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Asymmetric Synthesis of Heterobimetallic Planar Chiral Ferrocene Pallada-/Platinacycles and Their Application to Enantioselective Aza-Claisen Rearrangements

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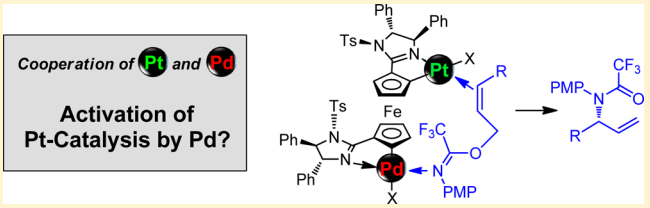
Supporting Information

ABSTRACT: Ligand exchange reactions are usually slower for Pt(II) in comparison to Pd(II) centers. Mainly for that reason Pt(II) catalysts have often shown a reduced catalytic activity as compared to their Pd(II) counterparts. We are interested in the question if this inherently slower ligand exchange might also provide a chance for heterobimetallic catalysts to accomplish an improved catalytic performance with substrates in which the reactive center has a lower binding constant than an additional Lewis basic moiety. For that purpose we have prepared the first diastereo- and enantiomerically pure mixed pallada-/platinacycles based on ferrocene. These complexes have been prepared by sequential direct diastereoselective cycloplatination and cyclopalladation. The investigation of the asymmetric aza-Claisen rearrangement of *Z*-configured trifluoroacetimidates showed that a heterodinuclear Pt−Pd bis-metallacycle is an excellent catalyst for this reaction type, in general allowing for very high enantioselectivities. Moreover, at a slightly elevated temperature (55 °C), the heterodinuclear platina-/palladacycle could in certain cases outperform the corresponding bis-Pd complex, previously known to be the by far most active highly enantioselective catalyst for the rearrangement of *Z*-configured trifluoroacetimidates. This effect, which might be surprising at first sight due to the low efficiency of other Pt catalysts for aza-Claisen rearrangements, might be explained by an enhanced lifetime of a productive monodentate olefin coordination of the substrate at the Pt center due to slower ligand exchange processes.



INTRODUCTION

The cooperation of two metal centers, which is well-known for a number of dinuclear metalloenzymes such as DNA polymerases, phosphatases, or ureases,[1] constitutes an intriguing design principle for artificial catalysts.[2] The bimetallic catalysts can be classified as homo- and heterobimetallic complexes. The former are generally more readily available, because both metals can often be introduced in the same step by a double metalation, whereas the latter frequently require a larger synthetic effort, because two different metalation steps are necessary. Despite this inherent disadvantage, heterobimetallic complexes obviously offer a large potential as dual activation catalysts. This is due to an enhanced variability for an optimization of the cooperation of both metals. In that way the complementary properties of the different Lewis acid centers can be employed most efficiently for the simultaneous activation of both reacting substrates (normally an electrophile and a nucleophile). In other words, the most advantageous metals for the activation of each reactant might be selected.

Recently we have reported that planar chiral ferrocene bisimidazoline bispalladacycles (**FBIP**, Figure 1)[3] act as highly enantioselective homobimetallic catalysts in different reaction types such as enantioselective [3,3] rearrangements of allylic imidates[4,5] or Michael additions of various nucleophiles to enones.[6] For the 1,4-addition of α-cyanoacetates to enones,[6a] detailed kinetic studies have provided strong evidence for the intramolecular cooperation of both metals by simultaneous activation of both substrates.

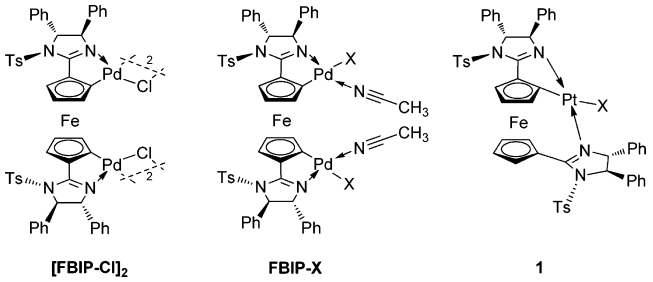


Figure 1. Planar chiral bis-palladacycle precatalyst [**FBIP-Cl**]$_2$, the activated monomeric catalysts **FBIP-X** (X^- is an anionic ligand), and monoplatinacycle **1**.

In addition, we have recently reported the first diastereoselective cycloplatination of an enantiomerically pure ferrocene derivative using the same ferrocenebisimidazoline ligand as for the synthesis of the **FBIP** systems.[7] The resulting Pt complex **1** gave only poor results in allylic imidate rearrangements.[8,9] On the other hand, it enabled the first enantioselective intramolecular Friedel−Crafts alkylations of

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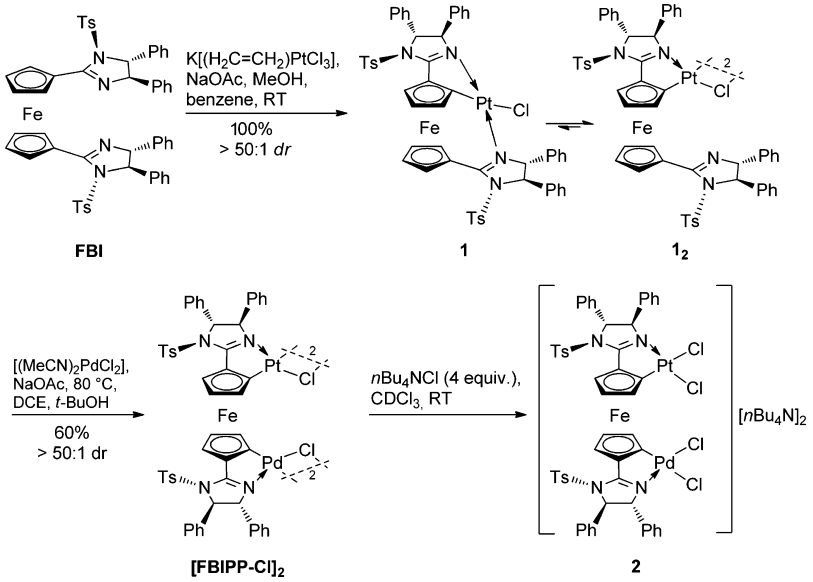
Scheme 1. Synthesis of the Dimeric Planar Chiral Mixed Platina-/Palladacycle [FBIPP-Cl]$_2$ and Formation of the Monomer 2 in the Presence of [nBu$_4$N]Cl



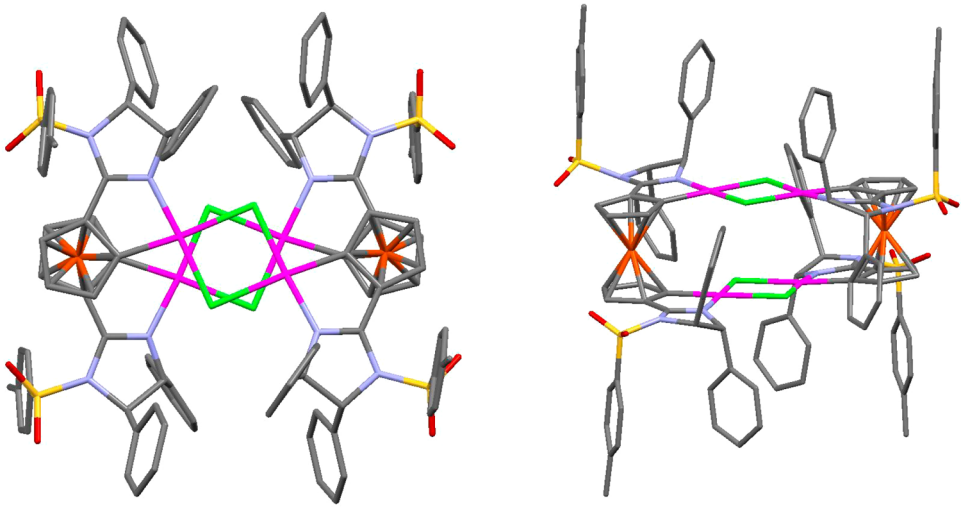


Figure 2. X-ray crystal structure analysis of dimeric mixed pallada-/platinacycle [**FBIPP-Cl**]$_2$ (color code C (gray), N (blue), O (red), S (yellow), Fe (orange), Pd and Pt (magenta), Cl (green); H atoms and included $CHCl_3$ molecules (7 per unit cell) omitted for clarity): (left) view along the ferrocene axes; (right) view nearly perpendicular to the ferrocene axes.

indoles with internal olefins that are not activated by π-acceptor substituents.[7] This application represents the first reported highly enantioselective reaction catalyzed by a platinacycle. In contrast, the related imidazoline mono-[10] and bispalladacycles[3,4] could not be used for the same purpose, demonstrating the different properties of pallada- and platinacycles for substrate activation.

Both Pd(II) and Pt(II) are well-known to serve as carbophilic Lewis acids capable of activating olefins as electrophiles for a large number of atom- and step-economic processes,[11,12] but they generally offer a complementary reactivity profile. Ligand exchange processes are usually much slower for Pt(II) in comparison to Pd(II), often resulting in sluggish catalytic processes. Another dissimilarity is given by the reactivity of the σ-alkyl−metal intermediates formed by attack of suitable nucleophiles at π-olefin complexes. Whereas alkyl−Pd(II) complexes display a comparatively high tendency to undergo a β-hydride elimination, their alkyl−Pt(II) counterparts prefer to undergo a protonolysis and a β-hydride elimination pathway is usually significantly slower.[12c,d,13] In addition, the tendency to generate a nucleophile by C−H activation is arguably more pronounced for Pt(II) than for Pd(II).[12c,d]

Due to the different catalytic preferences of Pd(II) and Pt(II) and the documented synthetic value of pallada- and platinacycles, we were interested in combining both metal centers in a planar chiral heterobismetallacycle to explore their cooperativity. Herein, we report the first synthesis of planar chiral diastereo- and enantiomerically pure mixed pallada-/platinacycles on a ferrocene basis. These complexes have been prepared from a ferrocene bisimidazoline ligand (**FBI**, Scheme 1) by sequential direct diastereoselective cycloplatination and cyclopalladation and were investigated in the catalytic asymmetric aza-Claisen rearrangement of trifluoroacetimidates for an initial comparison with the related bispalladacycle **FBIP**.

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RESULTS AND DISCUSSION

The ligand **FBI** was prepared according to the literature in three steps starting from ferrocene.[3] Cycloplatination was performed according to our previously published protocol using Zeise's salt as the Pt source (Scheme 1).[7] This reaction proceeds with excellent diastereoselectivity, most likely via a chelate in which Pt is coordinated by two imidazoline-N donors,[3] providing a mixture of a highly strained monomer **1** and the chloride-bridged dimer $\mathbf{1}_2$.[7,14]

This mixture was then applied to a diastereoselective cyclopalladation with $(MeCN)_2PdCl_2$ in the presence of NaOAc, providing the mixed dimeric bismetallacycle [**FBIPP-Cl**]$_2$. ^{1}H NMR spectra of this material are relatively complex because of the formation of different regioisomers, since chloride bridges are formed between either two identical or two different metals. X-ray single-crystal structure analysis confirms the dimeric nature of the complex[15] and shows a structure very similar to that of [**FBIP-Cl**]$_2$ (Figure 2).[4] The two different regioisomers (ratio 2:1 as determined by ^{1}H NMR) are statistically distributed in the crystal, and it is thus not possible to differentiate Pd and Pt in the structure. The distance between a Pd and Pt center bound to the same ferrocene fragment has been determined to be approximately 3.76−3.79 Å.

The crystal structure analysis of [**FBIPP-Cl**]$_2$ confirmed the expected *all-S*$_p$ configuration also found in the corresponding bispalladacycle.[16] The dimeric molecules can be described as macrocyclic systems comprising two ferrocenyl units and four chloride-bridged metal ions. The dimeric structure of [**FBIPP-Cl**]$_2$ forces two chloride-bridged metal square planes to be arranged in an almost coplanar fashion, which is otherwise unusual for dimeric pallada- or platinacycles. Moreover, halide-bridged pallada- or platinacycles usually form geometric isomers about the Pd^{II} centers.[17] In contrast, in the present case the planar chirality and the 1,1′,2,2′-substitution pattern of each ferrocene fragment dictate (as for [**FBIP-Cl**]$_2$) the coordination sphere about the Pd^{II} square planes for geometric reasons: the *all-S*$_p$-configured complexes exist exclusively as *all-trans*-configured isomers. That means both imino-type N atoms, which are positioned in the same $(MCl)_2$ plane, are always arranged *trans* to each other.

Treatment of [**FBIPP-Cl**]$_2$ with [*n*Bu$_4$N]Cl in chloroform generates monomer **2** with two anionic metal centers. Unfortunately, the product could not be separated from unreacted starting material on a preparative scale. However, the identity of **2** was confirmed by single-crystal X-ray structure analysis performed on the microcrystals obtained.[18] Since the structure could be refined to only R = 0.1334, an in-depth discussion of the structural parameters in **2** showing two independent conformers in the unit cell (Figure 3) is not possible, but the analysis confirms the constitution and absolute configuration. Moreover, it is possible to say that the distance of both soft metal centers is largely increased in the monomeric species (Pd−Pt distances ca. 6.0 and 6.7 Å for the two conformers). This large variation of possible metal−metal distances in ferrocene-derived bismetallacycles is considered to be a valuable aspect with regard to cooperative bimetallic catalysis, as each bimetallic reaction should prefer a different optimal distance of the reacting centers in the corresponding transition state. With the ferrocene backbone this distance is readily self-adjustable due to the partial rotational freedom around the Fe−Cp bond in the monomeric entities.

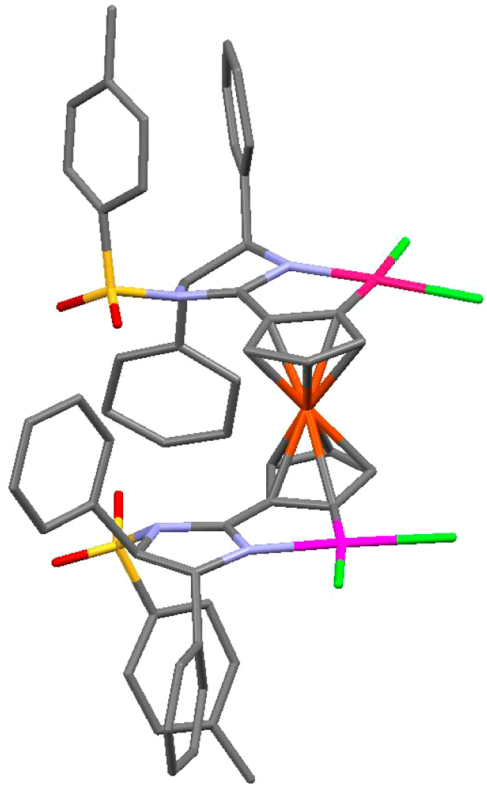
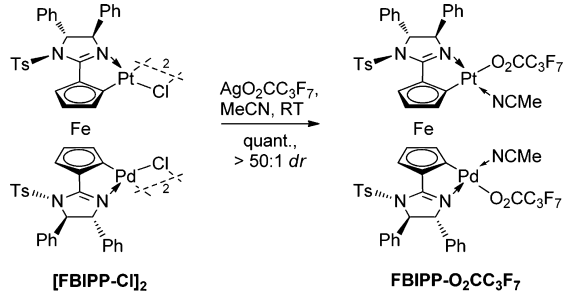


Figure 3. X-ray crystal structure analysis of monomeric mixed platina-/palladacycle **2** (color code C (gray), N (blue), O (red), S (yellow), Fe (orange), Pd and Pt (both magenta), Cl (green)). The unit cell contains two different conformers, and only one is depicted here. H atoms and the tetrabutylammonium counterion are also omitted for clarity.

A monomeric complex is also formed in quantitative yield by chloride counterion exchange utilizing silver heptafluorobutyrate in acetonitrile (Scheme 2).

Scheme 2. Generation of the Monomeric Complex FBIPP-$O_2CC_3F_7$ by Chloride Counterion Exchange in the Presence of MeCN



This transformation confirms that not only the cycloplatination but also the cyclopalladation proceeds with almost complete diastereoselectivity, as only a single isomer is obtained as judged by ^{1}H NMR. The generated species **FBIPP-$O_2CC_3F_7$** is a monomer, because one MeCN coordinates to each noble metal center.

To compare the catalytic properties with those of the established bis-Pd precatalyst [**FBIP-Cl**]$_2$, we have chosen the aza-Claisen rearrangement[5] of allylic imidates as the initial application, as part of our program to study cooperative effects

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in asymmetric catalysis.[4,6,19] The bis-Pd catalyst is the most active enantioselective catalyst known so far for the rearrangement of allylic trifluoroacetimidates with a *Z* configuration of the olefin moiety.[4] Since the aza-Claisen rearrangement proceeds stereospecifically (*E* and *Z* substrates yield different enantiomers in excess)[4,5,20] and since (*Z*)-olefins are more readily available in geometrically pure form than (*E*)-olefins (e.g., by semihydrogenation of alkynes), rearrangement of the *Z*-configured substrates provides a more practical access to highly enantioenriched allylic amines. However, this rearrangement is also considerably more difficult to achieve than the analogous transformation of the *E* isomers. This is explained by an unfavorable axial orientation of the (*Z*)-olefin substituent in the assumed half-chair-like transition state and the ensuing cyclic intermediate.[21]

The **FBIP** system has been demonstrated to be ca. 1−2 orders of magnitude more active than its mono-Pd counterparts for *Z*-configured substrates.[4] However, there is still a general problem for Pd-catalyzed aza-Claisen rearrangements causing low turnover frequencies even in the case of the more reactive *E*-configured substrates. Typical values are about just 40−100 h^{-1} for the most active enantioselective catalysts.[10d] A major issue of enantioselective aza-Claisen rearrangements is most likely the circumstance that the substrate has two possible coordination sites—the olefin and the imidate N atom—and that coordination of the imidate N is strongly preferred. The binding constant of the N atom of trichloroacetimidates has been reported to be about 10^4 times higher than the binding constant of an olefin.[21] That means that in a snapshot almost all of the catalyst would be blocked by an unproductive coordination (Figure 4). A bimetallic catalyst might change that situation in a way that coordination of the stronger N ligand to one metal site might also facilitate the coordination of the reactive olefin site by a chelating effect. Since both coordination events are reversible,[21] a subsequent attack of the imidate N atom on the coordinated olefin is still possible (Figure 4).

With the heterodinuclear Pd−Pt catalyst, higher ligand exchange rates are expected at the Pd center. However, the relatively rapid coordination of the imidate N atom at Pd might also lead to an accelerated ligand exchange at the Pt center by formation of the bridged substrate complex **3** depicted in Figure 4.[22] Once coordinated to the Pt center, the olefin exchange might be slower than in the case of the analogous bis-Pd catalyst while the N ligand still rapidly exchanges. In total this might lead to a larger lifetime of the complex with a productive monodentate olefin coordination. To investigate this idea, we studied the catalytic asymmetric rearrangement of *Z*-configured allylic imidate substrates **4**. Table 1 shows a comparison of data obtained with the heterodinuclear Pd−Pt complex [**FBIPP-Cl**]$_2$ and the corresponding homodinuclear Pd_2 complex [**FBIP-Cl**]$_2$. The experiments were conducted under conditions previously optimized for the bis-Pd precatalyst using silver tosylate for chloride ligand exchange. The rearrangements were investigated at 20 and 55 °C. In general, they are very clean in a way that side products are not detectable. As a general trend, the bispalladium catalyst is somewhat more active at 20 °C than the Pt−Pd catalyst (compare entries 1/2, 7/8, and 14/15). In contrast, at 55 °C which of the two catalyst systems performs in a superior manner is dependent on the substrate: e.g., substrate **4b** with R = *i*Bu requires a higher catalyst loading for the heterodinuclear catalyst (compare entries 9−11) to obtain high product yields.

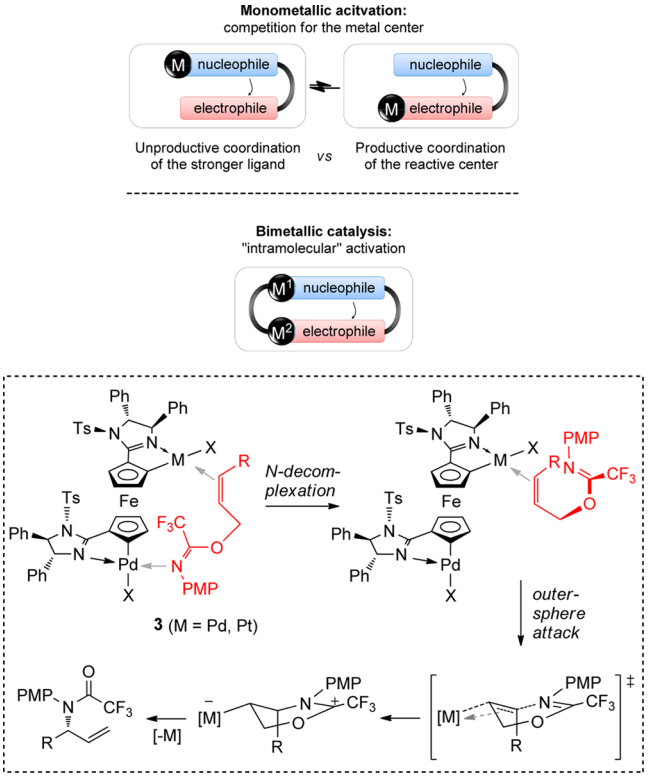

Figure 4. Comparison of the general coordination modes of a bidentate substrate, in which the reactive center (in the case of allylic imidates the olefin moiety) has a lower binding constant than another Lewis basic functionality leading to a small degree of productive coordination with a monometallic catalyst. In a bimetallic catalyst a chelate effect might increase the binding constant of the reactive center. However, the efficiency would just be increased in the allylic imidate rearrangement, if the decomplexation of the imidate N atom is sufficiently rapid to allow for a sufficiently fast outer-sphere attack at the coordinated olefin.

Similarly, a lower reactivity was also found for the rearrangement of **4c** with R = Me (entries 12 and 13). In that case, also the enantioselectivity was lower with the heterobimetallic catalyst (88 vs 94% ee). In contrast, for substrate **4a** with R = *n*Pr, a significantly higher activity was noticed with the Pt−Pd catalyst. Using 0.05 mol % of the precatalyst, the almost enantiopure product was formed in nearly quantitative yield, while the bispalladium catalyst gave a yield of just 68% under otherwise identical conditions. In addition, a higher activity of the Pt−Pd catalyst was also observed for substrate **4d** with R = $(CH_2)_2Ph$ (entries 16 and 17). Both catalysts can also be employed to generate N-substituted quaternary stereocenters starting from allylic imidates such as **4e** carrying residues R^E and R^Z (entries 18 and 19) both different from H. The successful enantioselective application of this challenging substrate class has been reported with very few catalysts.[10b,d,20g,23] While the product was formed in both cases in a yield of 94% using 2 mol % of the precatalysts, the enantioselectivity was higher for the Pt−Pd catalyst (87% vs 80% ee).

For a further comparison of the catalytic activity of the homo- and heterobimetallic complexes, the rearrangement of substrates **4a,d** was monitored starting after a reaction time of 2 h (Figure 5). For both substrates and with both catalysts, the reactions proceeded in a clean manner (no side products could be detected at any time). The Pt/Pd catalyst provided the

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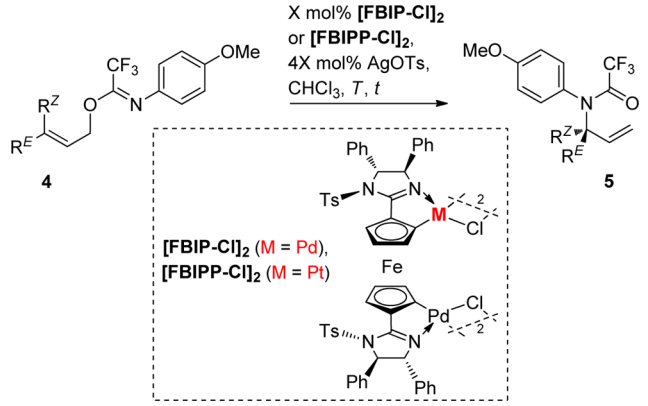
Table 1. Comparison of the Catalytic Asymmetric Rearrangement of Allylic Imidates 4 Using the Bis-Pd Catalyst [FBIP-Cl]$_2$ or the Heterodinuclear Pd−Pt Complex [FBIPP-Cl]$_2$



entry	M	4	R^Z	R^E	precat. loading: X (mol %)	T (°C)	t (h)	yield (%)[a]	ee (%)[b]
1	Pd	**4a**	*n*Pr	H	0.5	20	72	97	98
2	**Pt**	**4a**	*n*Pr	H	0.5	20	72	94	97
3	Pd	**4a**	*n*Pr	H	0.1	55	72	94	97
4	**Pt**	**4a**	*n*Pr	H	0.1	55	72	99	98
5	Pd	**4a**	*n*Pr	H	0.05	55	72	68	97
6	**Pt**	**4a**	*n*Pr	H	0.05	55	72	99	98
7	Pd	**4b**	*i*Bu	H	1	20	72	87	98
8	**Pt**	**4b**	*i*Bu	H	1.5	20	72	87	99
9	Pd	**4b**	*i*Bu	H	0.1	55	72	86	98
10	**Pt**	**4b**	*i*Bu	H	0.1	55	72	62	98
11	**Pt**	**4b**	*i*Bu	H	0.2	55	72	>99	98
12	Pd	**4c**	Me	H	0.1	55	24	97	94
13	**Pt**	**4c**	Me	H	0.1	55	48	78	88
14	Pd	**4d**	$(CH_2)_2Ph$	H	1.0	20	72	99	96
15	**Pt**	**4d**	$(CH_2)_2Ph$	H	1.0	20	72	83	95
16	Pd	**4d**	$(CH_2)_2Ph$	H	0.2	55	72	90	95
17	**Pt**	**4d**	$(CH_2)_2Ph$	H	0.2	55	72	98	95
18	Pd	**4e**	CH_2OBn	Me	2.0	55	72	94	80[c]
19	**Pt**	**4e**	CH_2OBn	Me	2.0	55	72	94	87[c]

[a]Yield of isolated product. [b]Determined by HPLC after hydrolysis of the amide. [c]Determined by HPLC without hydrolysis of the amide.

rearrangement product in both cases with a considerably higher rate under otherwise identical conditions.

The active participation of the Pt center in the catalytic event is likely as revealed by a comparison with the corresponding ferrocene monoimidazoline monopalladacycles. The latter are at least 1 order of magnitude less active for *Z*-configured substrates than the bimetallic catalysts, as the monopalladacycles require a precatalyst loading of 5 mol % for substrate **4a** in order to obtain high product yields.[10a,d] The fact that monoplatinacycle **1** is not a useful catalyst for aza-Claisen rearrangements of trifluoroacetimidates further supports the synergy of the Pd and Pt centers.

The activity difference of both catalysts at 20 °C favoring the homobimetallic catalyst might reflect the traditional issues of slower substrate coordination/product release at Pt. However, these issues appear to be less relevant at 55 °C and the higher activity in certain cases with the heterobimetallic catalyst supports the initial hypothesis of an improved synergistic action of both metal centers in the case of Pd and Pt, depending on the temperature-dependent kinetic profile of each elementary step. An increased lifetime of the substrate olefin coordination might thus be beneficial for the catalyst activity at least under certain conditions (vide supra).

CONCLUSION

In conclusion, we have reported the first asymmetric synthesis of planar chiral mixed pallada-/platinacycles based on ferrocene. These complexes were prepared via sequential direct cycloplatination and cyclopalladation. Both metalations proceeded with almost complete diastereoselectivity. In preliminary studies the Pt−Pd system was investigated in the catalytic asymmetric aza-Claisen rearrangement of *Z*-configured trifluoroacetimidates for an initial comparison with the related bispalladacycle **FBIP**. Although monoplatinacycles were previously found to be not useful as catalysts for the aza-Claisen rearrangement of trifluoroacetimidates, the heterodinuclear Pt−Pd complex [**FBIPP-Cl**]$_2$ proved to be an excellent precatalyst for this reaction type, in general allowing for very high enantioselectivities. In particular, at a slightly elevated temperature, the heterodinuclear bismetallacycle could for certain substrates outperform the bispalladacycle **FBIP**, previously known as the by far most active enantioselective catalyst for the title reaction using *Z*-configured allylic trifluoroacetimidate substrates. This effect might be explained by an enhanced lifetime of a productive monodentate olefin coordination of the substrate at the Pt center due to slower ligand exchange processes in comparison to Pd(II).

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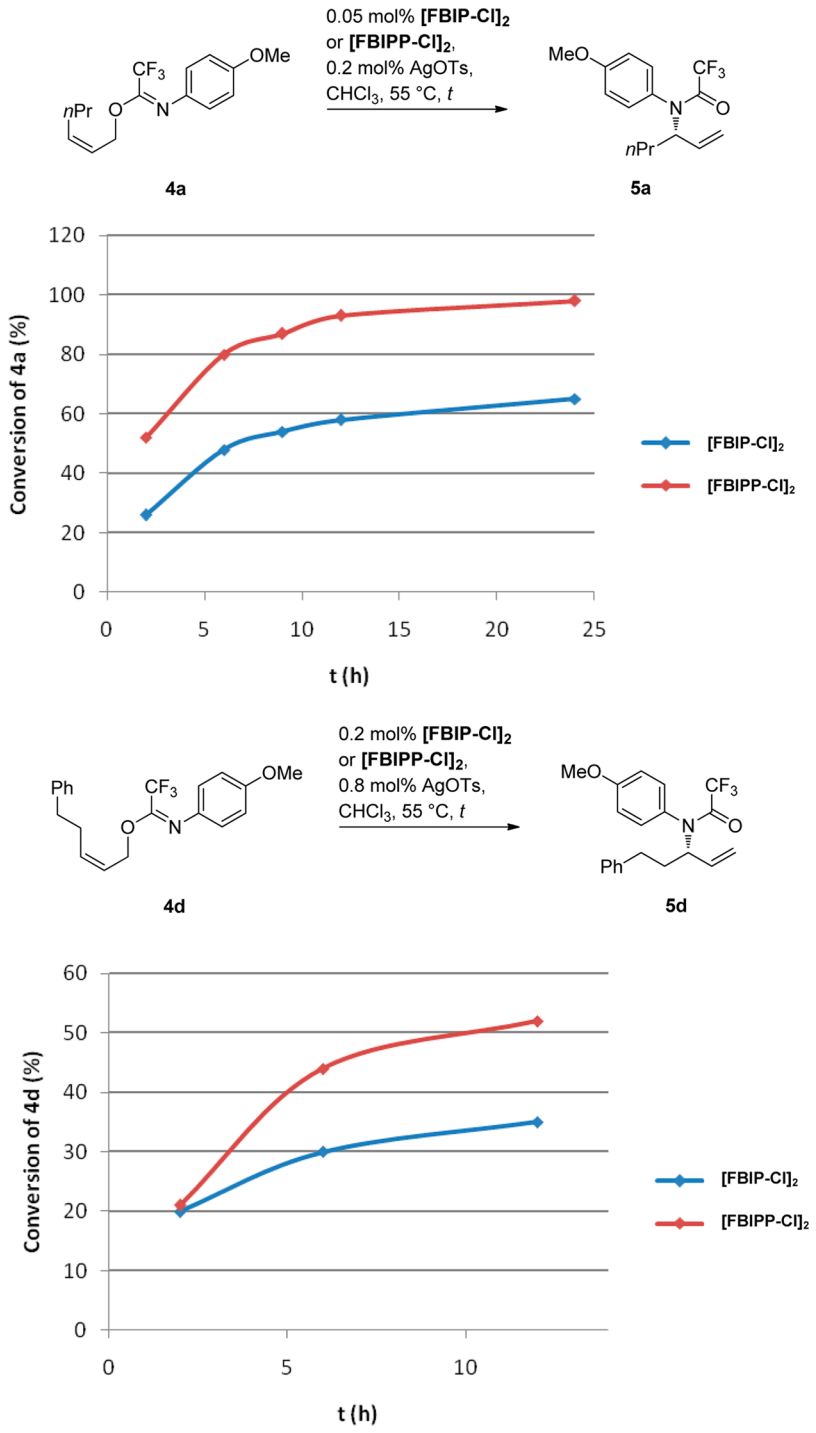

Figure 5. Comparison of the reactivity using the bis-Pd precatalyst [**FBIP-Cl**]$_2$ (blue curves) and the Pt/Pd precatalyst [**FBIPP-Cl**]$_2$ (red curves) for the rearrangement of substrates **4a** (top) and **4d** (bottom) by monitoring via ^{1}H NMR of samples taken.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed in oven-dried (150 °C) glassware under a positive pressure of dinitrogen using standard Schlenk techniques. For catalysis all glassware used (also for catalyst activation and preparation of stem solutions) was intensively washed with demineralized water to remove all remaining chloride. Methanol and benzene were stored in crown-capped bottles under argon over 4 Å molecular sieves. Acetonitrile and dichloromethane (DCM) were purified by distillation and subsequently by a solvent purification system under a dinitrogen atmosphere. *n*-Hexane (HPLC grade), 2-propanol (HPLC grade), and chloroform (>99%) were used as purchased. NMR spectra were recorded at 21 °C on spectrometers operating at 500 or 300 MHz (^{1}H), 125 or 75 MHz (^{13}C), and 235 MHz (^{19}F). Deuterated solvents were used as purchased. IR spectra were recorded by the IR service of the Universität Stuttgart on a spectrometer with an ATR unit. Optical rotation was measured on a polarimeter operating at the sodium D line with a 100 mm path cell length. Melting points were measured in open glass capillaries and are uncorrected. Mass spectra were obtained from the MS service of the Universität Stuttgart. Single-crystal X-ray analyses were performed by Dr. Wolfgang Frey (Universität Stuttgart). Enantiomeric excesses (ee's) were determined by high-performance liquid chromatography (HPLC).

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General Procedure for the Enantioselective Aza-Claisen Rearrangement. Silver *p*-toluenesulfonate (4.00 equiv) was dissolved in MeCN (0.1 mL/mg), and the solvent was subsequently removed by a stream of dinitrogen. A solution of [**FBIPP-Cl**]$_2$ (1.00 equiv) in DCM (0.1 mL/mg) was then added under a dinitrogen atmosphere. The mixture was stirred overnight at room temperature and subsequently filtered through Celite/CaH_2. The filter cake was extracted with DCM until the organic solution was colorless. The solvent was removed by a steady stream of dinitrogen and finally by high vacuum. A stem solution of the activated catalyst was prepared by dissolving the solid in dry $CHCl_3$ (20 mmol/L). The required amount of this solution was added to the substrate (prepared according to Overman et al.[20a]) under a nitrogen atmosphere. The reaction tube was sealed, and the reaction mixture was stirred for the indicated time at the indicated temperature. Afterwards, the reaction mixture was suspended in petroleum ether/ethyl acetate (10/1) and subsequently purified by filtration over silica gel.

[**FBIP-Cl**]$_2$ was prepared according to literature procedures.[4]

***trans-N,N-μ*-[(1*S*)-2-[(4*R*,5*R*)-1-(4-Tolylsulfonyl)-4,5-dihydro-4,5-diphenyl-1*H*-imidazol-2-yl-κ*N3*]-1′-[(4*R*,5*R*)-1-(4-tolylsulfonyl)-4,5-dihydro-4,5-diphenyl-1*H*-imidazol-2-yl-κ*N3*]-1-ferrocene-κ*C1*]chloroplatinum(II) (1) and Bis[(1*S*)-2-[(4*R*,5*R*)-1-(4-tolylsulfonyl)-4,5-dihydro-4,5-diphenyl-1*H*-imidazol-2-yl-κ*N3*]-1′-[(4*R*,5*R*)-1-(4-tolylsulfonyl)-4,5-dihydro-4,5-diphenyl-1*H*-imidazol-2-yl]-1-ferrocene-κ*C1*]-μ-dichlorodiplatinum(II) (1$_2$).** (4′′*R*,5′′*R*)-1,1′-Bis(2′′-4′′,5′′-dihydro-4′′,5′′-diphenyl-1′′-tosylimidazolyl)ferrocene[4] (**FBI**; 200.0 mg, 0.214 mmol, 1.00 equiv) was suspended in benzene (2.20 mL). To this mixture was added a solution of K[$(C_2H_4)PtCl_3$] (157.7 mg, 0.428 mmol, 2.00 equiv) and sodium acetate (70.2 mg, 0.856 mmol, 4.00 equiv) in methanol (2.20 mL), and the resulting solution was stirred for 24 h at room temperature. Afterwards the reaction mixture was filtered through Al_2O_3 (ethyl acetate). Solvent removal under reduced pressure yielded the product as a red solid (249.1 mg, 0.214 mmol, 100%). This product is a mixture of the *cis*/*trans* dimeric and the monomeric species **1**$_2$ and **1** (4.2/1), respectively, mp > 250 °C dec. Data for dimer **1**$_2$ are as follows. ^{1}H NMR (300 MHz, $CDCl_3$, mixture of *cis* and *trans* isomers): δ 7.80−6.53 (m, 82H, arom *H*), 6.38 (d, *J* = 7.4, 2H, arom *H*), 5.58 (d, *J* = 2.4, 1H, Cp *H*/C*H*Ph), 5.53−5.49 (m, 1H, Cp *H*/C*H*Ph), 5.48 (d, *J* = 2.7, 1H, Cp *H*/C*H*Ph), 5.44 (d, *J* = 2.7, 1H, Cp *H*/C*H*Ph), 5.37−5.35 (m, 1H, Cp *H*/C*H*Ph), 5.32 (d, *J* = 2.7, 1H, Cp *H*/C*H*Ph), 5.27 (d, *J* = 2.7, 1H, Cp *H*/C*H*Ph), 5.17−5.13 (m, 1H, Cp *H*/C*H*Ph), 5.02 (d, *J* = 2.7, 2H, Cp *H*/C*H*Ph), 4.98 (d, *J* = 3.8, 3H, C*H*Ph), 4.96−4.94 (m, 2H, Cp *H*/C*H*Ph), 4.92 (d, *J* = 3.8, 2H, C*H*Ph), 4.87−4.85 (m, 1H, Cp *H*/C*H*Ph), 4.78−4.73 (m, 1H, Cp *H*/C*H*Ph), 4.63−4.59 (m, 2H, Cp *H*/C*H*Ph), 4.59−4.57 (m, 1H, Cp *H*/C*H*Ph), 4.56−4.51 (m, 2H, Cp *H*/C*H*Ph), 4.48−4.40 (m, 3H, Cp *H*/C*H*Ph), 4.33−4.29 (m, 1H, Cp *H*/C*H*Ph), 4.27 (d, *J* = 2.4, 2H, Cp *H*/C*H*Ph), 4.15−4.09 (m, 2H, Cp *H*/C*H*Ph), 2.37 (s, 6H, 2 × C*H*$_3$), 2.34 (s, 3H, C*H*$_3$), 2.31 (s, 3H, C*H*$_3$), 2.29 (s, 3H, C*H*$_3$), 2.25 (s, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, mixture of *cis* and *trans* isomers): δ 183.8 (^{q}C), 176.89 (^{q}C), 171.0 (^{q}C), 166.5 (^{q}C), 163.3 (^{q}C), 158.3 (^{q}C), 146.0, 145.9, 145.2, 145.0, 144.5, 142.5, 141.1, 140.7, 140.6, 140.1, 139.7, 138.7, 134.5, 134.23, 134.20, 133.2, 130.4, 130.3, 130.1, 130.00, 129.97, 129.8, 129.61, 129.56, 129.53, 129.41, 129.39, 129.32, 129.30, 129.26, 129.1, 129.0, 128.9, 128.82, 128.77, 128.72, 128.67, 128.60, 128.57, 128.54, 128.52, 128.47, 128.3, 128.21, 128.17, 128.0, 127.9, 127.7, 127.64, 127.61, 127.59, 127.5, 127.4, 127.32, 127.27, 127.17, 127.1, 126.78, 126.76, 126.4, 125.94, 125.89, 125.87, 125.84, 125.77, 125.63, 125.57, 125.4, 125.1 (C_{Ar}), 85.3, 83.1, 82.7, 80.0, 78.1, 78.0, 77.3, 76.9, 76.8, 76.5, 76.1, 76.0, 75.7, 75.3, 74.7, 74.4, 74.3, 74.19, 74.16, 73.5, 73.3, 73.0, 72.9, 72.49, 72.45, 72.36, 72.2, 71.9, 70.84, 70.78, 67.7 (Cp C/HC(N)), 31.0, 21.77, 21.72, 21.68, 21.62, 21.59, 21.49 (Ts-CH_3). IR (in $CDCl_3$): $\tilde{\nu}$ 3033, 2254, 1971, 1596, 1531, 1495, 1453, 1367, 1170, 1090, 1028 cm^{-1}. MS (ESI, only monomeric species detectable): *m*/*z* 1129.19 (100%, [M + H − Cl]$^+$), 935.23 (3%, [M + H − PtCl]$^+$). HRMS (ESI): *m*/*z* calcd for [M + H − Cl]$^+$ 1129.1889, measd 1129.1886. Data for monomer **1** are as follows. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60−7.31 (m, 16H, arom *H*), 7.17 (m, 3H, arom *H*), 7.01 (m, 5H, arom *H*), 6.89 (m, 2H, arom *H*), 6.69 (d, *J* = 7.5, 2H, arom *H*), 6.45 (d, *J* = 2.7, 2H, arom *H*), 5.58 (m, 1H, Cp), 5.55 (d, *J* = 2.7, 1H, Cp *H*), 5.51 (d, *J* = 2.7, 1H, CHPh), 5.35 (d, *J* = 2.7, 1H, C*H*Ph), 5.22 (d, *J* = 3.3, 1H, C*H*Ph), 5.10 (d, *J* = 2.7, 2H, C*H*Ph, Cp *H*), 4.94 (m, 1H, Cp *H*), 4.68 (m, 1H, Cp *H*), 4.62 (dd, *J* = 2.7, *J* = 2.4, 1H, Cp *H*), 4.34 (m, 1H, Cp *H*), 2.45 (s, 3H, Ts-C*H*$_3$), 2.33 (s, 3H, Ts-C*H*$_3$). All further data are in accordance with the literature.[2]

Bis{[*μ*-chloro-[(η^5-(4′′*R*,5′′*R*)-(1-*S*$_P$)-2-(2′′-4′′,5′′-dihydro-4′′,5′′-diphenyl-1′′-tosyl-1′′*H*-imidazolyl)cyclopentadienyl-κ*C1*,κ*N3*]palladium(II)][*μ*-chloro-[(η^5-(4′′′*R*,5′′′*R*)-(1′-*S*$_P$)-2′-(2′′′-4′′′,5′′′-dihydro-4′′′,5′′′-diphenyl-1′′′-tosyl-1′′′*H*-imidazolyl)-cyclopentadienyl-κ*C1*′,κ*N3*′]platinum(II)]iron(II)} ([FBIPP-Cl]$_2$). A mixture of platinacycles **1**/**1**$_2$ (249.1 mg, 0.214 mmol, 1.00 equiv), bis(acetonitrile)dichloropalladium (55.5 mg, 0.214 mmol, 1.00 equiv), and sodium acetate (34.0 mg, 0.428 mmol, 2.00 equiv) was dissolved in degassed 1,2-dichloroethane/tBuOH (1/1) (28.5 mL) and the solution stirred for 7.5 h at 80 °C. After the mixture was cooled to room temperature, the solvent was removed in vacuo and the reaction mixture was filtered through silica gel (DCM). The solvent was subsequently removed under reduced pressure. The product was obtained as a red solid (161.1 mg, 0.0617 mmol, 58%). The product is a mixture of two regioisomers (isomeric ratio 1/0.5). [α]$_D^{25}$ (*c* = 0.020 g/dL, $CHCl_3$) = −225.0°. Mp: >200 °C dec. ^{1}H NMR (500 MHz, CD_2Cl_2, main isomer (*), minor isomer (#)): δ 7.44−7.36 (m, 12H, arom *H*), 7.34−7.11 (m, 20H, arom *H*), 7.06−6.90 (m, 13H, arom *H*), 6.90−6.84 (m, 3H, arom *H*), 6.36−6.30 (m, 4H, arom *H*), 5.14* (d, *J* = 2.2, 1H, Cp *H*), 6.34 (d, *J* = 7.7, 4H, arom *H*), 5.12# (d, *J* = 2.2, 1H, Cp *H*), 5.06−5.03 (m, 2H, Cp *H*), 4.97* (d, *J* = 2.8, 1H, C*H*Ph), 4.91# (d, *J* = 3.1, 1H, C*H*Ph), 4.88# (d, *J* = 3.5, 1H, C*H*Ph), 4.81* (d, *J* = 3.8, 1H, C*H*Ph), 4.66−4.63 (m, 2H, C*H*Ph/Cp *H*), 4.60* (d, *J* = 2.8, 1H, C*H*Ph), 4.56−4.53# (m, 2H, C*H*Ph/Cp *H*), 4.49* (d, *J* = 3.9, 1H, C*H*Ph/Cp *H*), 4.48−4.46* (m, 1H, Cp *H*), 4.46−4.44# (m, 1H, Cp *H*), 4.38 (d, *J* = 2.4, 1H, Cp *H*), 4.37* (d, *J* = 2.4, 1H, Cp *H*), 4.29# (d, *J* = 2.2, 1H, Cp *H*), 4.27* (d, *J* = 2.2, 1H, Cp *H*), 2.41 (s, 3H, Ts-C*H*$_3$), 2.39 (s, 3H, Ts-C*H*$_3$), 2.37 (s, 3H, Ts-C*H*$_3$). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 172.3 (2C), 170.4 (2C), 145.8 (2C), 145.6 (2C), 140.9, 140.7 (2C), 140.5 (2C), 140.3, 134.1, 133.9 (2C), 133.8 (2C), 133.7, 130.3 (4C), 130.2 (4C), 129.6 (4C), 129.5 (4C), 128.9, 128.8, 128.7 (2C), 128.6, 128.5, 128.4 (2C), 127.6, 127.3, 127.2 (2C), 127.1, 127.0 (2C), 126.9 (3C), 126.6, 126.5 (2C), 125.7, 125.6 (2C), 125.5 (2C), 125.4, 126.2 (2C), 97.9 (2C), 97.2, 78.1 (2C), 77.7, 77.5, 77.3 (2C), 76.7 (2C), 76.4 (2C), 75.8, 75.5, 74.9 (2C), 74.7 (2C), 74.4 (2C), 73.3, 73.1 (2C), 73.0 (2C), 72.9 (2C), 71.2, 70.9, 70.0 (2C), 69.9, 69.0, 68.9 (2C), 68.5 (2C), 21.4 (4C). IR (in $CDCl_3$): $\tilde{\nu}$ 3065, 2925, 2362, 2256, 1597, 1551, 1494, 1457, 1362, 1335, 1259, 1170, 1096, 1029, 971, 905, 812, 728, 670, 649, 607, 545 cm^{-1}. MS (ESI): *m*/*z* 2610.04 (100%, [M]$^+$), 1305.00 (51%, [M + H]$^+$). HRMS (ESI): *m*/*z* calcd for [M]$^+$ 2610.0433, found 2610.0427.

{Acetonitrile-[(η^5-(4′′*R*,5′′*R*)-(1-*S*$_P$)-2-(2′′-4′′,5′′-dihydro-4′′,5′′-diphenyl-1′′-tosyl-1′′*H*-imidazolyl)cyclopentadienyl-κ*C1*,κ*N3*]heptafluorobutyratopalladium(II)]}{acetonitrile-[(η^5-(4′′′*R*,5′′′*R*)-(1′-*S*$_P$)-2′-(2′′′-4′′′,5′′′-dihydro-4′′′,5′′′-diphenyl-1′′′ tosyl-1′′′*H*-imidazolyl)cyclopentadienyl-κC1′,κ*N3*′]-heptafluorobutyratoplatinum(II)]}iron(II) (FBIPP-O$_2$CC$_3$F7). A solution of silver heptafluorobutyrate (4.9 mg, 0.0153 mmol, 4.00 equiv) in MeCN (0.1 mL) was added to [**FBIPP-Cl**]$_2$ (10.0 mg, 3.83 μmol, 1.00 equiv) under an N_2 atmosphere. The mixture was stirred for 2 h at room temperature. The reaction mixture was then filtered through Celite, and subsequently the solvent was removed by a stream of N_2 and finally by vacuum. [α]$_D^{22}$ (*c* = 0.050 g/dL, $CHCl_3$) = +540.0°. Mp: >200 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63−6.98 (m, 24H, arom *H*), 6.61−6.56 (m, 2H, arom *H*), 6.56−6.50 (m, 2H, arom *H*), 5.83−5.77 (m, 1H, C*H*Ph), 5.61−5.55 (m, 1H, C*H*Ph), 5.19−5.14 (m, 1H, C*H*Ph), 5.16−5.13 (m, 1H, Cp *H*), 5.11−5.07 (m, 1H, Cp *H*), 5.00−4.96 (m, 1H, Cp *H*), 4.92−4.88 (m, 1H, Cp *H*), 4.86−4.80 (m, 2H, Cp *H*), 4.67−4.62 (m, 1H, Cp *H*), 4.55−4.53 (m, 1H, C*H*Ph), 2.49 (s, 3H, Ts-C*H*$_3$), 2.46 (s, 3H, Ts-C*H*$_3$), 2.01 (s, 3H, NCC*H*$_3$ + 2 × solvent NCC*H*$_3$), 1.73 (s, 3H, NCC*H*$_3$). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 174.7, 172.0, 147.2, 146.9, 140.8, 140.3, 139.9, 139.7, 134.6, 134.4, 131.3, 131.15 (2C), 131.07 (2C), 130.2 (2C), 130.0 (4C), 129.7 (2C), 129.6 (2C), 129.3 (4C), 128.6, 128.4, 128.0

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(2C), 127.8, 127.6 (2C), 127.5 (2C), 126.5, 126.3 (2C), 125.9, 125.5 (2C), 22.0 (2C), 3.2, 2.2. ^{19}F NMR (235 MHz, $CDCl_3$): −80.5 to −81.0 (m, 3F, CF_3), −80.6 to −80.2 (m, 3F, CF_3), −115.4 to −115.9 (m, 2F, CF_3CF_2), −116.6 to −117.2 (m, 2F, CF_3CF_2), −126.6 to −126.9 (m, 2F, CF_2COO), −127.1 to −127.6 (m, 2F, CF_2COO). IR (in $CDCl_3$): $\tilde{\nu}$ 3033, 2929, 2254, 1672, 1596, 1544, 1494, 1466, 1456, 1374, 1333, 1305, 1261, 1211, 1189, 1171, 1118, 1083, 1053, 967, 931, 906, 814, 758, 719, 700, 670, 650, 600, 543 cm^{-1}. MS (ESI): *m*/*z* 1447.0 (100%, $[M - O_2CC_3F_7 - 2MeCN]^+$) 1269.0 (59%, $[M - 2O_2CC_3F7 - 2MeCN + Cl]^+$). HRMS (ESI): *m*/*z* calcd for $[M - O_2CC_3F_7 - 2MeCN]^+$ 1446.0635, found 1446.0631.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further experimental procedures, characterization data, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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