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Isomerization of Ferrocenyl Phosphinites to Phosphane-oxides and retro-Phospha-Brook Rearrangement

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ABSTRACT

Ferrocene-containing phosphorus derivatives are important as ligands in transition-metal catalysis. We have investigated the synthesis of ferrocene-based phosphanes from corresponding phosphinites via retro-phospha-Brook rearrangement. Ferrocenyl phosphinites isomerize to thermodynamically more stable phosphine oxides. Interestingly, retro-phospha-Brook rearrangement proceeds on the adjacent phenyl ring with the assistance of the ferrocenyl moiety. DFT calculations provided insight into the reaction mechanisms of these transformations. Isomerization probably proceeds intramolecularly with the participation of developing charge stabilization with ironś d-orbitals. BH_3 complexation seems to favor the phosphinite structure as was evidenced by ^{31}P-^{11}B scalar coupling. Retro-phospha-Brook rearrangement also likely proceeds as intramolecular migration of the phosphanyl group from oxygen to carbon, from both BH_3 complexes and the uncomplexed starting material.

1. Introduction

Ferrocene derivatives are invaluable as materials, pharmaceuticals, and catalysts [1]. Chiral ferrocene compounds serve as highly efficient catalysts for many transformations [2]. Phosphorus-containing ligands have found the widespread use in metal-catalyzed reactions. Chiral ferrocene phosphanes are a privileged ligand class for many transformations in asymmetric catalysis, including chemical industry applications [3–11]. Diphosphanes such as Josiphos, [12] Taniaphos, [13–15] or Walphos [16] are prototypical catalysts. Rich coordination chemistry of ferrocenyl phosphorus compounds is in the center of interest of many chemists as well [17–20]. Recently, ferrocene-based nitrogen and phosphorus derivatives became useful as nucleophilic organocatalysts, thus sidestepping the need for transition metal catalysts [21]. Given this interest, a variety of preparative methods were developed for synthesis and transformations of ferrocenyl phosphorus derivatives [22].

Recently, we have investigated the retro-Brook rearrangement of ferrocenyl silyl ethers as a means to obtain new ferrocenyl silicon derivatives [23]. Bromine-lithium exchange or *ortho*-lithiation produced suitably positioned carbanions that acted as nucleophilic centers and initiated an attack on the silyl group in the retro-Brook rearrangement. Motivated by these results, we have decided to investigate the possibility of performing a related retro-phospha-Brook rearrangement on ferrocenyl derivatives. The successful application of retro-phospha-Brook rearrangement would constitute a new strategy to obtain valuable ferrocenyl phosphorus derivatives.

Brook rearrangement is typically a migration of a silyl group between carbon and oxygen [24–26]. The transfer of the silyl group from oxygen to carbon is termed retro-Brook rearrangement. Brook rearrangement has been instrumental also in asymmetric synthesis, [27] and natural product synthesis [28]. Besides silicon, other heteroatoms can promote rearrangements as well. Arguably, the transfer of phosphorus groups is one of the most relevant from a synthetic point of view as it leads to useful organophosphorus derivatives. Phospha-Brook rearrangement was described in several instances where a carbanion was generated at a suitable distance from the phosphorus group [29–36]. Recently, Terada and coworkers showed that [1,2]-phospha-Brook rearrangement generated α-oxygenated propargyl anions that engaged in a Mannich or aldol type additions, which ultimately provided access to pyrroles and furan derivatives [37,38]. This type of Brook rearrangement was also utilized in the formation of allylic alcohols from α,β-epoxyketones [39]. Carbanions generated by [1,2]-phospha-Brook rearrangement were employed in aromatic nucleophilic substitutions of fluoroarenes [40]. Base-catalyzed phospha-Brook rearrangement of isatine and diethyl phosphite afforded intermediate electrophilic species that underwent a Friedel–Crafts alkylation. In this way, α-aryl oxindoles were obtained in a one-pot procedure [41]. However, phospha-Brook rearrangement has never been used for the synthesis of ferrocenyl phosphorus derivatives.

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In this context, we decided to study the utilization of Br-Li exchange-initiated retro-phospha-Brook rearrangement as a possible means for the synthesis of ferrocenyl phosphane derivatives. Herein, we describe the results of our experimental and DFT investigation of phosphinite - phosphane-oxide isomerization and retro-phospha-Brook rearrangement of selected ferrocenyl derivatives.

2. Results and Discussion

We have started our investigation by a synthesis of ferrocenyl alcohol **2** using literature procedures [15]. Racemic alcohol **2** was obtained in 71% yields by reduction of the corresponding ferrocenyl ketone **1** (Scheme 1). This ferrocenyl ketone was obtained by Friedel-Crafts acylation of ferrocene. With racemic ferrocenyl alcohol **2** in our hands, we have tried to synthesize the corresponding phosphinite **3** by a reaction with chlorodiphenylphosphine under various conditions. The reactions with Ph_2PCl in toluene, with Et_3N or BuLi as base were not successful. The best reaction conditions comprised Ph_2PCl, 4-dimethylaminopyridine (DMAP), and Et_3N in dichloromethane (DCM). Interestingly, the spectral characteristics, in particular NMR data, of the obtained compound matched more closely with corresponding phosphane-oxide **4** than with expected phosphinite **3** (Scheme 1).

NMR spectroscopic characteristics of compound **4** resemble those of similar ferrocenyl phosphane-oxides obtained by a different method [42]. We have calculated the chemical shifts for phosphinite **3** and phosphane-oxide **4** at the ωB97X-D/6-31G* level. DFT calculated chemical shifts of phoshane-oxide **4** are closer to the experimental ones. Key NMR characteristics are gathered in Table 1.

Compound *rac*-**4** afforded base-induced phospha-Brook rearrangement when treated with three equivalents of *n*BuLi (Scheme 2a). The corresponding alcohol **5** was obtained in 26% isolated yield. This result is surprising as phospha-Brook rearrangement is expected to proceed via a phosphinite. In another attempt to obtain ferrocenyl phosphinites, we have tried to stabilize the resulting phosphinite via coordination with BH_3. Alcohol **2** was treated with chlorodiphenylphosphine in the presence of DMAP and triethylamine and then with dimethylsulfide-borane complex. Even though in only low isolated yield (25%), we have obtained the corresponding BH_3-complex of phosphinite **3**. In addition to this product, 40% of 2-bromobenzylferrocene (**6**) and 15% of uncomplexed **3** were obtained (Scheme 2b). 2-Bromobenzylferrocene probably resulted from the secondary reduction of the alcohol with borane.

Experimental evidence in favor of BH_3-complexed phosphinite derivative was obtained by ^{31}P NMR. The scalar nuclear spin-spin coupling between ^{31}P and ^{11}B nuclei is an indication of a dative bond in BH_3-complexed phosphanes [43]. Indeed, such coupling, with a constant $^1J_{PB}$ = 42 Hz, was observed in BH_3-complexed compound **3**. This result hints at a partly covalent bond between phosphorus and boron.

As an alternative, Arbusov-type reaction can be considered on phosphinite **3** involving intermolecular nucleophilic attack of phosphorus on the αC. We think that it is unlikely because such an event should produce a mixture of **3** and **4** that we did not observe. Furthermore, these kind or reactions usually require higher temperature and S_N2 reaction at the αC next to the ferrocene moiety is also unlikely.

Phospha-Brook rearrangement proceeded on BH_3-complexed phosphinite BH_3.**3** as well, however alcohol **5** was obtained only in 11% yield along with 17% of a debrominated compound **7**. Compound **7** was likely formed via protodelithiation from an organolithium intermediate, which was formed via Br-Li exchange (Scheme 2b).

To gain insight into the details of the phosphinite – phosphane-oxide isomerization, we have carried out DFT calculations. Optimized structures were obtained using long-range corrected hybrid density ωB97X-D functional [44]. This functional performs well for both main group elements as well as for organometallic compounds. Geometry optimizations were performed with LACVP basis set, which combines Hay and Wadtś LANL2DZ effective core basis set for Fe, [45] and 6-31G* basis set for all other atoms. Energies were refined at ωB97X-D/6-311+G** level using C-PCM scheme to account for solvent effects (dichloromethane). [46].

DFT calculations suggest that isomerization of phosphinite **3** to the corresponding phosphane-oxide **4** proceeds via a cyclic transition state (Scheme 3a). Developing a positive charge on the α-carbon might be stabilized by donor-acceptor orbital interaction with d-electrons of iron. Similar orbital interactions were described in related compounds by computational methods as well as X-ray crystallography [47–50].

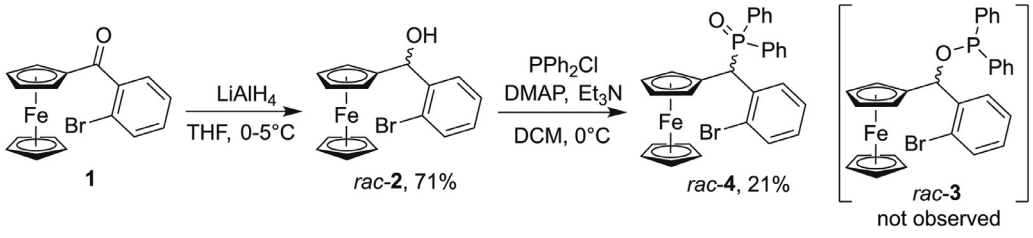
DFT calculations (ωB97X-D/LACVP//ωB97X-D/6-311+G**(DCM)) suggest that phosphane-oxide form **4-H** is 84.5 kJ/mol more stable than the model phosphinite **3-H**. The difference is even more pronounced in brominated phosphane-oxide **4-Br**, which is even more stable (106.2 kJ/mol) than the corresponding phosphinite **3-Br** (Scheme 3b).

The natural charge on the α-carbon in the transition state **TS-isom-H** is +0.170 (ωB97X-D/6-311+G** (DCM)). In comparison, α-carbon in the corresponding carbocation has a natural charge +0.017. To visualize the stabilization of the transition state of the isomerization via Fe-CH interaction, we have used intrinsic bond orbitals (IBO) [51,52]. Scheme 3c shows IBOs for the Fe-CH

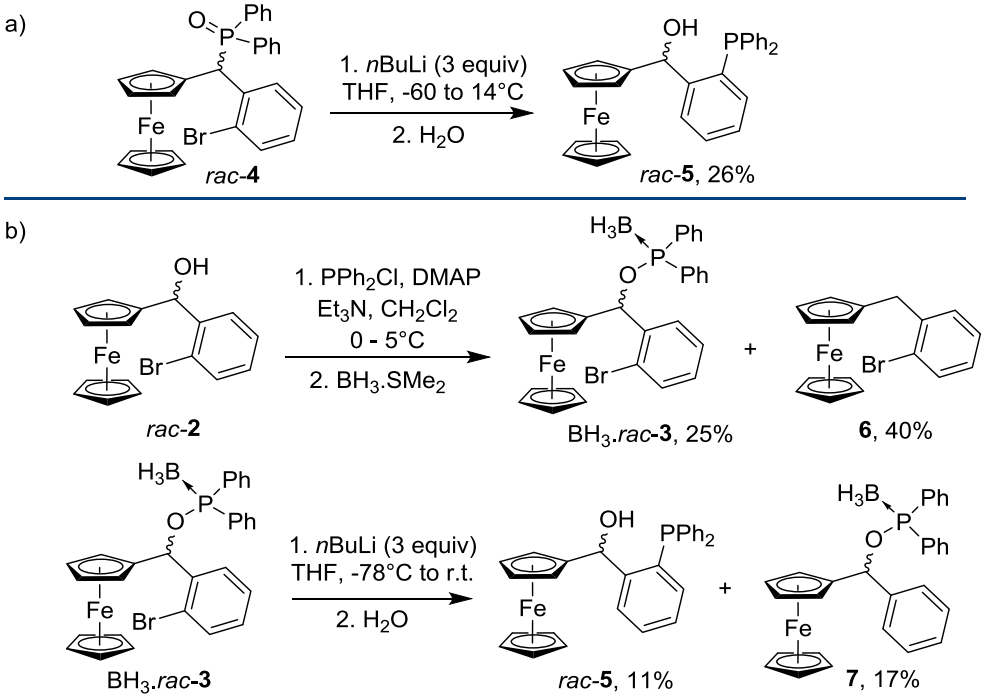
Table 1
Comparison of selected NMR characteristics of compound **4** with similar phosphane-oxides.

Compound	δ^P [ppm]	$\delta^C(\alpha C)$ [ppm]	$^1J_{PC}$ [Hz]	δ^H [ppm]	$^2J_{PH}$ [Hz]
rac-**4** (experimental)	30.9	45.9	63.0	5.12	9.2
rac-**4** (DFT)[a]	126.7	43.8		4.15	
rac-**3** (DFT)[a]	220.0	79.4		6.03	
FcCH($POPh_2$)-Me	33.9	35.6	66.4	3.39	15.8
FcCH($POPh_2$)-*i*Pr	32.3	46.2	66.6	3.37	15.0

[a] NMR chemical shifts were calculated at ωB97X-D/6-31G* level using ωB97X-D/6-31G* optimized geometries; stated chemical shifts are weighted arithmetic mean of chemical shifts of most populated conformers, see SI for details.



Scheme 1. Synthesis of starting material for phospha-Brook rearrangement.



Scheme 2. Experimental results in the phospha-Brook rearrangement.

interaction in the transition state of isomerization and in the corresponding carbocation for comparison.

DFT calculation (ωB97X-D/LACVP//ωB97X-D/6-311+G**(DCM)) of the BH_3 phosphinite and phosphane-oxide showed that the difference in stability is higher than in uncomplexed species. BH_3-complexed phosphane oxide is 50.9 kJ/mol more stable than BH_3-complexed phosphinite (Fig. 1).

To understand retro-phospha-Brook rearrangement on both free phosphinite **3** as well as BH_3-protected phosphinite BH_3.**3**, DFT calculations were conducted. We have again employed long-range corrected hybrid density ωB97X-D functional with LACVP basis set for geometrical optimizations. Energies were refined at ωB97X-D/6-311+G** level with C-PCM scheme to account for solvent effects (tetrahydrofuran). To better model organolithium species involved in this reaction, we have used explicit solvent coordination with two molecules of THF complexed to lithium. As a starting compound for retro-phospha-Brook rearrangement, the organolithium intermediate **Int-PhLi** was modeled. Intramolecular transposition of the diphenylphosphanyl group from oxygen to carbon occurs via a transition state **TS-Brook** with an activation barrier 45.7 kJ/mol. This process is accompanied by the simultaneous transposition of lithium from carbon to oxygen. The retro-phospha-Brook rearrangement's primary product is a lithium alkoxide **Int-OLi**, which is upon aqueous work-up transformed into product **5** (Scheme 4).

DFT calculations (ωB97X-D/LACVP//ωB97X-D/6-311+G** (THF)) showed that coordinated borane likely accelerates the rearrangement pathway. Activation barrier (32.0 kJ/mol) is slightly lower in comparison with the reaction of uncoordinated substrate (Fig. 2).

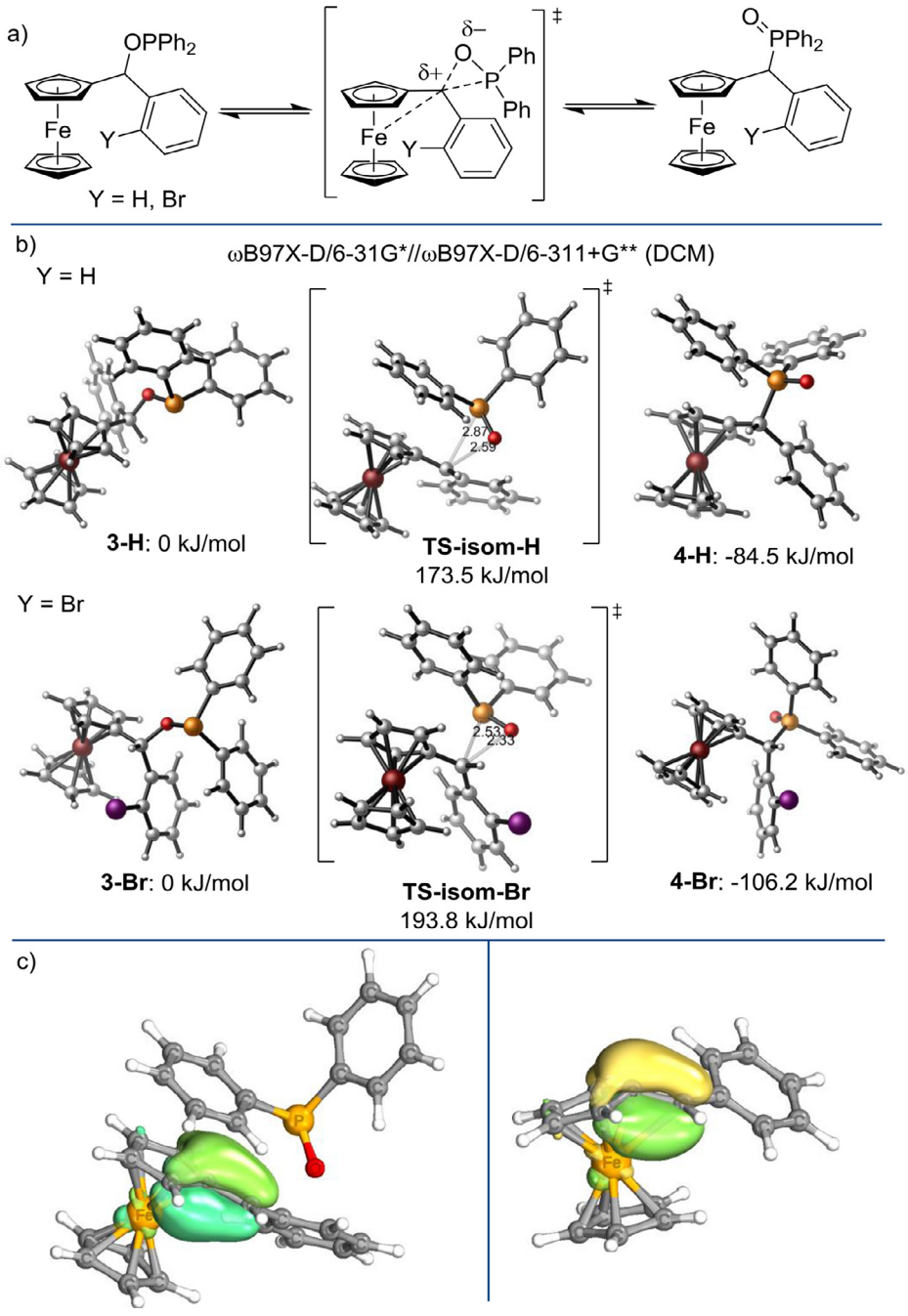
The reason why retro-phospha-Brook rearrangement via BH_3-complexed starting material affords products in lower yield is probably because of side reactions between BuLi and BH_3. An interesting question remains, why retro-phospha-Brook rearrangement proceeds even if DFT calculations and spectroscopic studies of **4** suggest that the starting material is in the form of phosphane-oxide from which it is difficult to imagine a successful retro-phospha-Brook rearrangement. One hypothesis may be that in the presence of BuLi or on the carbanionic intermediate, the phosphinite/phosphane-oxide isomerization is faster and some amount of phosphinite is present. This would then allow retro-phospha-Brook rearrangement to proceed.

3. Conclusions

Experiments and DFT calculations showed that ferrocenyl phosphinites rearrange to more stable phosphine-oxides. Borane-protection seems to stabilize these phosphinites and the presence of scalar coupling between ^{31}P and ^{11}B supports this notion. *n*BuLi initiated retro-phospha-Brook rearrangement can be realized both with uncomplexed as well as BH_3-complexed starting materials. Interestingly, this suggests that rearrangement can be accomplished also from a phosphine-oxide. Despite the relatively low isolated yields of rearrangement products, this study presents an example of an unusual reaction mechanism worth further investigation.

4. Experimental

All experiments were performed under an argon atmosphere, using standard Schlenk techniques. Alcohol **2** (CAS: 1277-49-2) was prepared according to procedures in the literature [15,23]. Other chemicals were purchased from commercial suppliers (Sigma-Aldrich, Alfa-Aesar, Acros, TCI Chemicals) and used without further purification. Solvents were dried (DCM, and Et_3N with CaH_2, THF with Na/benzophenone) and distilled. Thin-layer chromatography was performed on Merck TLC-plates silica gel 60, F-254, or on Al_2O_3 TLC-plates. Compounds were visualized by irradiation with UV light. Products were separated by flash chromatography using Merck silica gel 60 (0.040-0.063 mm). NMR spectra were recorded on Varian NMR System 300 and 600 (300 or 600 MHz for ^1H, 151 MHz for ^{13}C, and 121 or 243 MHz for ^{31}P). Chemical shifts (δ) are given in ppm relative to tetramethylsilane. High-resolution mass spectra (HRMS) were recorded using HESI heated electrospray ionization (HESI).



Scheme 3. a) Phosphinite-phosphane-oxide isomerization; b) DFT (ωB97X-D/6-31G*//ωB97X-D/6-311+G**(DCM)) structures and relative Gibbs free energies; lengths of formed and broken bonds in transition states are in Å; molecules visualized with CYLview; [53] c) intrinsic bond orbitals for transition state of the isomerization (left) and the corresponding ferrocenyl(phenyl)methylium cation (right); generated with IboView [54].

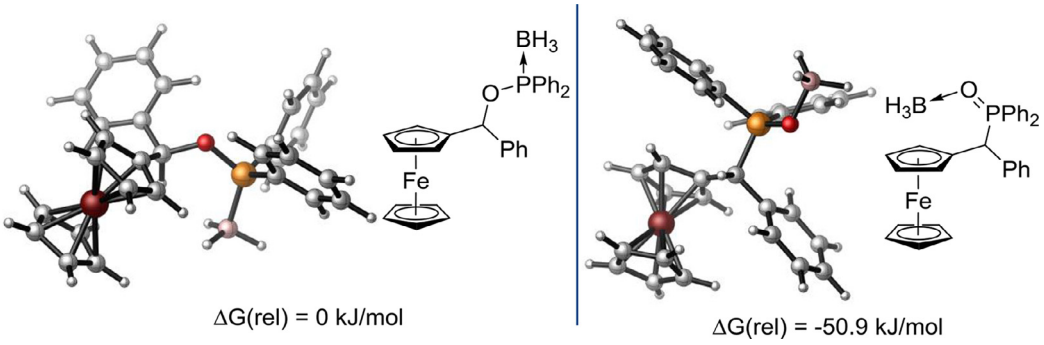
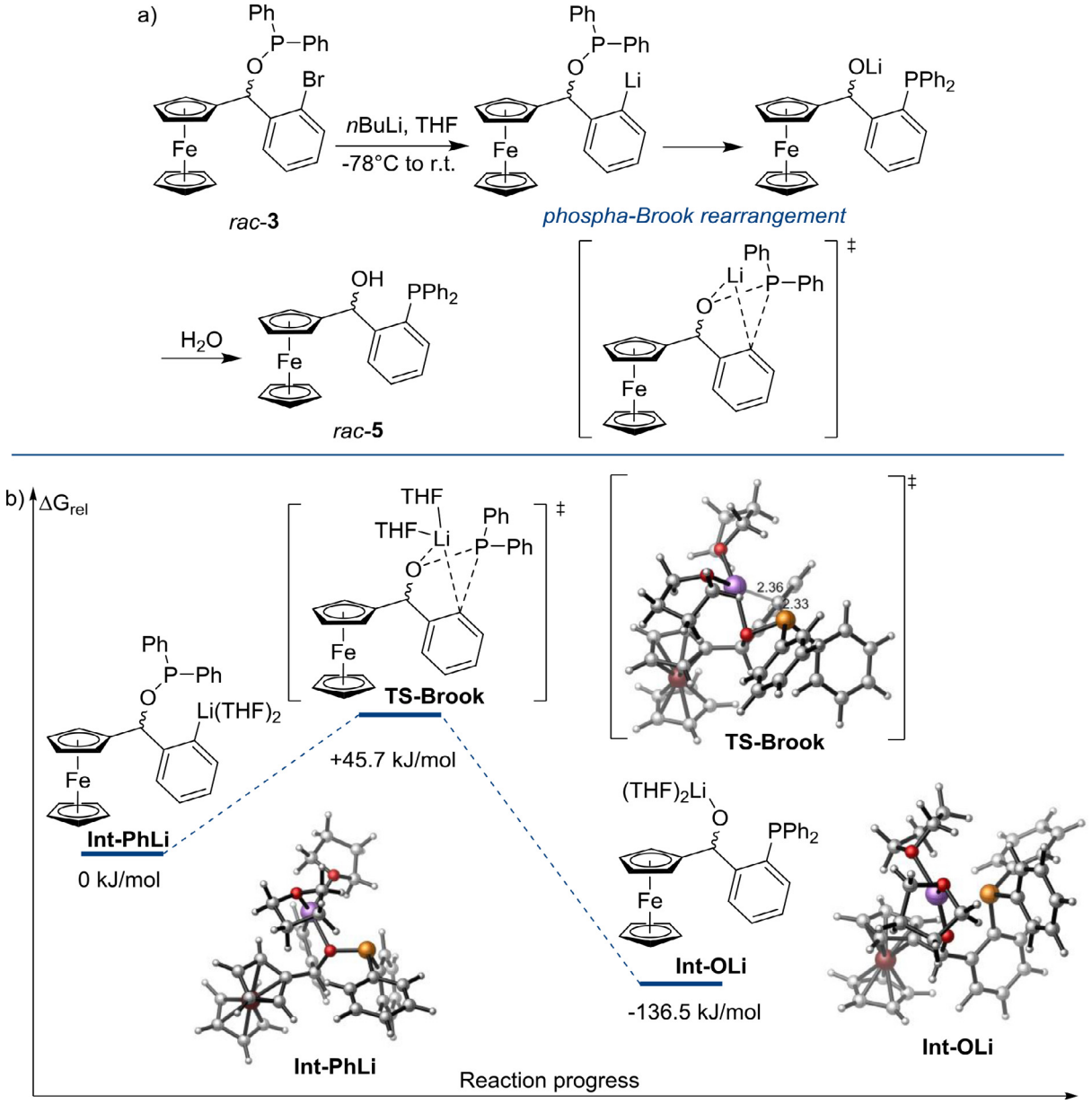


Fig. 1. BH_3-complexes of phosphinite and phosphane-oxide calculated at (ωB97X-D/LACVP//ωB97X-D/6-311+G**(DCM)) level with relative Gibbs free energies.



Scheme 4. a) Reaction scheme for the retro-phospha-Brook rearrangement; b) reaction energy profile with relative Gibbs free energies obtained at ωB97X-D/LACVP//ωB97X-D/6-311+G**(THF) level; lengths of formed and broken bonds in the transition state are in Å.

4.1. 1-(2-Bromobenzyl)phenyl diphenylphosphinite (rac-*3*)

Into a solution of alcohol **2** (0.27 mmol, 100 mg) and DMAP (0.014 mmol, 1.7 mg) in anhydrous DCM, anhydrous Et_3N (1.89 mmol, 0.26 mL) was added. The reaction mixture was cooled to 0°C and PPh_2Cl (0.27 mmol, 50 μL) was added. After 1h, the reaction mixture did not contain any starting alcohol 2. The reaction mixture was filtered through Celite® and crude product purified by column chromatography (SiO_2, hexanes/AcOEt, 6:1). Product *rac*-**3** (31.5 mg, 21%) was obtained as a yellow crystalline solid. Mp 187°C (decomp.); R_f = 0.43 (hexanes/AcOEt, 1:1); HRMS: (*m*/*z*): $[M]^+$ calc. for $C_{29}H_{24}BrFeOP$, 554.0098, found 554.0095; IR (ATR): υ 3052, 2915, 2651, 1719, 1466, 1435, 1259, 1177, 1149, 1105, 1025, 927, 811, 791, 747, 693, 645, 609, 542, 523, 504 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.18 (dt, *J* = 7.9; 1.7 Hz, 1H, Ph), 7.74-7.59 (m, 4H, Ph), 7.50-7.27 (m, 8H, Ph), 7.07 (ddd, *J* = 8.9; 2.6; 1.3 Hz, 1H, Ph), 5.12 (d, *J* = 9.2 Hz, 1H, HC-O), 4.44 (d, *J* = 1.2 Hz, 1H, Fc), 4.14 (dd, *J* = 3.7; 2.5 Hz, 1H, Fc), 3.89 (td, *J* = 2.4; 1,2 Hz, 1H, Fc), 3.75 (s, 5H, Cp), 3.74 (m, 1H, Fc) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ 138.1 (Ph), 132.6 (Ph), 131.6 (d, *J* = 14.8 Hz, Ph), 131.6 (d, *J* = 8.8 Hz, Ph), 131.2 (Ph), 131.1 (Ph), 128.8 (Ph), 128.3 (d, *J* = 12.0 Hz, Ph),128.2 (d, *J* = 12.2 Hz, Ph),127.7 (Ph), 125.7 (d, *J* = 8.9 Hz, Ph), 84.1 (Fc), 70.9 (Fc), 68.8 (Fc), 68.7 (Cp), 68.2 (Fc), 66.7 (Fc), 45.9 (d, *J* = 63.0 Hz, C-O) ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ 30.9 ppm.

4.2. (2-(Diphenylphosphanyl)phenyl)(ferrocenyl)methanol (rac-*5*)

Into a solution of compound *rac*-**3** (0.09 mmol, 50 mg) in anhydrous THF (9.4 mL) was at -60°C slowly added *n*BuLi (1,6 M in hexane, 0.27 mmol, 0.16 mL). The reaction mixture was stirred while the temperature increases slowly to 14°C and then cold water was added (8 mL). Aqueous phase was diluted with brine and extracted with Et_2O. Combined organic phases were dried over anhydrous Na_2SO_4. The product was isolated by column chromatography (SiO_2, hexanes/AcOEt 5:6). Alcohol *rac*-**5** (11 mg, 26%) was obtained as a yellow crystalline solid. Mp 205°C (decomp.); R_f = 0.29

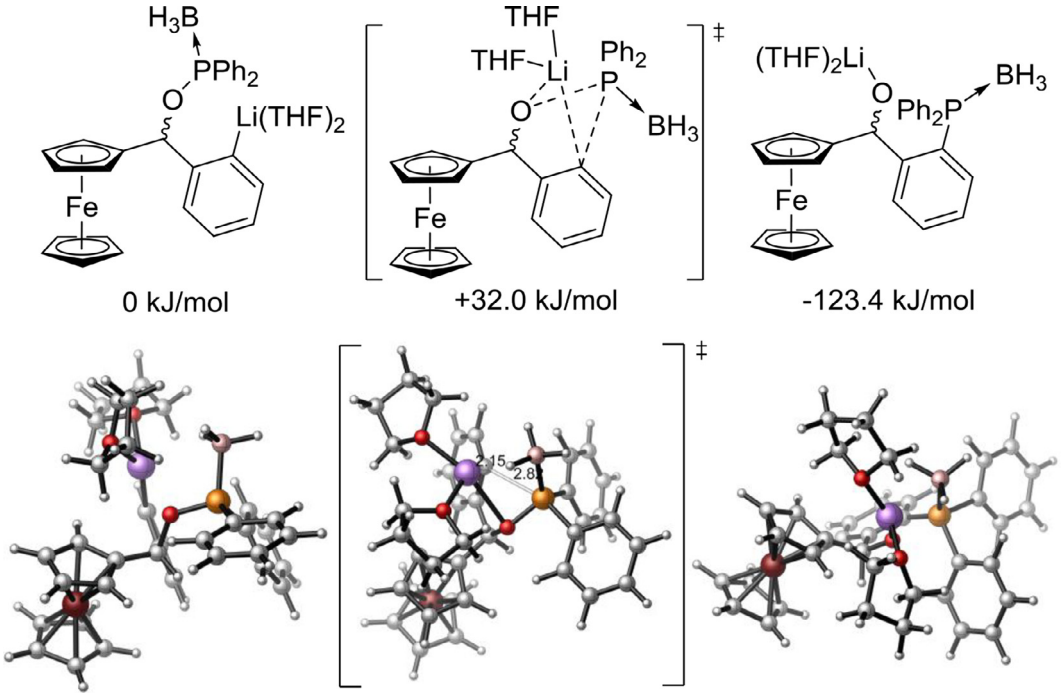


Fig. 2. DFT calculated structures for retro-phospha-Brook rearrangement under BH_3-complexation with relative Gibbs free energies; lengths of formed and broken bonds in the transition state are in Å.

(hexanes/AcOEt 5:6); IR (ATR): υ 3297 (br s, OH), 2921, 2852, 1908, 1719, 1465, 1435, 1379, 1260, 1180, 1102, 1075, 1039, 1019, 867, 801, 751, 716 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.79-7.45 (m, 10H, Ph), 7.40 (ddd, *J* = 7.6; 1.5; 1.5 Hz, 1H, Ph), 7.28-7.23 (m, 1H, Ph), 7.16 (dddd, *J* = 7.5; 7.5; 2.6; 1.3 Hz, 1H, Ph), 6.97 (ddd, *J* = 14.1; 7.6; 1.4 Hz, 1H, Ph), 6.07 (d, *J* = 4.1 Hz, 1H, HC-O), 5.41 (d, *J* = 4.1 Hz, 1H, HO), 4.61-4.57 (m, 1H, Fc), 4.13-4.09 (m, 1H, Fc), 4.02 (s, 5H, Cp), 3.99-3.95 (m, 1H, Fc), 3.58-3.55 (m, 1H, Fc) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.6 (d, *J* = 7.6 Hz, Ph), 133.2 (d, *J* = 102.8 Hz, Ph), 133.0 (d, *J* = 13.0 Hz, Ph), 132.6 (d, *J* = 2.5 Hz, Ph), 132.3 (d, *J* = 9.8 Hz, Ph), 132.2 (d, *J* = 2.8 Hz, Ph), 132.2 (d, *J* = 2.9 Hz, Ph), 131.7 (d, *J* = 10.0 Hz, Ph), 131.6 (d, *J* = 106.3 Hz, Ph), 130.3 (d, *J* = 101.3 Hz, Ph), 129.3 (d, *J* = 9.5 Hz, Ph), 128.8 (d, *J* = 12.2 Hz, Ph), 128.6 (d, *J* = 12.4 Hz, Ph), 126.7 (d, *J* = 13.0 Hz, Ph), 89.9 (Fc), 70.0 (d, *J* = 5.9 Hz, C-O), 68.9 (Cp), 67.6 (Fc), 67.1 (Fc), 67.0 (Fc), 66.8 (Fc) ppm; ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.1 ppm.

4.3. 4-(((Diphenylphosphanyl)oxy)(2-(diphenylphosphanyl) phenyl)methyl)ferrocene-borane complex (BH_3.rac-*3*)

Alcohol *rac*-**2** (0.27 mmol, 100 mg) and DMAP (0.014 mmol, 1.7 mg) were dissolved in anhydrous DCM. Into this solution, anhydrous Et_3N (1.89 mmol, 0.26 mL) was added dropwise and then PPh_2Cl (0.27 mmol, 0.05 mL) was added slowly at 0°C. After the complete conversion of starting alcohol **3** (approx. 1 h), $BH_3.SMe_2$ (0.27 mmol, 0.03 mL) was added at 0°C. The mixture was stirred for 30 min and then the solvent was evaporated, and the products were separated by column chromatography (SiO_2, hexanes/AcOEt, 6:1). The product BH_3.*rac*-**3** (38 mg, 25%) was obtained as an orange crystalline solid. In addition, compound *rac*-**3** (22 mg, 15%) and a 2-bromobenzylferrocene (**6**, 38 mg, 40%) [55] were also isolated. R_f 0.56 (hexanes/AcOEt, 6:1). HRMS: (*m*/*z*): $[M - BH_3]^+$ calc. for $C_{29}H_{24}BrFeOP$, 554.0098, found 554.0097. IR (ATR): υ 3055, 2961, 2923, 2853, 2651, 1891, 1718, 1467, 1432, 1307, 1260, 1190, 1102, 1056, 1020, 948, 925, 831, 813, 743, 713, 688, 670, 630, 585, 556, 520, 482, 439 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.8 Hz, 1H, Ph), 7.70 (dd, *J* = 9.1; 7.6 Hz, 2H, Ph), 7.58-7.49 (m, 4H, Ph), 7.44-7.40 (m, 2H, Ph), 7.37-7.30 (m, 2H, Ph), 7.28-7.24 (m, 2H, Ph), 7.11 (t, *J* = 7.6 Hz, 1H, Ph), 5.47 (d, *J* = 16.1 Hz, 1H, HC-O), 4.26 (s, 1H, Fc), 4.13 (s, 1H, Fc), 3.93 (s, 1H, Fc), 3.81 (s, 5H, Cp), 3.58 (s, 1H, Fc), 0.6-1.3 (m, 3H, BH_3) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 137.6 (d, *J* = 1.6 Hz, Ph), 134.1 (d, *J* = 8.5 Hz, Ph), 132.9 (d, *J* = 8.2 Hz, Ph), 132.9 (Ph), 131.6 (d, *J* = 3.0 Hz, Ph), 131.6 (Ph), 131.0 (d, *J* = 2.3 Hz, Ph), 129.0 (Ph), 128.5 (d, *J* = 9.8 Hz, Ph), 128.5 (d, *J* = 52.0 Hz, Ph), 128.3 (d, *J* = 9.6 Hz, Ph), 127.7 (d, *J* = 52.7 Hz, Ph), 127.4 (Ph), 126.1 (d, *J* = 6.9 Hz, Ph), 84.4 (Fc), 70.6 (d, *J* = 2.0 Hz, C-O), 68.8 (Cp), 68.6 (Fc), 68.4 (Fc), 87.3 (Fc), 43.9 (d, J = 28.2 Hz, C-O) ppm. ^{31}P NMR (243 MHz, $CDCl_3$): 27.2 (br d, J_{PB} = 42 Hz) ppm.

4.4. Procedure for preparation of rac-*5* from BH_3.rac-*3*

Compound BH_3.*rac*-**3** (0.10 mmol, 56 mg) was dissolved in anhydrous THF (3 mL) and the resulting solution was cooled to -78°C. Into this solution, *n*BuLi was added (1.6 M in hexane, 0.12 mmol, 70 µL). The reaction mixture was stirred for 1.5 h at -78°C and then the temperature was allowed to slowly rise to r.t. (18 h). The reaction was quenched with cold H_2O (3 mL). Aqueous phase was extracted with AcOEt and combined organic extracts were dried over anhydrous Na_2SO_4. After filtration, the mixture was concentrated under reduced pressure and product was isolated by column chromatography (SiO_2, hexanes/AcOEt 10:1). Product *rac*-**5** (5 mg, 11%) was obtained as a yellow crystalline solid along with debrominated compound **7** (8 mg, 17%).

4.5. DFT calculations

DFT calculations were performed using ωB97X-D functional, [44] as implemented in Spartan 18 program package [56]. For geometrical optimizations, LACVP basis set (a combination of 6-31G* for H, C, N, O, Li, P, and LANL2DZ basis set for Fe) was used. Energies were refined at ωB97X-D/6-311+G** level. Solvent effects were evaluated within the context of self-consistent reaction field theory using the polarizable continuum model

(PCM)[46] and dichloromethane (ε = 8.93), and tetrahydrofuran (ε = 7.52) as solvents. Conformational searches were performed for all starting compound and products using molecular mechanics. Lowest energy conformers were gradually reoptimized at HF/3-21G level and then at ωB97X-D/LACVP level.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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