_3CN (15 ml), and K_2CO_3 (84 mg, 0.614 mmol) and 1,6-dibromohexane (178 µl, 286 mg, 1.17 mmol) were added into this solution. The resulting mixture was refluxed for 2 h and then stirred at room temperature for 18 h. The solution was diluted with H_2O (50 ml) and extracted with *t*-BuOMe (2 × 20 ml). The combined

organic extracts were washed with brine, dried with anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 19:1 + 0.5% Et_3N). The pure product **8** (124 mg, 36%) was obtained as an orange oil. $[\alpha]_D$ –160 (*c* 0.63, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 7.57 m, 2 H (Ph); 7.36 m, 3 H (Ph); 7.14 m, 5 H (Ph); 4.39 dd, *J* = 3.4, 2.1, 1 H (CH_{Fc}); 4.26 m, 2 H (CH_{Fc}); 3.91 s, 5 H (Cp); 3.85 m, 1 H (CH_{Fc}); 3.32 t, *J* = 7.0, 2 H (CH_2); 2.29 td, *J* = 11.5, 7.3, 1 H; 2.14 ddd, *J* = 11.6, 7.8, 6.0, 1 H; 1.70 s, 3 H (N-CH_3); 1.66 m, 2 H (CH_2); 1.26 d, *J* = 6.7, 3 H (CH_3); 1.19 m, 2 H (CH_2); 1.00–0.77 m, 4 H. ^{13}C NMR (75 MHz, $CDCl_3$): 141.8 d, *J* = 7.9 (P-C_{Ph}); 139.5 d, *J* = 9.0 (P-C_{Ph}); 135.9 d, *J* = 21.6 (CH_{Ph}); 132.8 d, *J* = 17.8 (CH_{Ph}); 129.3 (CH_{Ph}); 128.3 d, *J* = 7.7 (CH_{Ph}); 127.8 d, *J* = 6.2 (CH_{Ph}); 127.5 (CH_{Ph}); 97.7 d, *J* = 23.9 (C_{Fc}); 76.6 d, *J* = 9.1 (C_{Fc}); 72.33 (CH_{Fc}); 72.28 (CH_{Fc}); 70.1 (Cp); 69.0 (CH_{Fc}); 58.0 d, *J* = 7.3 (N-CH); 54.8 (CH_2); 34.7 (CH_2); 34.4 (N-CH_3); 33.2 (CH_2); 28.6 (CH_2); 27.8 (CH_2); 26.8 (CH_2); 9.2 (CH_3). ^{31}P NMR ($CDCl_3$, 121.5 MHz): –23.2. HR-MS (ESI), *m/z*: calculated for $C_{31}H_{38}BrFeNOP$ (MH^+) 590.1250, found 590.0762.

Preparation of Imidazolium Salts **9**–**11**. General Procedure 2

Bromide **10** (238 mg, 0.403 mmol) was dissolved in 1-methylimidazole (321 µl, 4.03 mmol) and the resulting solution was subjected to microwave irradiation (10 × 10 s, 650 W) under N_2 atmosphere. After cooling, the resulting mixture was washed with Et_2O (5 × 5 ml). The oily residue was dissolved in MeOH (10 ml), the solution was filtered through Celite, and the filtrate was concentrated. The crude product was dissolved in degassed deionized H_2O (40 ml). Into this, KPF_6 (103 mg, 0.558 mmol) in H_2O (5 ml) was added and the resulting solution was stirred at room temperature for 18 h. The pale yellow precipitate was filtered off and washed with H_2O (100 ml). The solid was dissolved in EtOAc, dried (Na_2SO_4), and this solution was filtered through celite and concentrated. The residue was dried in vacuo.

(R,S$_p$)-3-[6-({1-[2-(Diphenylphosphanyl)ferrocen-1-yl]ethyl}methylamino)-6-oxohexyl]-1-methyl-1H-imidazol-3-ium hexafluorophosphate (**9**). General procedure 2 gave compound **9** (198 mg, 72%) as a yellow solid. M.p. 86–95 °C. $[\alpha]_D$ –300 (*c* 0.77, $CHCl_3$). IR (neat): ν(CO) 1626. ^{1}H NMR (300 MHz, $CDCl_3$), peaks of minor rotamer are in italics: 8.79 s, 1 H (Im); 7.34–6.92 m, 12 H (Ph); 6.12 q, *J* = 6.9, 1 H (CH); *5.35 q*; 4.50 dd, *J* = 2.6, 1.4, 1 H (CH_{Fc}); *4.38 t*, 4.33 t, *J* = 2.4, 1 H (CH_{Fc}); *4.07 s*, 4.05 s, 5 H (Cp); 4.04 m, 2 H; 3.99 s, 3 H (Me_{Im}); *3.90 s*; 3.78 m, 1 H; *2.24 s*, 2.19 s, 3 H (NCH_3); 1.77 m, 4 H; *1.54 d*, 1.42 d, *J* = 7.2, 3 H (CH_3); 1.28–1.06 m, 4 H. ^{13}C NMR (75 MHz, $CDCl_3$): 171.1; 139.6; 137.0; 136.5; 135.1 d, *J* = 26.0; 132.4 d, *J* = 19.8; 129.5–128.1; 123.6; 122.6; 93.4 d, *J* = 25.9; 72.5; 70.2; 70.1; 69.2; 49.7; 47.2; 36.5; 32.2; 29.8; 28.7; 25.5; 23.3; 16.3. ^{31}P NMR (121.5 MHz, $CDCl_3$): *–24.2*, –25.5, –143.8 sep, *J* = 712 (PF_6). HR-MS (ESI), *m/z*: calculated for $C_{35}H_{41}FeN_3OP$ (M^+) 606.2331, found 606.234.

(R,S$_p$)-1-[6-({1-[2-(Phenylselanyl)ferrocen-1-yl]ethyl}methylamino)-6-oxohexyl]-1-methyl-1H-imidazol-3-ium hexafluorophosphate (**10**). General procedure 2 gave product **12** (491 mg, 68%) as a yellow foam. $[\alpha]_D$ –49.8 (*c* 0.59, $CHCl_3$). IR (neat): ν(CO) 1626. ^{1}H NMR (300 MHz, $CDCl_3$), peaks of minor rotamer are in italics: 8.72 s, 1 H (CH_{Im}); 7.34 t, *J* = 1.8, 1 H (CH_{Im}); 7.30 m, 1 H (CH_{Im}); 7.13–6.93 m, 5 H (Ph); 5.90 q, *J* = 6.9, 1 H (CH); *5.19 q*; 4.52 dd, *J* = 2.3, 1.5, 1 H (CH_{Fc}); 4.43 m, 2 H (CH_{Fc}); *4.23 s*, 4.21 s, 5 H (Cp); 4.12 t, *J* = 7.2, 2 H (CH_2); 3.95 s, 3 H (Me_{Im}); *3.90 s*; *2.34 s*, 2.21 s, 3 H (NMe); 1.76 m, 4 H (CH_2); *1.52 d*, 1.39 d, *J* = 6.9, 3 H (CH_3); 1.26–1.02 m, 4 H (CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): 171.2, 136.5, 135.3, 128.9, 128.0, 125.7, 123.6, 122.5, 92.3, 78.1, 70.4, 70.1, 69.7, 69.6, 49.8, 47.7, 36.5, 32.5, 29.8, 28.8, 25.5, 23.4, 16.3. HR-MS (ESI), *m/z*: calculated for $C_{29}H_{36}FeN_3OSe$ (M^+) 578.1406, found 578.0417.

(R,S$_p$)-3-[6-{1-[2-(Diphenylphosphanyl)ferrocen-1-yl]ethyl}methylaminohexyl]-1-methyl-1H-imidazol-3-ium hexafluorophosphate (**11**). General procedure 2 gave product **11** (252 mg, 85%) as a yellow foam. $[\alpha]_D$ –188 (*c* 0.42, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 8.59 s, 1 H (CH_{Im}); 7.58 m, 2 H (Ph); 7.37 m, 3 H (Im, Ph); 7.21 t, *J* = 1.8, 1 H (CH_{Im}); 7.14 m, 3 H (Ph); 7.09 m, 3 H (Ph); 4.40 m, 1 H (CH); 4.27 t, *J* = 2.4, 1 H (CH_{Fc}); 4.24 dd, *J* = 6.7, 2.8, 1 H (CH_{Fc}); 4.10 dd, *J* = 13.9, 6.9, 1 H (CH_{Fc}); 4.02 m, 2 H (CH_2); 3.92 s, 3 H (Me_{Im}); 3.90 s, 5 H (Cp); 3.87 m, 1 H; 2.36–2.13 m, 2 H; 1.73 s, 3 H (NMe); 1.61 m, 4 H; 1.39 m, 1 H; 1.28 d, *J* = 6.7, 3 H (CH_3); 1.08 m, 2 H. ^{13}C NMR (75 MHz, $CDCl_3$): 141.4 d, *J* = 8.2; 138.9 d, *J* = 8.7; 136.1, 135.5 d, *J* = 21.8; 132.2 d, *J* = 17.5; 128.9, 127.9 d, *J* = 7.9; 127.3 d, *J* = 6.1; 127.1, 123.5, 121.9, 96.9 d, *J* = 24.7; 76.0 d, *J* = 9.4; 71.8 d, *J* = 5.5; 69.7 d, *J* = 4.4; 69.6, 68.7, 57.5 d, *J* = 7.5; 54.1, 50.0, 36.2, 33.8, 29.7, 27.0, 26.3, 25.9, 9.8. ^{31}P NMR (121.5 MHz, $CDCl_3$): –22.6, –143.7 sep, *J* = 713 (PF_6). HR-MS (ESI), *m/z*: calculated for $C_{25}H_{30}BrFeNOSe$ (M^+) 592.2578, found 592.1627.

(R,S$_p$)-6-Bromo-N-{1-[2,1′-bis(diphenylphosphanyl)ferrocen-1-yl]ethyl}-N-methylhexanamide (**13**). $[\alpha]_D$ –263 (*c* 0.80, $CHCl_3$). IR (neat): ν(CO) 1618. ^{1}H NMR (300 MHz, $CDCl_3$), peaks of minor rotamer are in italics: 7.42 m, 3 H (Ph); 7.33–7.21 m, 15 H (Ph); 7.14 m, 2 H (Ph); 6.02 m, 1 H (CH); *5.23 m*; 4.52 m, 1 H (CH_{Fc}); 4.45 m, 1 H (CH_{Fc}); 4.10 m, 3 H (CH_{Fc}); 3.60 m, 2 H; *3.43 t*, 3.37 t, *J* = 6.8, 2 H (CH_2); *2.18 s*, 2.17 s, 3 H (NMe); *1.89 m*, 1.76 m, 2 H; 1.54 m, 2 H; *1.41 d*, 1.30 d, *J* = 6.9, 3 H (CH_3); 1.20 m, 2 H; 0.94 m, 2 H. ^{13}C NMR (75 MHz, $CDCl_3$): 171.0 d, *J* = 15.2; *170.9 d*, *J* = *29.6*; 139.2 dd, *J* = 21.0, 10.6; 137.5 dd, *J* = 122.6, 9.8; *135.0 d*, *J* = *22.5*; 134.9 d, *J* = 21.5; 133.6 d, *J* = 20.0; 133.0 d, *J* = 19.1; 132.4 dd, *J* = 19.8, 7.6; 130.0 dd, *J* = 12.4, 5.4; 128.5 d, *J* = 21.5; 128.4 d, *J* = 88.5; 128.1 d, *J* = 20.7; 128.06 d, *J* = 6.5; 120.6 d, *J* = 14.4; 119.4 d, *J* = 16.3; *96.3 d*, *J* = *25.2*; 94.2 d, *J* = 25.6; 79.9 d, *J* = 14.6; 75.5 d, *J* = 20.2; *75.4 d*, *J* = *19.7*; 74.4 d, *J* = 14.6; 73.5 d, *J* = 2.4; 73.1 d, *J* = 8.7; 72.3 d, *J* = 3.5; 72.2; 71.0 d, *J* = 2.0; 69.9; 60.4; 34.0 d, *J* = 8.2; 32.7; *32.6*; 27.8; *27.7*; 23.5; *23.4*; 21.1; *15.9*; 15.8; 14.2. ^{31}P NMR (121.5 MHz, $CDCl_3$): –18.1, –27.3. HR-MS (ESI), *m/z*: calculated for $C_{43}H_{45}BrFeNOP_2$ (MH^+) 788.1484, found 788.1261.

(R,S$_p$)-3-[6-({1-[2,1′-Bis(diphenylphosphanyl)ferrocen-1-yl]ethyl}methylamino)-6-oxohexyl]-1-methyl-1H-imidazol-3-ium hexafluorophosphate (**14**). General procedure 2 gave product **14** (164 mg, 80%) as a yellow foam. $[\alpha]_D$ –282 (*c* 0.33, $CHCl_3$). IR (neat): ν(CO) 1634. ^{1}H NMR (300 MHz, $CDCl_3$), peaks of minor rotamer are in italics: 8.75 s, 1 H (Im); 7.43–7.20 m, 20 H (Ph, Im); 7.04 m, 2 H (Ph); 6.01 q, *J* = 7.2, 1 H (CH); *5.25 q*, 4.50 m, 1 H (Fc); 4.45 m, 1 H (Fc); 4.16 m, 3 H (Fc); 4.07 t, *J* = 6.7, 2 H (CH_2); 3.96 s, 3 H (Im-CH_3); 3.63 m, 1 H; 3.58 m, 1 H; *2.20 s*, 2.15 s, 3 H (N-CH_3); 1.76 m, 2 H; 1.61 m, 2 H; 1.40 m, 2 H; 1.31 d, *J* = 6.9, 3 H (CH_3); 1.07 m, 2 H. ^{13}C NMR (75 MHz, $CDCl_3$): 170.7, *170.6* (CO); 139.2 d, *J* = 21.7; 139.1; 138.3 d, *J* = 9.6; 137.9; 136.6 d, *J* = 9.6; *135.0*, 134.9 d, *J* = 21.5; 133.6 d, *J* = 20.0; *133.2*, 133.1 d, *J* = 19.1; 132.4 d, *J* = 19.6; *131.9*; 128.9 d, *J* = 30.9; 128.2 d, *J* = 37.2; 128.16 d, *J* = 15.8; 128.14; 128.1 d, *J* = 16.4; 123.3; 122.2 (Ph, Im); 94.0 d, *J* = 25.6 (C_{Fc}); 76.9 d, *J* = 5.9 (C_{Fc}); 76.8 (CH_{Fc}); 75.5 d, *J* = 19.8 (CH_{Fc}); *75.4 d*; 74.4 dd, *J* = 4.7, 1.8 (CH_{Fc}); 73.4; 73.2 d, *J* = 5.4 (C_{Fc}); 73.1; 72.3 dd, *J* = 3.6, 1.3 (CH_{Fc}); 71.2 d, *J* = 1.9 (CH_{Fc}); 69.9 (CH); 49.6, *49.4* (CH_2); 36.6 (CH_3); 32.2 (CH_2); *30.6*, 30.0 (CH_2); 26.6 (CH_2); 25.6 (CH_2); *23.5*, 23.2 (CH_2); *17.5*, 16.0 (CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): –17.3, *–17.5*; *–25.6*, –26.7; –143.7 sep, *J* = 713 (PF_6). HR-MS (ESI), *m/z*: calculated for $C_{47}H_{50}FeN_3OP_2$ (M^+) 790.2813, found 790.1541.

Allylic Alkylation

Ligand (0.020 mmol) and $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol) were dissolved in an ionic liquid (2 ml) and stirred at room temperature for 30 min. To this solution compound **15** (252 mg, 1.00 mmol), BSA (0.49 ml, 407 mg, 2.00 mmol), DMM (0.23 ml, 264 mg, 2.00 mmol) and KOAc (5 mg, 0.050 mmol) were added. The resulting mixture was stirred at room temperature and monitored by TLC. When no starting material could be detected, or after 48 h, the solution was extracted with toluene (10 × 5 ml). Combined organic extracts were concentrated and the residue purified by column chromatography (SiO_2, hexane/EtOAc 9:1). The enantiomeric excess was determined by HPLC (AD-H, hexane/i-PrOH 90:10, 0.5 ml/min); t_R 16.10 min (*R*), t_R 22.02 min (*S*). $[\alpha]_D$ –14.4 (*c* 0.72, $CHCl_3$), 92% ee (*S*); ref.[26] $[\alpha]_D$ –19.6 (*c* 0.55, $CHCl_3$), 96% ee (*S*). ^{1}H NMR (300 MHz, $CDCl_3$): 7.35–7.20 m, 10 H (Ph); 6.50 d, *J* = 15.8, 1 H (=CH); 6.33 dd, *J* = 15.7, 8.5, 1 H (=CH); 4.27 dd, *J* = 10.9, 8.5, 1 H (CH); 3.95 d, *J* = 10.9, 1 H (COCHCO); 3.71 s, 3 H (OCH_3); 3.52 s, 3 H (OCH_3).

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