Paramagnetic Palladacycles with Pd^{III} Centers are Highly Active Catalysts for Asymmetric Aza-Claisen Rearrangements

Simon H. Eitel,[‡] Matthias Bauer,*[,#] David Schweinfurth,[†] Naina Deibel,[†] Biprajit Sarkar,*[,†] Harald Kelm,[§] Hans-Jörg Krüger,*[,§] Wolfgang Frey,[‡] and René Peters*[,‡]

[‡] *Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany*

[#] *Institut für Technische Chemie und Polymerchemie, Karlsruher Institut für Technologie (KIT), Engesserstr. 18 / 20, D-76128 Karlsruhe, Germany*

[†] *Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany*

[§] *Fachbereich Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger Straße Gebäude 54/655, D-67663 Kaiserslautern, Germany*

Email: matthias.bauer@kit.edu; sarkar@iac.uni-stuttgart.de; krueger@chemie.uni-kl.de; rene.peters@oc.uni-stuttgart.de

Table of Contents

Experimental

All reactions were performed in oven dried (150 °C) glassware and were magnetically stirred. A positive pressure of nitrogen (ca. 0.2 mbar) was used as protective atmosphere. For all reactions liquids and solutions were added *via* syringe and septa. Solvents were removed by rotary evaporation at 40 °C bath temperature and 600 – 10 mbar pressure or by a constant stream of nitrogen. Non-volatile compounds were dried *in vacuo* at 0.1 mbar. Diethyl ether, tetrahydrofuran (THF) and dichloromethane (DCM) were distilled and further purified by a solvent purification system. Silver nitrate (> 99.99%) was ground to powder and stored in a glove box. DMF (anhydrous, 99.8%) was stored in crown capped bottles under nitrogen atmosphere. Absolute ethanol and *n*-pentane were used as purchased. For work-up procedures and column chromatography distilled technical grade solvents (diethyl ether, petrol ether and ethyl acetate) were used. **PPFIP-Cl**,[1] **PPFOP-Cl**,[2] pentaphenylferrocene,[2] thianthrenium tetrafluoroborate **6**[3] and the allylic trifluoroacetimidate[6] **3b** and **3c** were prepared according to literature procedures. All other chemicals were purchased and used without further purification. Reactions were magnetically stirred and either monitored by HPLC (reverse phase, acetonitrile/water as eluent) or by thin layer chromatography (TLC) with silica-plates (*silica gel 60 F_{254}*). Visualization was achieved by fluorescence quenching under UV light (λ = 254 nm) and/or by staining with $KMnO_4$/NaOH-solution (0.5 g $KMnO_4$ in 100 mL 0.1 M NaOH). Preparative column chromatography for compound purification was performed on silica (0.040 – 0.063 mm), using a positive pressure of nitrogen (ca. 0.2 mbar). Yields refer to pure isolated products and are calculated in mol% of the used starting material.

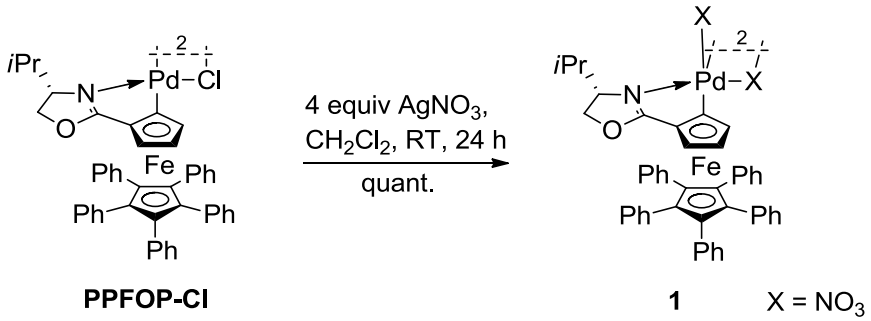
^{1}H and ^{13}C NMR spectra were recorded at 21 °C on spectrometers operating at 300 and 500 MHz for ^{1}H and 75 and 125 MHz for ^{13}C. ^{19}F NMR spectra were recorded at 21 °C on a spectrometer operating at 235 MHz. Deuterated solvents were used as purchased and are stated after the corresponding frequency. Chemical shifts in ppm refer to tetramethylsilane (δ = 0) as internal standard. Coupling constants *J* are given in Hz and the following abbreviations are used for multiplicities: *s* (singulet), *d* (doublet), *t* (triplet), *q* (quartet), *p* (pentet), *m* (multiplet), *b* (broad signal). IR spectra were recorded by the analytical service of the Universität Stuttgart on a spectrometer with an ATR-unit. Aggregation state of the sample is stated in parentheses, signals are given by wavenumbers (cm^{-1}).

The *ee*-values of **4** were determined by chiral stationary phase HPLC after cleavage of the trifluoroacetate group. The assignment of the configuration of products **4** is based on comparison of the specific optical rotations and HPLC retention times with literature data, after cleavage of

the trifluoroacetate group.[6] Optical rotation was measured at 20 °C on a polarimeter operating at the sodium-D line ($\lambda = 589$ nm). Path length of the quartz cell was 100 mm, solvent and concentration (in g mL^{-1}) are stated in parentheses. Melting points were measured in open glass capillaries and are uncorrected. Mass spectra were performed by the analytical service of the Universität Stuttgart. The ionization method is stated in parentheses. Microanalyses were performed by the analytical service of the Universität Stuttgart. Single crystal X-ray analysis was performed by Dr. Wolfgang Frey. XAS and EDX measurements were performed by Dr. Matthias Bauer. Cyclic voltammogram, EPR spectra and UV-vis-NIR spectroelectrochemical measurements were recorded by David Schweinfurth, Naina Deibel and Dr. Biprajit Sarkar. Mössbauer spectra were recorded by Dr. Harald Kelm and Prof. Dr. Hans-Jörg Krüger. ICP-OES measurements were performed by Stefan Naumann and Prof. Dr. M. R. Buchmeiser.

Synthesis of Scalemic Pd^{III} Complexes

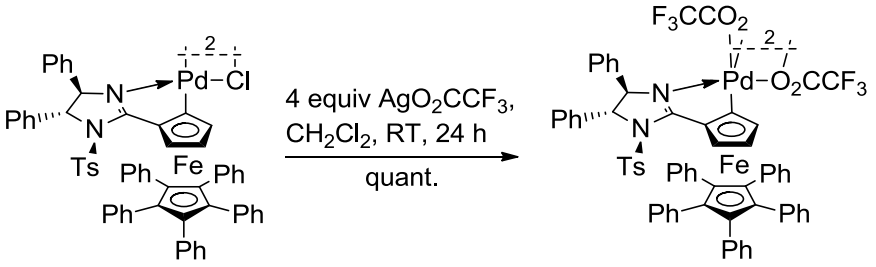
Bis[nitrato]bis[μ-(nitrato-κ*O*:κ*O*')]bis[(*1S*$_p$)-2-[(*4S*)-4,5-dihydro-4-(1-methylethyl)-2-oxazolyl-κ*N*3]-1',2',3',4',5'-pentaphenylferrocenyl-κ*C*]di-palladium(III) (1)



A solution of **PPFOP-Cl** (5.28 mg, 3.2 µmol) in dry DCM (1 mL) was transferred into a dry pear-shaped flask equipped with a magnetic stirring bar and $AgNO_3$ (2.19 mg, 12.9 µmol, 4 equiv) under N_2. The flask was sealed with a plastic cap and shielded from light. The suspension was stirred for 24 h at room temperature, filtrated under N_2 through celite/CaH_2 (1:1) and the filter cake was washed with dry DCM (1 mL). The solvent was removed by a constant N_2 stream providing the dimeric Pd^{III} complex **1** as an orange-brown solid (5.80 mg, 3.2 µmol, quant.).

$C_{92}H_{76}Fe_2N_6O_{14}Pd_2$, **MW**: 1812.22 g/mol. **Mp**: decomposition > 200 °C. **$[\alpha]_D^{20}$ (c = 0.10, DCM)**: – 1962.9. **IR (solid)**: ν = 3056, 2923, 1602, 1444, 1374, 1267, 987, 696, 573. **MS (ESI) *m*/*z***: 1750.3 ([**1** – NO_3]$^+$, 1%), 1626.3 ([**1** – $(NO_3)_3$]$^+$, 100%), 1583.4 ([**1** – $Pd(NO_3)_2$]$^+$, 10%), 844.1 ([monomer – (NO_3)]$^+$, 3%), 782.1 ([ligand+Pd]$^+$, 3%). **Microanalysis**: calc. for $C_{92}H_{76}Fe_2N_6O_{14}Pd_2$: C: 60.91; H: 4.22; N: 4.63. Found: C: 60.76; H: 4.15; N: 4.65.

Bis[trifluoroacetato]bis(μ-trifluoroacetato-κ*O*:κ*O*')bis[(*1S*$_p$)-2-[(*4R*,*5R*)-4,5-dihydro-1-[(4-methylphenyl)sulfonyl]-4,5-diphenyl-1*H*-imidazol-2-yl-κ*N*3]-1',2',3',4',5'-pentaphenylferrocenyl-κ*C*]di-palladium(III) (2)

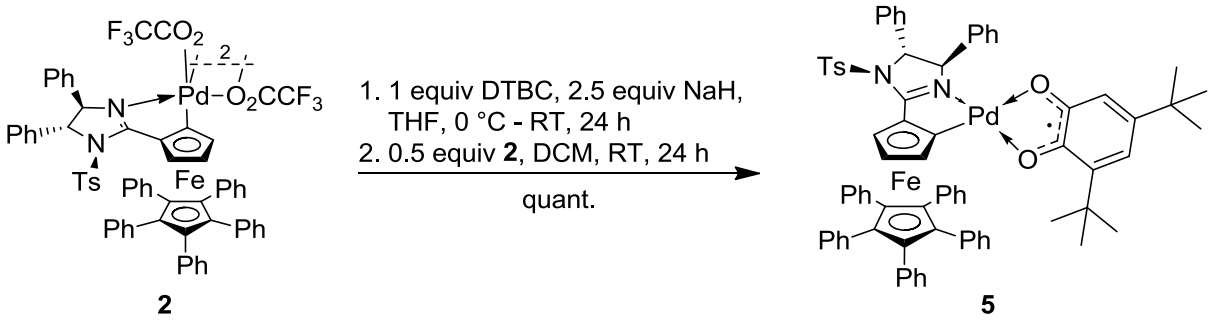


PPFIP-Cl **2**

A solution of **PPFIP-Cl** (69.8 mg, 32 μmol) in dry DCM (10 mL) was transferred into a dry pear-shaped flask equipped with a magnetic stirring bar and AgO_2CCF_3 (28.4 mg, 0.13 mmol, 4 equiv) under N_2. The flask was sealed with a plastic cap and shielded from light. The suspension was stirred for 24 h at room temperature, filtrated under N_2 through celite/CaH_2 (1:1) and the filter cake was washed with dry DCM. The solvent was removed by a constant N_2 stream to provide the dimeric Pd^{III} complex **2** as a red-brown solid (81.4 mg, 32 μmol, quant.).

$C_{132}H_{94}F_{12}Fe_2N_4O_{12}Pd_2S_2$, **MW**: 2544.82 g/mol. **Mp**: decomposition > 200 °C. **$[\alpha]_D^{20}$ (c = 0.10, DCM)**: + 2051.1. **^{19}F NMR (235 MHz, $CDCl_3$)**: δ = –72.85 (*b*, C*F*$_3$), –74.47 (*b*, C*F*$_3$). **IR (solid)**: ν = 3056, 1666, 1651, 1444, 1191, 1139, 696. **MS (ESI) *m*/*z***: 2429.21 ([**2** – TFA]$^+$, 2%), 2205.3 ([**2** – $(TFA)_3$]$^+$, 39%), 1158.15 ([**2** – $(TFA)_2$]$^+$, 5%), 1045.17 ([ligand+Pd]$^+$, 100%), 890.14 ([ligand+Pd – Ts]$^+$, 26%). **Microanalysis**: Calc. for $C_{132}H_{94}F_{12}Fe_2N_4O_{12}Pd_2S_2$: C: 62.30; H: 3.72; N: 2.20. Found: C: 62.49; H: 4.06; N: 2.15.

(3,5-Di-*tert*-butylsemiquinone-κ*O*:*O*')-[(*1S*$_p$)-2-[(*4R*,*5R*)-4,5-dihydro-1-[(4-methylphenyl)sulfonyl]-4,5-diphenyl-1*H*-imidazol-2-yl-κ*N*3]-1',2',3',4',5'-pentaphenylferrocenyl-κ*C*]-palladium(II) (5)



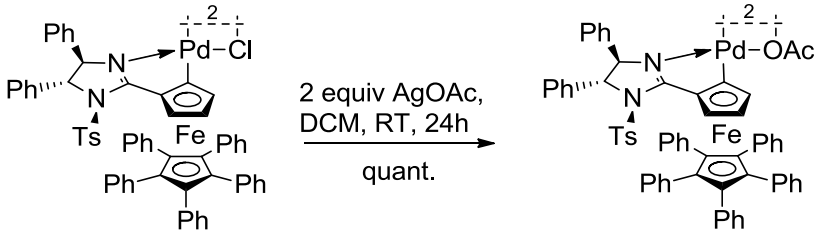
2 **5**

3,5-Di(*tert*-butyl)benzene-1,2-diol (5.11 mg, 23 µmol) was dissolved in dry THF (1 mL) and added to NaH (1.40 mg, 58 µmol, 2 equiv) in dry THF (1 mL) at 0 °C under N_2-atmosphere. The reaction was allowed to warm to room temperature and stirred overnight. The resulting reaction mixture was filtered through celite and the solvent was removed to give the di-sodium salt of 3,5-di(*tert*-butyl)catechol (DTBC) as a dark blue solid.

The Pd^{III} complex **2** (29.0 mg, 11 µmol, 0.5 equiv) in dry DCM (1 mL) was added to the di-sodium salt in dry DCM (1 mL) under N_2-atmosphere. The reaction was stirred overnight at room temperature. Afterwards the mixture was filtered through celite under N_2 and the solvent was removed by a constant stream of N_2 providing the pure product **5** as a dark red solid (28.9 mg, 23 µmol, quant.).

$C_{76}H_{67}FeN_2O_4PdS$, **MW**: 1266.69 g/mol. **Mp**: decomposition > 200 °C. **$[\alpha]_D^{20}$ (c = 0.10, DCM)**: + 19.7. **^{1}H NMR (500 MHz, CD_2Cl_2)**: The following signals could be detected of the paramagnetic complex: δ = 7.52 (*d*, *J* = 8.2, 2H, Ar*H*), 7.25 − 7.18 (*b*, Ar*H*), 7.11 (*d*, *J* = 7.7, 10H, Ar*H*), 7.06 − 6.96 (*b*, Ar*H*), 6.93 − 6.85 (*m*, Ar*H*), 6.77 (*t*, *J* = 7.7, 2H, Ar*H*), 6.45 (*d*, *J* = 7.7, 2H, Ar*H*), 6.21 (*d*, *J* = 7.7, 2H, Ar*H*), 5.68 (*d*, *J* = 2.4, 1H, C*H*), 4.59 (*t*, *J* = 2.4, 1H, *m*-C_5H_3), 4.43 − 4.40 (*m*, 2H, C*H*-Ph), 4.33 − 4.32 (*m*, 1H, C*H*), 2.41 (*s*, 3H, CH_3), 1.18 (*s*, 9H, *t*-butyl), 1.14 (*s*, 9H, *t*-butyl). **IR (solid)**: ν = 3056, 2922, 2853, 1655, 1444, 1196, 1170, 1154, 740, 695. **MS (ESI) *m*/*z***: 1265.3 ([**5** + H]$^+$, 85%), 1045.2 ([ligand+Pd]$^+$, 100%). **HRMS (ESI) *m*/*z***: calculated for [**5** + H]$^+$: 1265.3226, found: 1265.3233.

Bis(μ-acetato-κ*O*:κ*O*')bis[(*1S*$_p$)-2-[(*4R*,*5R*)-4,5-dihydro-1-[(4-methylphenyl)sulfonyl]-4,5-diphenyl-1*H*-imidazol-2-yl-κ*N*3]-1',2',3',4',5'-pentaphenylferrocenyl-κ*C*]di-palladium(II) (PPFIP-OAc)

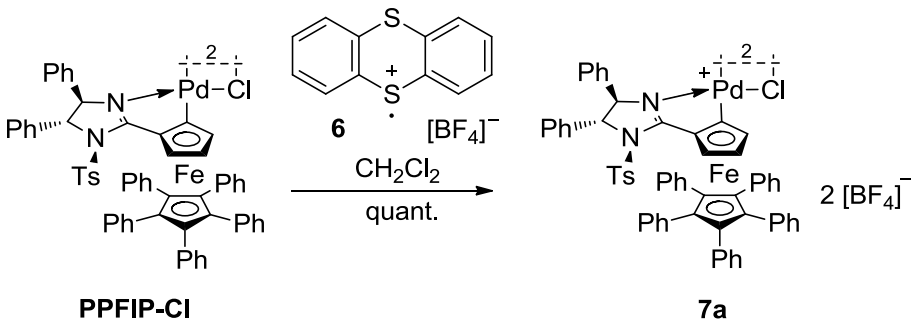


PPFIP-Cl **PPFIP-OAc**

PPFIP-Cl (28.5 mg, 13 μmol) was dissolved in dry DCM (6 mL) and silver acetate (4.3 mg, 26 μmol, 2 equiv) was added under N_2. The reaction was stirred at room temperature overnight. The resulting suspension was filtrated under N_2 through celite/CaH_2 (1:1) and the filter cake was washed with dry DCM (1 mL). The solvent was removed by a constant stream of N_2 to give **PPFIP-OAc** as a wine red solid (31.9 mg, 13 μmol, quant.).

$C_{128}H_{100}Fe_2N_4O_8Pd_2S_2$, **MW**: 2210.85 g/mol. **Mp**: decomposition > 250 °C. **$[\alpha]_D^{20}$ (c = 0.029, DCM)**: + 331.0. **IR (solid)**: ν = 3054, 2924, 2854, 1731, 1599, 1547, 1501, 1443, 1377, 1168, 1153, 1075, 1027, 967, 738. **^{1}H NMR ($CDCl_3$, 300 MHz,)**: δ = 7.56 (*d*, *J* = 8.3, 4H, Ar*H*), 7.33 – 7.19 (*m*, 7H, Ar*H*), 7.12 – 7.01 (*m*, 20H, Ar*H*), 6.50 (*d*, *J* = 7.2, 4H, Ar*H*), 6.42 (*d*, *J* = 7.2, 4H, Ar*H*), 5.69 (*d*, *J* = 2.0, 2H, Pd-C-C*H*), 4.81 (*d*, *J* = 1.9, 2H, *o*-C_5H_3), 4.61 (*t*, *J* = 2.4, 2H, *m*-C_5H_3), 4.50 (*b*, 4H, C*H*-Ph), 2.51 (*s*, 6H, CH_3), 1.83 (*s*, 6H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 175.6, 170.6, 146.2, 142.5, 140.2, 135.9, 135.4, 133.1, 133.0, 130.7, 129.8, 129.4, 128.6, 128.4, 127.7, 127.6, 127.5, 127.5, 127.3, 126.8, 126.7, 125.7, 99.0, 89.1, 88.7, 81.5, 77.8, 76.5, 75.9, 74.4, 72.7, 32.4, 30.1, 23.1, 21.9. **MS (ESI) *m*/*z***: 2151.4 ([M – OAc]$^+$, 2%), 1045.2 ([ligand+Pd]$^+$, 100%), 889.2 ([ligand+Pd – Ts]$^+$, 3%). **HRMS (ESI) *m*/*z***: calc. for [M – OAc]$^+$: 2151.3668, found: 2151.3669.

Bis[tetrafluoroborato]bis(μ-chlorido)bis[(*1S*$_p$)-2-[(*4R*,*5R*)-4,5-dihydro-1-[(4-methylphenyl)sulfonyl]-4,5-diphenyl-1*H*-imidazol-2-yl-κ*N*3]-1',2',3',4',5'-pentaphenylferrocenyl-κ*C*]di-palladium(III) (7a)

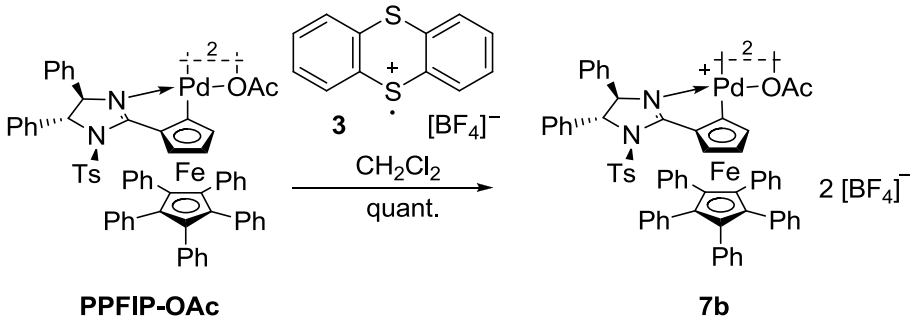


PPFIP-Cl **7a**

PPFIP-Cl (16.6 mg, 7.7 μmol) was dissolved in dry DCM (1 mL) and transferred to a solution of thianthrenium tetrafluoroborate **6** (4.7 mg, 15 μmol, 2 equiv) in dry DCM (1 mL) under N_2 atmosphere. The reaction was stirred at room temperature overnight. The resulting brown solution was filtrated under N_2 through celite/CaH_2 (1:1) and the filter cake was washed with dry DCM (1 mL). The solvent was removed by a constant stream of N_2 and the residue was washed three times with *n*-pentane to furnish the dimeric Pd^{III} complex **7a** as a brown solid (18.0 mg, 7.7 μmol, quant.).

$C_{124}H_{94}B_2Cl_2F_8Fe_2N_4O_4Pd_2S_2$, **MW**: 2337.27 g/mol. **Mp**: decomposition > 200 °C. **$[\alpha]_D^{20}$ (c = 0.10, DCM)**: + 41.3. **IR (solid)**: ν = 3057, 1595, 1546, 1497, 1445, 1379, 1170, 1053, 813, 738, 695, 668. **MS (ESI) *m/z***: 2129.4 ([**7a** – $[BF_4]_2$ – Cl]$^+$, 8%), 1261.2 ([ligand+Pd+thianthrene]$^+$, 6%), 1045.2 ([ligand+Pd]$^+$, 100%), 890.14 ([ligand+Pd – Ts]$^+$, 2%).

Bis[tetrafluoroborato]bis(μ-acetato-κ*O*:κ*O*')bis[(*1S*$_p$)-2-[(*4R*,*5R*)-4,5-dihydro-1-[(4-methylphenyl)sulfonyl]-4,5-diphenyl-1*H*-imidazol-2-yl-κN3]-1',2',3',4',5'-pentaphenylferrocenyl-κ*C*]di-palladium(III) (7b)

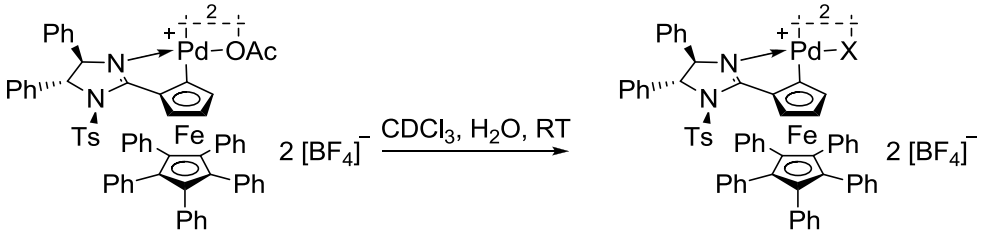


PPFIP-OAc **7b**

PPFIP-OAc (13.4 mg, 6.1 μmol) was dissolved in dry DCM (1 mL) and transferred to a solution of thianthrenium tetrafluoroborate (3.7 mg, 12 μmol, 2 equiv) in dry DCM (1 mL) under N_2. The reaction was stirred at room temperature overnight. The resulting brown solution was filtrated under N_2 through celite/CaH_2 (1:1) and the filter cake was washed with dry DCM (1 mL). The solvent was removed by a constant stream of N_2 and the residue was washed three times with *n*-pentane to yield the dimeric Pd^{III} complex **7b** as a brown solid (14.5 mg, 6.1 μmol, quant.).

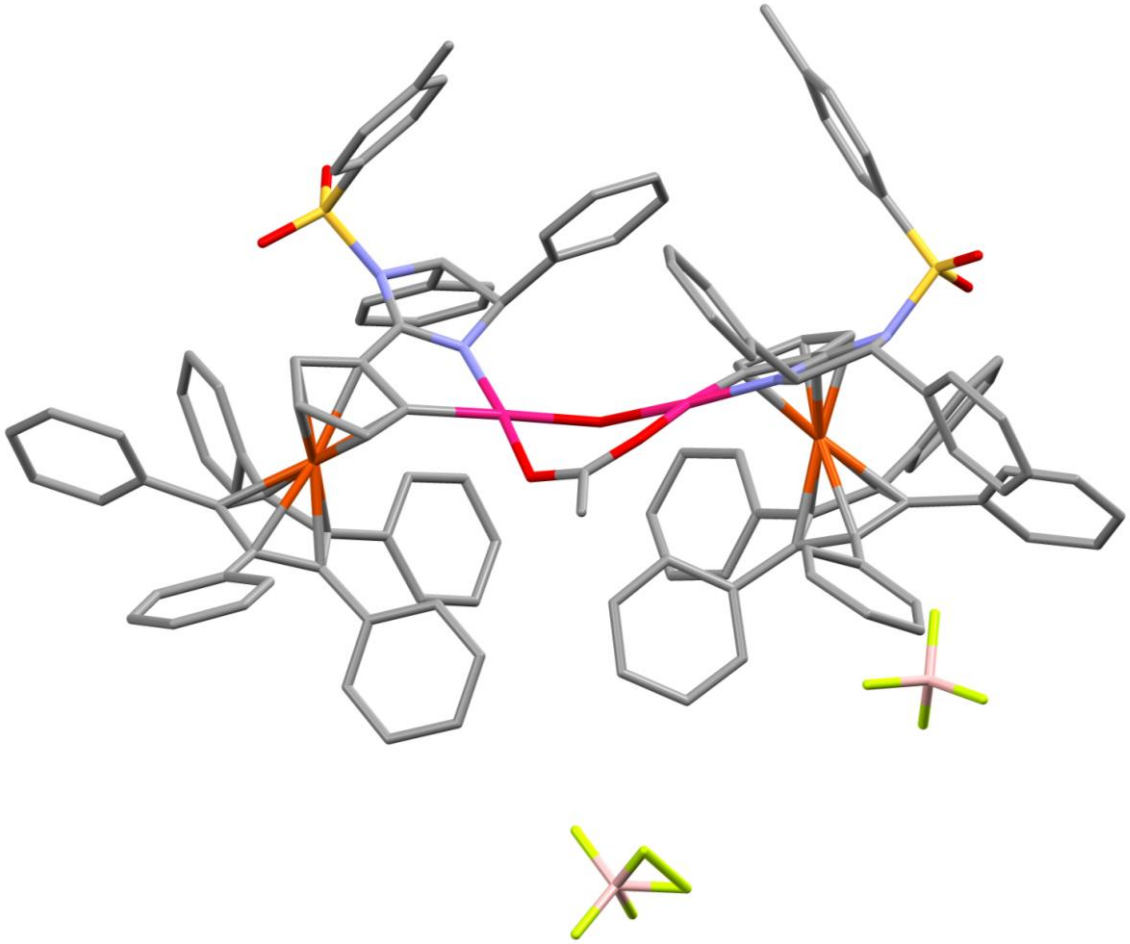
$C_{128}H_{100}B_2F_8Fe_2N_4O_8Pd_2S_2$, **MW**: 2384.45 g/mol. **Mp**: decomposition > 200 °C. **$[\alpha]_D^{20}$ (c = 0.07, DCM)**: + 40.0. **IR (solid)**: ν = 3058, 1549, 1501, 1445, 1380, 1171, 1055, 696, 668. **MS (ESI)** ***m/z***: 2153.4 ([7**b** – $[BF_4]_2$ – OAc]$^+$, 11%), 1295.3 ([ligand+Pd+thianthrene]$^+$, 51%), 1104.2 ([ligand+Pd+OAc]$^+$, 22%), 1045.2 ([ligand+Pd]$^+$, 100%), 890.2 ([ligand+Pd – Ts]$^+$, 30%).

Bis[tetrafluoroborato](μ-acetato-κ*O*:κ*O*')(μ-hydroxo)bis[(*1S*$_p$)-2-[(*4R*,*5R*)-4,5-dihydro-1-[(4-methylphenyl)sulfonyl]-4,5-diphenyl-1*H*-imidazol-2-yl-κ*N*3]-1',2',3',4',5'-pentaphenylferrocenyl-κ*C*]di-palladium(III) (7c)



7b **7c:** X = OAc/OH

7c crystallized from **7b** in wet $CDCl_3$ at room temperature giving dark brown crystals, suitable for X-ray crystal structure analysis. CCDC 831695 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

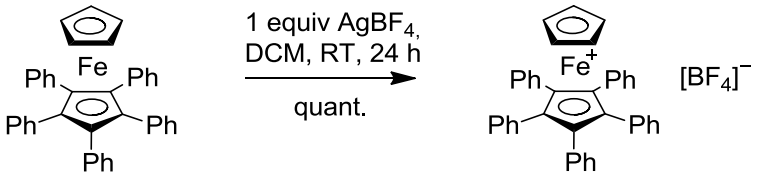


X-ray crystal structure of **7c** [color code: C (grey); B (grey-brown); F (green); N (blue); O (red); S (yellow); Fe (orange); Pd (pink)]. H atoms and one included water molecule per unit cell are omitted for clarity. One tetrafluoroborate counterion shows a disorder.

$C_{126}H_{98}B_2F_8Fe_2N_4O_7Pd_2S_2$, **MW**: 2342.42 g/mol. **Mp**: decomposition > 200 °C. **IR (solid)**: ν = 3667, 3543, 3057, 2926, 1538, 1379, 1169, 1046, 737, 694. **MS (ESI) *m/z***: 2343.33 ([**7c**+H]$^+$, 1%), 2149.33 ([**7c** – $(BF_4)_2$ – OH^-]$^+$, 1%), 1104.20 ([ligand+Pd+OAc]$^+$, 100%), 1045.17 ([ligand+Pd]$^+$, 46%), 890.16 ([ligand+Pd – Ts]$^+$, 14%).

Synthesis of Reference Compounds

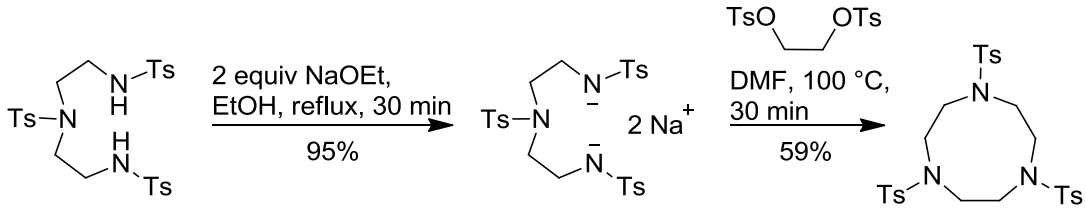
Pentaphenylferrocenium tetrafluoroborate



Pentaphenylferrocene (17.5 mg, 31 µmol) was dissolved in dry DCM (1.5 mL) and added to $AgBF_4$ (6.0 mg, 31 µmol, 1 equiv) under N_2. The reaction was stirred for 24 h at room temperature. The suspension was filtrated under nitrogen over celite. The solvent was removed by a constant stream of N_2 to give brown pentaphenylferrocenium tetrafluoroborate (20.3 mg, 31 µmol, quant.).

$C_{40}H_{30}BF_4Fe$, MW: 653.32 g/mol. **Mp**: decomposition > 300 °C. **IR (solid)**: ν = 3054, 2919, 1600, 1577, 1500, 1443, 1410, 1180, 1050, 1027, 839, 738, 693. **MS (ESI) *m/z***: 566.2 ($[M - BF_4]^+$, 100%). **Microanalysis**: Calc. for $C_{40}H_{30}FeBF_4$: C: 73.54; H: 4.63. Found: C: 73.57; H: 4.60.

N,*N*',*N*''-Tritosyl-1,4,7-triazacyclononane[4]

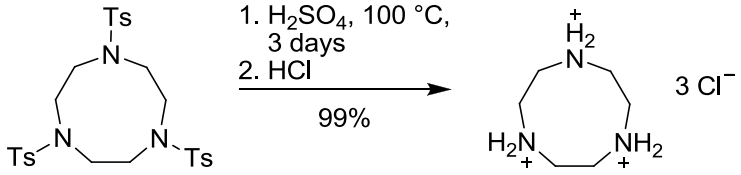


Abs. ethanol (12 mL) was added to *N*,*N*',*N*''-tritosyldiethylenetriamine (4.39 g, 7.76 mmol) under nitrogen and heated to reflux. After 30 min the heat source was removed and a solution of NaOEt, prepared from sodium (0.36 g, 15.5 mmol) and abs. ethanol (12 mL) was added as rapidly as possible. The resulting solution was decanted from an undissolved residue. The solution was kept at room temperature overnight, from which the product crystallized. The disodium salt was filtrated under nitrogen, washed with abs. ethanol and dried *in vacuo* at 40 °C to give pure *N*,*N*',*N*''-tritosyldiethylenetriamine disodium salt (4.52 g, 7.41 mmol, 95%).

N,*N*',*N*''-tritosyldiethylenetriamine disodium salt (4.00 g, 6.56 mmol) was dissolved in DMF (53 mL) and warmed to 100 °C. A solution of ethylene glycol ditosylate (2.43 g, 6.56 mmol, 1 equiv) in DMF (21 ml) was added *via* syringe pump during 5 min. The reaction mixture was held at 100 °C for an additional 30 min. Afterwards water (18 mL) was added and the reaction mixture was allowed to cool to room temperature and stirred overnight. The product was collected by filtration, washed with 95% ethanol and dried *in vacuo* at 40 °C to provide pure *N*,*N'*,*N''*-tritosyl-1,4,7-triazacyclononane (2.28 g, 3.87 mmol, 59%).[4]

$C_{27}H_{33}N_3O_6S_3$, **MW**: 591.76 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 7.70 (*d*, *J* = 8.1, 6H, Ar*H*), 7.33 (*d*, *J* = 8.1, 6H, Ar*H*), 3.45 (*s*, 12H, CH_2), 2.45 (*s*. 9H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 143.9, 132.6, 129.9, 127.3, 51.9, 21.5. The other analytical data are in accordance with the literature.[4]

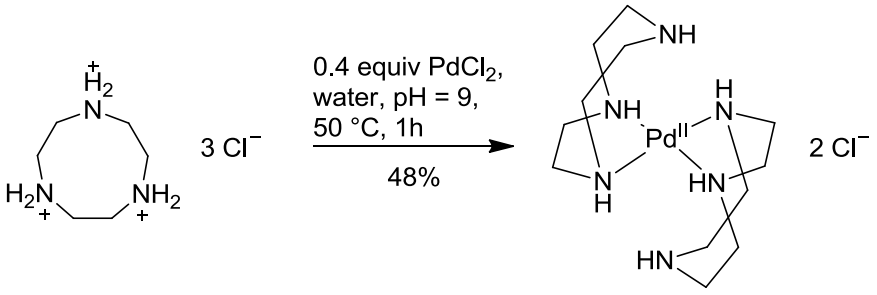
1,4,7-Triazacyclononane tris(hydrochloric acid) salt[4]



Under nitrogen protective atmosphere concentrated sulfuric acid (0.7 mL) was added to *N*,*N*',*N*''-tritosyl-1,4,7-triazacyclononane (0.28 g, 0.47 mmol). The mixture was held for three days at 100 °C. The solution was cooled to 0 °C and diethyl ether (2 mL) was slowly added. The precipitated, hygroscopic polyhydrosulfate salt was filtrated under nitrogen and washed with anhydrous diethyl ether. Then the salt was stirred in water (0.3 mL) and neutralized with NaOH solution (0.6 ml, 50%). Activated carbon (4 mg) was added and the solution was heated to 80 °C and filtrated through celite. The filtrate was cooled by ice and reacidified to pH 1 by adding conc. hydrochloric acid. The white tris(hydrochloric acid) triamine salt precipitated as colorless solid and the solvent was removed *in vacuo* providing the pure product (0.11 g, 0.47 mmol, 99%).[4]

$C_6H_{18}Cl_3N_3$, **MW**: 238.59 g/mol. **^{1}H NMR (300 MHz, D_2O)**: δ = 4.70 (*s*, 12H, CH_2), 3.28 (*s*, 6H, NH_2). **^{13}C NMR (75 MHz, D_2O)**: δ = 42.4. The other analytical data are in accordance with the literature.[4]

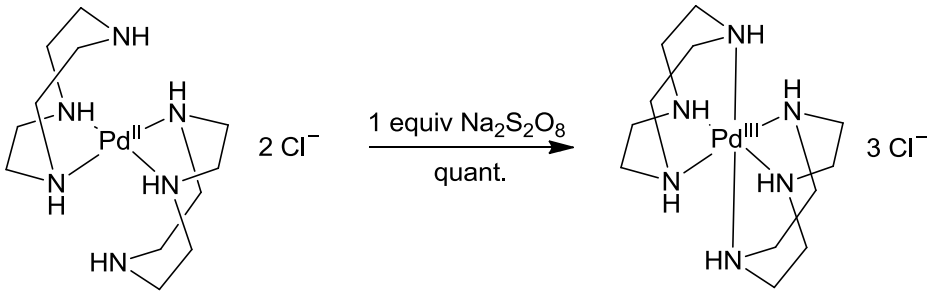
Bischlorobis(1,4,7-triazacyclononane)palladium(II) [Pd([9]aneN$_3$)](Cl)$_2$[5]



Deionized water (1.2 mL) was added to $PdCl_2$ (30.0 mg, 0.17 mmol) and adjusted to pH = 9 with NaOH solution (2M). The mixture was heated to 50 °C. 1,4,7-Triazacyclononane-trishydrochloric acid salt (100 mg, 0.42 mmol, 2.5 equiv) was directly added to the palladium suspension and kept for an additional hour at < 50 °C. Remaining $PdCl_2$ dissolved and Pd metal was formed which was removed by filtration. From the resulting solution [Pd([9]aneN$_3$)](Cl)$_2$ (35.5 mg, 0.08 mmol, 48%) crystallized as yellow solid at room temperature after several days.[5]

C$_{12}$H$_{30}$Cl$_2$N$_6$Pd, **MW**: 435.73 g/mol. **^{1}H NMR (300 MHz, D$_2$O):** δ = 3.24 − 3.15 (*m*, 12H, C*H*$_2$), 2.94 − 2.85 (*m*, 12H, C*H*$_2$). **^{13}C NMR (75 MHz, D$_2$O):** δ = 42.3. **MS (ESI) *m*/*z***:, 437.10 ([M]$^+$, 13%), 295.24 ([ligand$_2$+Cl]$^+$, 42%), 259.26 ([ligand$_2$]$^+$, 10%), 130.14 ([ligand]$^+$ 100%). **HRMS (ESI) *m*/*z***: calc. for [M+H]$^+$: 437.1008, found: 437.1016. The other analytical data are in accordance with the literature.[5]

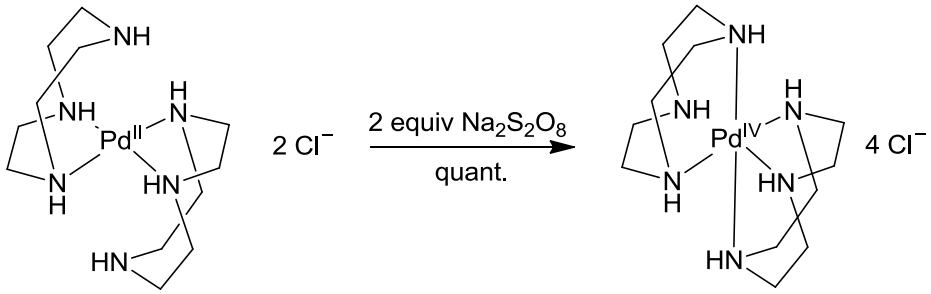
Trichlorobis(1,4,7-triazacyclononane)palladium(III) [Pd([9]aneN$_3$)](Cl)$_3$[5]



In a modified literature procedure [Pd([9]aneN$_3$)](Cl)$_2$ (24.9 mg, 57 µmol) was dissolved in diluted NaCl solution (1M, 0.6 mL) and $Na_2S_2O_8$ (13.6 mg, 57 µmol, 1 equiv) was slowly added. After a few minutes the solvent was removed by rotary evaporation to furnish the [Pd([9]aneN$_3$)](Cl)$_3$ complex in a NaCl matrix.[5]

$C_{12}H_{30}Cl_3N_6Pd$, **MW**: 471.19 g/mol. **MS (ESI) *m/z***: 130.13 ([ligand]$^+$, 100%), 234.02 ([ligand+Pd]$^+$, 10%), 269.99 ([ligand+Pd+HCl]$^+$, 13%), 287.99 ([ligand+Pd+NH_4Cl]$^+$, 10%), 361.13 ([M – Cl_3 – H_2]$^+$, 5%), 399.11 ([M – Cl_2 – H]$^+$, 2%). The other analytical data are in accordance with the literature.[5]

Tetrachlorobis(1,4,7-triazacyclononane)palladium(IV) [Pd([9]aneN_3)](Cl)$_4$[5]

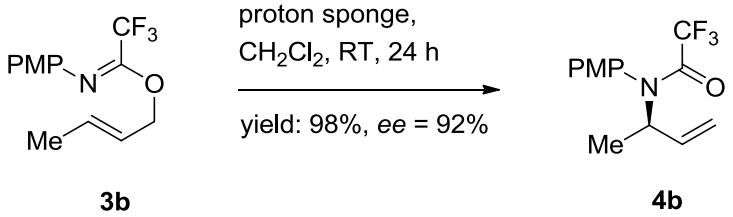


In a modified literature procedure [Pd([9]aneN_3)](Cl)$_2$ (26.4 mg, 61 µmol) was dissolved in diluted NaCl solution (1M, 0.6 mL) and $Na_2S_2O_8$ (29.0 mg, 122 µmol, 2 equiv) was slowly added. After a few minutes the solvent was removed by rotary evaporation to gain the [Pd([9]aneN_3)](Cl)$_4$ complex in a NaCl matrix.[5]

$C_{12}H_{30}Cl_4N_6Pd$, **MW**: 504.03 g/mol. **^{1}H NMR (MHz,):** δ = 4.12 − 3.95 (*m*, 12H, CH_2), 3.93-3.78 (*m*, 12H, CH_2). **^{13}C NMR (75 MHz, D_2O):** δ = 42.2. **MS (ESI) *m/z***: 130.13 ([ligand]$^+$, 100%), 234.02 ([ligand+Pd]$^+$, 4%), 269.99 ([ligand+Pd+HCl]$^+$, 6%), 287.99 ([ligand+Pd+NH_4Cl]$^+$, 5%), 361.16 ([M – Cl_4 – H_3]$^+$, 3%). The other analytical data are in accordance with the literature.[5]

Study of the Catalyst Deactivation and Reactivation

(*R*)-2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-(1-methylallyl)acetamide (4b)[6]



3b **4b**

2nd run:
catalyst precipitation after 1st run for recycling
yield **4b**: 37%, *ee* = 12%

3rd run:
catalyst precipitation after 2nd run *and catalyst reactivation with excess* AgO_2CCF_3
yield **4b**: 99%, *ee* = 79%

Catalyst activation:

A solution of **PPFIP-Cl** (20.1 mg, 9.2 µmol) in dry DCM (10 mL) was transferred into a dry pear-shaped flask equipped with a magnetic stirring bar and AgO_2CCF_3 (8.2 mg, 37 µmol, 4 equiv) under N_2. The flask was sealed with a plastic cap and shielded from light. The suspension was stirred for 24 h at room temperature, filtrated under N_2 through celite/CaH_2 (1:1) and the filter cake was washed with dry DCM. The solvent was removed by a constant N_2 stream to provide the dimeric Pd^{III} complex **2** (23.4 mg, 9.2 µmol, quant.). Proton sponge (as 0.1M solution in DCM, 4 equiv) was added to the red-brown solid.[2]

1st catalysis run:

The activated catalyst (11.2 mg, 4.4 µmol, 5 mol%) as solution in DCM was transferred to a flask containing imidate **3b** (21.9 mg, 80 µmol, 1 equiv). A stream of N_2 was passed through the flask until the solvent volume reached 0.2 mL. The flask was sealed with a plastic cap and the reaction mixture was stirred for 24 h at room temperature.[2]

After the 1st catalysis run, *n*-pentane was added to precipitate the catalyst and the supernatant was removed after centrifugation. The precipitated catalyst (12.0 mg) was dried *in* vacuo. The rearrangement product **4b** (21.3 mg, 78 µmol, 98%, 92%*ee*) was isolated by filtration of the supernatant over silica and removal of the solvent *in* vacuo. The *ee* value of the rearrangement product **4b** was determined after hydrolysis with NaOEt in EtOH (see procedure below).

2nd catalysis run:

The precipitated catalyst (6.6 mg) and proton sponge (1.0 mg, 4.7 µmol) were dissolved in dry DCM and transferred to the imidate **3b** (21.9 mg, 80 µmol). A stream of N_2 was passed through the flask until the solvent volume reached 0.2 mL. The flask was sealed with a plastic cap and the reaction mixture was stirred for 24 h at room temperature.

After the 2nd catalysis run, *n*-pentane was added to precipitate the catalyst and the supernatant was removed after centrifugation. The precipitated catalyst (6.0 mg) was dried *in* vacuo. The remaining solvent was removed *in vacuo* at room temperature and the residue was purified by column chromatography (petrol ether:EtOAc = 9:1) to result in pure product **4b** (9.3 mg, 34 µmol, 42%, 12%*ee*). The *ee* value of the rearrangement product **4b** was determined after hydrolysis with NaOEt in EtOH (see procedure below).

3rd catalysis run:

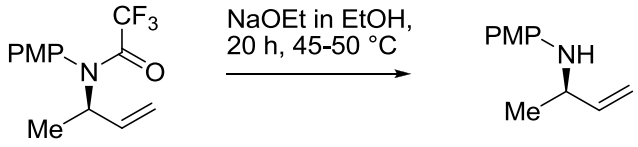
The isolated catalyst (6.0 mg) of the 2nd catalysis run was filtrated over silica, using dry DCM and then transferred into a dry pear-shaped flask equipped with a magnetic stirring bar and AgO_2CCF_3 (4.0 mg, 18 µmol) under N_2. The flask was sealed with a plastic cap and shielded from light. The suspension was stirred for 20 h at room temperature, filtrated under N_2 through celite/CaH_2 (1:1) and the filter cake was washed with dry DCM. The solvent was removed by a constant N_2 stream.

For catalysis proton sponge (1.1 mg, 5.1 µmol) was added to the oxidized catalyst, dissolved in dry DCM and transferred to the imidate **3b** (21.9 mg, 80 µmol). A stream of N_2 was passed through the flask until the solvent volume reached 0.2 mL. The flask was sealed with a plastic cap and the reaction mixture was stirred for 24 h at room temperature.

n-Pentane was added after complete reaction to precipitate the catalyst. The rearrangement product **4b** (21.6 mg, 79 µmol, 99%, 79%*ee*) was isolated by filtration of the mixture over silica and removal of the solvent *in vacuo*. The *ee* value of the rearrangement product **4b** was determined after hydrolysis with NaOEt in EtOH (see procedure below).

$C_{13}H_{14}F_3NO_2$, **MW**: 273.24 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 21 °C)**: δ = 7.05 (*m*, 2H, C_6H_4OMe), 6.89 − 6.53 (*m*, 2H, C_6H_4OMe), 5.75 (*ddd*, *J* = 17.1; 10.5; 6.6, 1H, HHC=C*H*), 5.20 − 5.16 (*m*, 3H, H_2C=CH and C*H*N), 3.83 (*s*, 3H, OCH_3), 1.18 (*d*, *J* = 6.9, 3H, CH_3). The other analytical data are in accordance with the literature.[6]

(*R*)-*N*-(4-Methoxyphenyl)-3-amino-1-butene[6]



4b

The *ee* values of the rearrangement products **4b** were determined after hydrolysis with NaOEt in EtOH. To the allylic trifluoroacetamide **4b** (86 µmol or less) was added 0.5 mL of a 1M solution of NaOEt in EtOH. The flask was closed and the reaction mixture was stirred overnight at 45 – 50 °C. An aqueous solution of saturated ammonium chloride (1 mL) was added and the mixture was extracted with DCM. After removal of the solvent under reduced pressure, the crude oily residue could be directly used for *ee*-determination by chiral stationary phase HPLC (Chiralcel OD-H, 99.8:0.2 *n*-hexane/*i*PrOH, 0.8 mL/min, detection at 250 nm).

Retention times: (*S*)-enantiomer = 31.1 min; (*R*)-enantiomer = 35.6 min.[2,6]

1st run: 92% *ee*

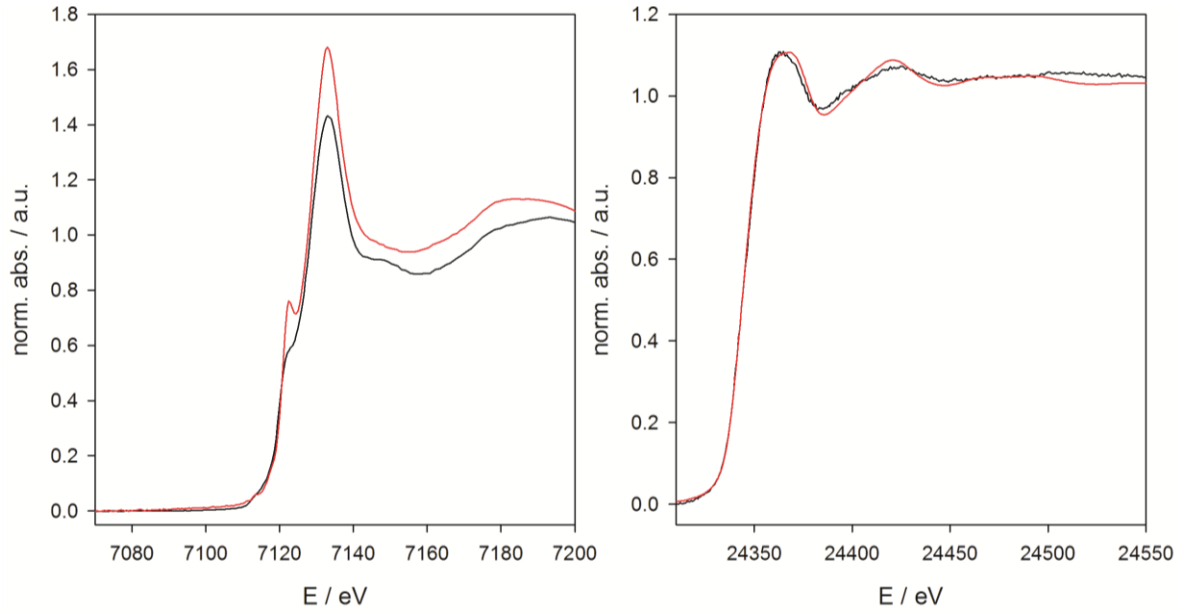
2nd run: 27% *ee*

3rd run: 79% *ee*

$C_{11}H_{15}NO$, **MW**: 177.24 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 21 °C)**: δ = 7.05 (*m*, 2H, Ar-*H*), 6.89 − 6.53 (*m*, 2H, Ar-*H*), 5.75 (*ddd*, *J* = 17.1; 10.5; 6.6, 1H, HHC=C*H*), 5.20 − 5.16 (*m*, 3H, H_2C=CH and C*H*N), 3.83 (*s*, 3H, OCH_3), 1.18 (*d*, *J* = 6.9, 3H, CH_3). The other analytical data are in accordance with the literature.[6]

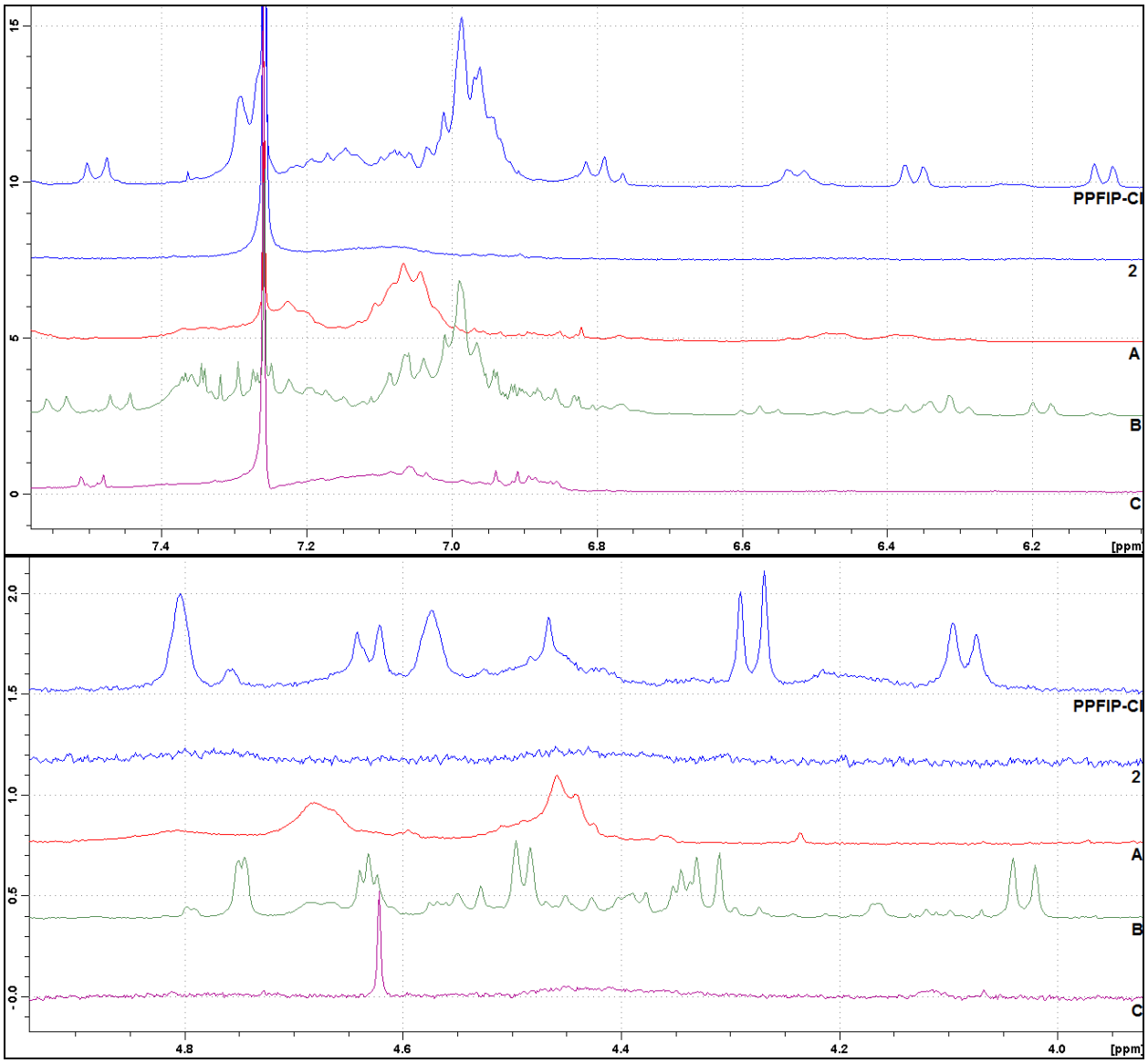
Spectroscopic Investigations of the Catalysts after the Allylic Imidate Rearrangement

Shown below are XANES spectra of the isolated solid catalysts after the allylic imidate rearrangement reaction (after the 1st run). On the left recorded at the iron K-edge, on the right at the palladium K-edge. The iron XANES spectrum does not show the pronounced 1s→Cp(π*) signal, as would be expected for an Fe^{III} species. The latter can therefore be excluded to be present after the catalytic reaction. The Pd XANES spectrum is resembling very much the spectrum of **PPFIP-Cl**, thus a Pd^{III} complex like after the activation, can also be excluded. Detailed EXAFS investigations of the used catalyst could not be carried out due to the low signal to noise ratio.



*XANES spectra of the isolated catalyst after reaction (after 1st run): (Left) Fe XANES spectra of the catalyst after reaction (black) in comparison to a ferrocenium reference (red line). (Right) Pd K-edge XANES spectrum of the catalyst after reaction (black line) in comparison to the Pd^{II} precatalyst **PPFIP-Cl**.*

The catalyst species were also used for ^{1}H NMR investigations. The spectrum of the precatalyst **PPFIP-Cl** is compared to the oxidized complex **2**, the precipitated catalyst after the first catalysis run (**A**), the filtrated catalyst after the 2nd run (**B**) and the reoxidized catalyst for the 3rd experiment (**C**). The region of the aromatic protons (top) and of the benzylic imidazoline protons and the three protons of the Cp-ring (bottom) are shown. While the oxidized complex **2** does not show any NMR signal, the precipitated complex after the 1st catalysis experiment shows slightly broadened signals due to the reduction of the Pd^{III}-complex during the catalysis. Filtration of the complex after the second catalysis experiment results in sharp signals, which disappear after reoxidation of the complex by excess silver salt, caused by the formation of paramagnetic Pd^{III}.



^{1}H NMR spectra of the different catalyst species: Precatalyst ***PPFIP-Cl*** *, activated catalyst **2**, precipitated catalyst after 1st run (**A**), filtrated catalyst after 2nd run (**B**) and reoxidized complex for the 3rd run (**C**). Only aromatic protons (top), benzylic imidazoline protons and the three protons of the Cp-ring (bottom) are shown.*

ESI-MS of the reoxidized complex for the 3rd catalysis experiment confirm the successful oxidation of the previous Pd^{II}-complex. The monomeric form of complex **2** with an additional neutral ligand (derived from the rearrangement product **4b**, which was present in traces) could be detected. Following masses were found:

MS (ESI) ***m/z***: 1513.18 ([ligand+Pd+$(O_2CCF_3)_2$+N-anisyltrifluoroacetamide+Na]$^+$, 20%), 1406.13 ([ligand+Pd+$(O_2CCF_3)_2$+trifluoroacetamide+Na]$^+$, 3%), 1318.26 ([ligand+Pd+**4b**]$^+$, 2%), 1045.17 ([ligand+Pd]$^+$, 100%), 890.14 ([ligand+Pd – Ts]$^+$, 5%).

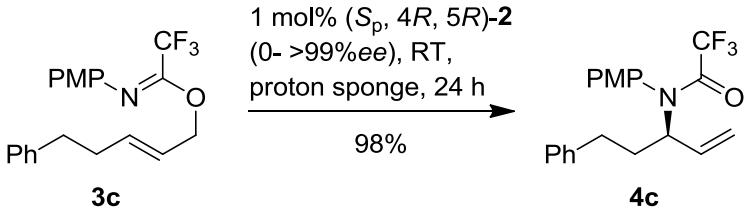
Further ESI-MS analysis during the rearrangement of **3c** in the presence of catalyst **2** (measurements after ~15 min) confirms the monomeric form of the catalyst, since the

coordination of the substrate **3c** (or product **4c**) to the monomeric catalyst plus one Na was detected.

MS (ESI) *m*/*z*: 1657.27 ([ligand+Pd+$(O_2CCF_3)_2$+**3c**+Na]$^+$, 3%), 1408.3 ([ligand+Pd+**3c**]$^+$, 14%), 1045.2 ([ligand+Pd]$^+$, 100%).

Investigations to the Non-Linear Effect of 2 in the Aza-Claisen Rearrangement

(*R*)-2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-(1-phenethylallyl)acetamide (4c)[6]



A stem solution of the (S_p,4*R*,5*R*)-configured activated Pd^{III} complex **2** in DCM (1.40 mg **2** per 200 µL DCM) was mixed with a stem solution of the (R_p,4*S*,5*S*)-configured catalyst **2** in DCM (1.40 mg **2** per 200 µL DCM) to form catalyst solutions (1.40 mg, 0.55 µmol, 1 mol%) with varying enantiomeric excess (0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and > 99% *ee* for the (S_p,4*R*,5*R*)-isomer). To this catalyst solution was added a proton sponge stem solution (0.47 mg, 2.20 µmol, 4 mol%) in DCM and a stem solution of **3c** (20.0 mg, 55 µmol, 1 equiv) in DCM. A stream of N_2 was passed through the flask until the solvent volume reached 0.2 mL. The flask was sealed with a plastic cap and the reaction mixture was stirred for 24 h at room temperature. After complete reaction, *n*-pentane was added to precipitate the catalyst. The rearrangement product **4c** (19.6 mg, 54 µmol, 98%) was isolated by filtration over silica and removal of the solvent *in vacuo*.[2] The *ee* value of the rearrangement product **4c** was determined after hydrolysis with NaOEt in EtOH (see procedure below).

$C_{20}H_{20}F_3NO_2$, MW: 363.37 g/mol. **^{1}H NMR (500 MHz, $CDCl_3$, 21 °C)**: δ = 7.31 – 7.26 (*m*, 2H, C_6H_4OMe), 7.22 − 7.05 (*m*, 5H, C_6H_4OMe and Ar*H*), 6.87 (*dd*, *J* = 7.7; 1.5, 2H, Ar*H*), 5.59 (*ddd*, *J* = 17.3; 10.1; 8.4, 1H, H_2C=C*H*), 5.34 − 5.25 (*m*, 2H, H_2C=CH), 5.08 (*q*, *J* = 6.7, 1H, C*H*N), 3.83 (*s*, 3H, OCH_3), 2.65 (*t*, *J* = 8.4, 2H, CH_2Ph), 2.02 – 1.92 (*m*, 1H, CH_2CH), 1.82 – 1.71 (*m*, 1H, CH_2CH). The other analytical data are in accordance with the literature.[6]

Figure 1 displays the presence of a negative non-linear effect for the asymmetric Aza-Claisen rearrangement of allylic trifluoroacetimidate **3c** catalyzed by the Pd^{III} complex **2**. This result supports the formation of an equilibrium between mono- and dimeric catalyst species. The value of the enantiomeric excess of the different reactions is shown in Table 1.

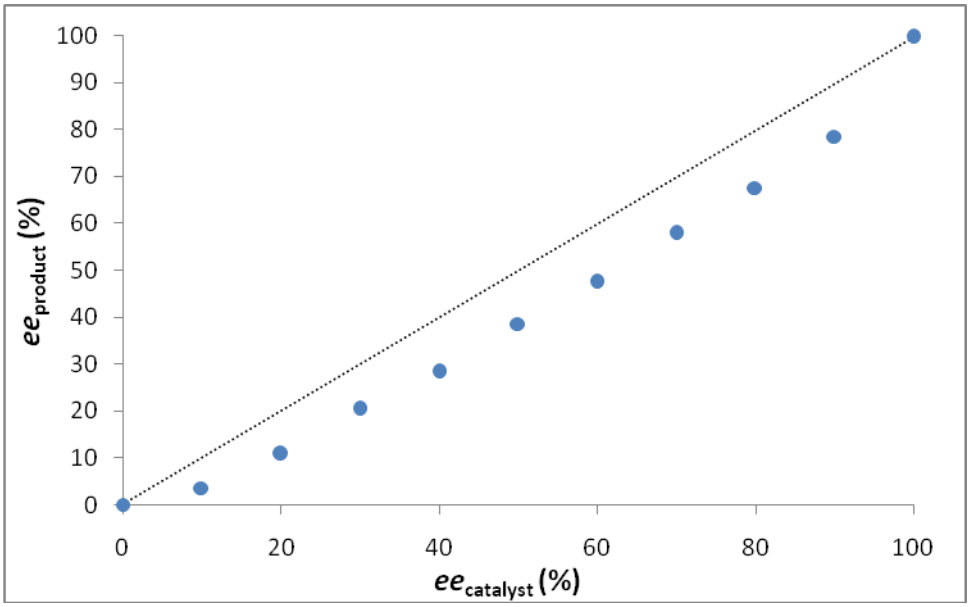
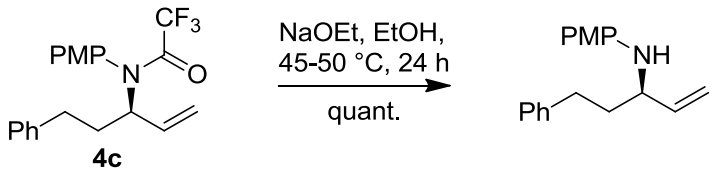


Figure 1: Investigations to the non-linear effect of catalyst 2 in the Aza-Claisen rearrangement.

(*R*)-*N*-(4-Methoxyphenyl)-3-amino-5-phenyl-1-pentene[6]



The *ee* values of the rearrangement products **4c** were determined after hydrolysis with NaOEt in EtOH. To the allylic trifluoroacetamide **4c** (86 µmol or less) was added 0.5 mL of a 1M solution of NaOEt in EtOH. The flask was closed and the reaction mixture was stirred overnight at 45 – 50 °C. An aqueous solution of saturated ammonium chloride (1 mL) was added and the mixture was extracted with DCM. After removal of the solvent under reduced pressure, the crude oily residue could be directly used for *ee*-determination by chiral stationary phase HPLC (Chiralcel OD-H, 98.2:1.8 *n*-hexane/*i*PrOH, 0.8 mL/min, detection at 250 nm).

Retention times: (*S*)-enantiomer = 23.7 min; (*R*)-enantiomer = 25.3 min.[2,6]

$C_{18}H_{21}NO$, MW: 267.37 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 21 °C)**: δ = 7.29 – 7.25 (*m*, 2H, Ar*H*), 7.20 – 7.15 (*m*, 3H, Ar*H*), 6.73 (*d*, *J* = 8.8, 2H, C_6H_4OMe), 6.51 (*d*, *J* = 8.8, 2H, C_6H_4OMe), 5.80 – 5.70 (*m*, 1H, H2C=C*H*), 5.18 (*d*, *J* = 17.1, 1H, H_2C=CH), 5.12 (*d*, *J* = 10.3, 1H, H_2C=CH), 3.75 (*q*, *J* = 6.7, 1H, C*H*N), 3.73 (*s*, 3H, OCH_3), 3.36 (*s*, 1H, N*H*), 2.73 (*t*, *J* =

7.7, 2H, CH_2Ph), 1.91 – 1.85 (*m*, 2H, CH_2CH). The other analytical data are in accordance with the literature.[6]

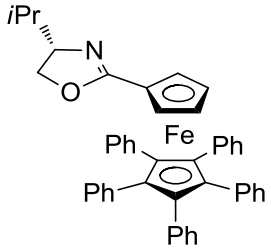
Table 1: Investigations to the non-linear effect of catalyst 2 in the Aza-Claisen rearrangement.

#	*ee* of catalyst **2** (%)	*ee* of product **4c** (%)
1	0	0.1
2	10	3.6
3	20	10.9
4	30	20.5
5	40	28.4
6	50	38.6
7	60	47.5
8	70	57.8
9	80	67.6
10	90	78.5
11	> 99	99.6

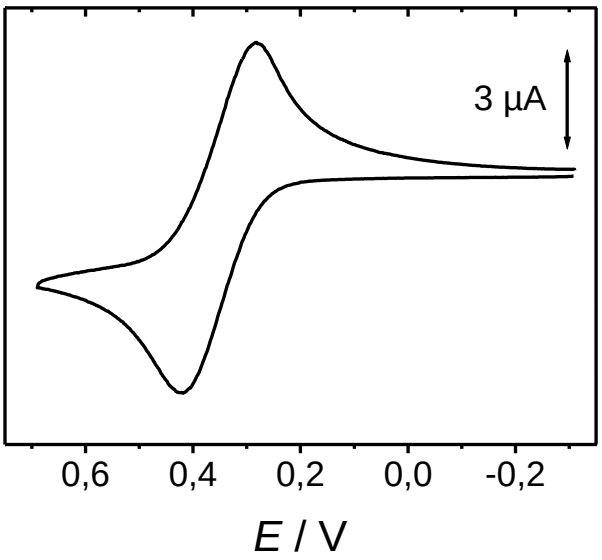
Additional CV and UV-vis-NIR Spectroscopy

CV of the ligand PPFO and PPFI

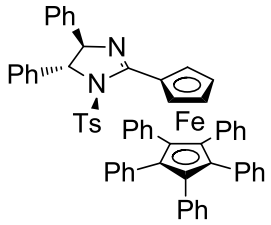
Cyclic voltammogram of **PPFO** in dichloromethane at 295 K. Scan rate = 100 mV/s, working electrode: gold, $E_{1/2}$ = 0.42 V.



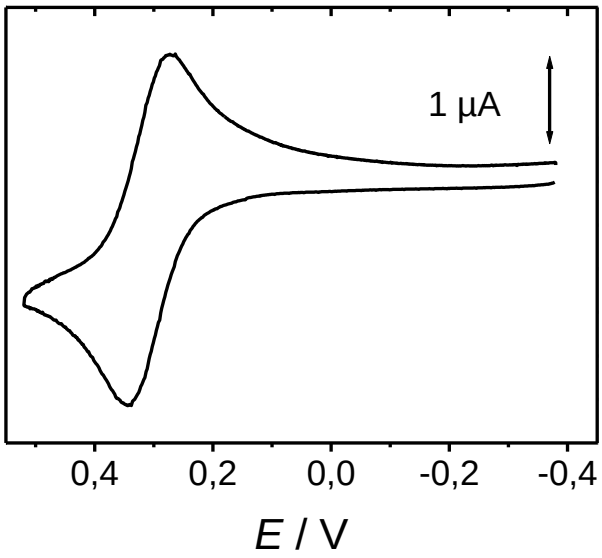
PPFO



Cyclic voltammogram of **PPFI** in dichloromethane at 295 K. Scan rate = 100 mV/s, working electrode: gold, $E_{1/2}$ = 0.31 V.

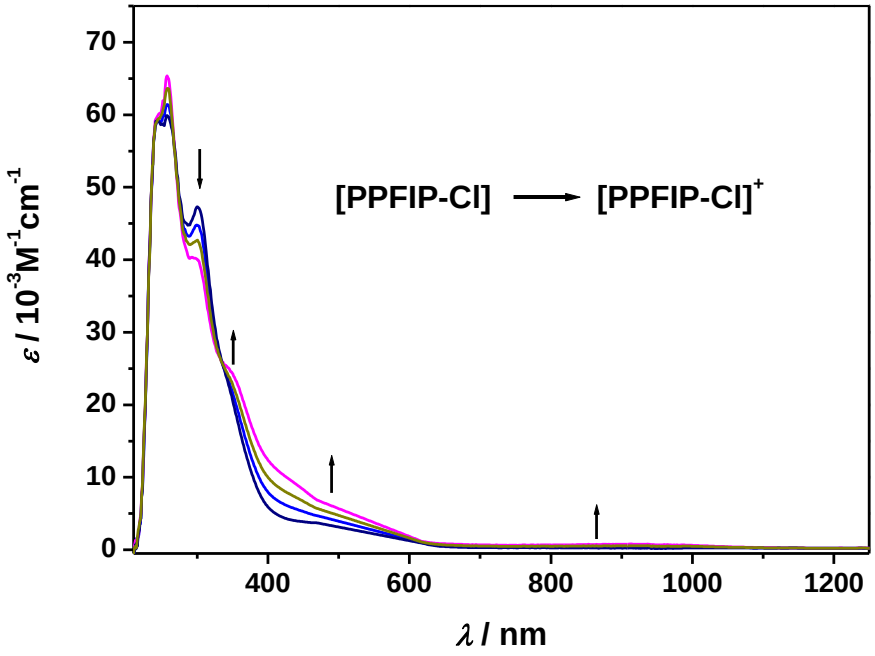


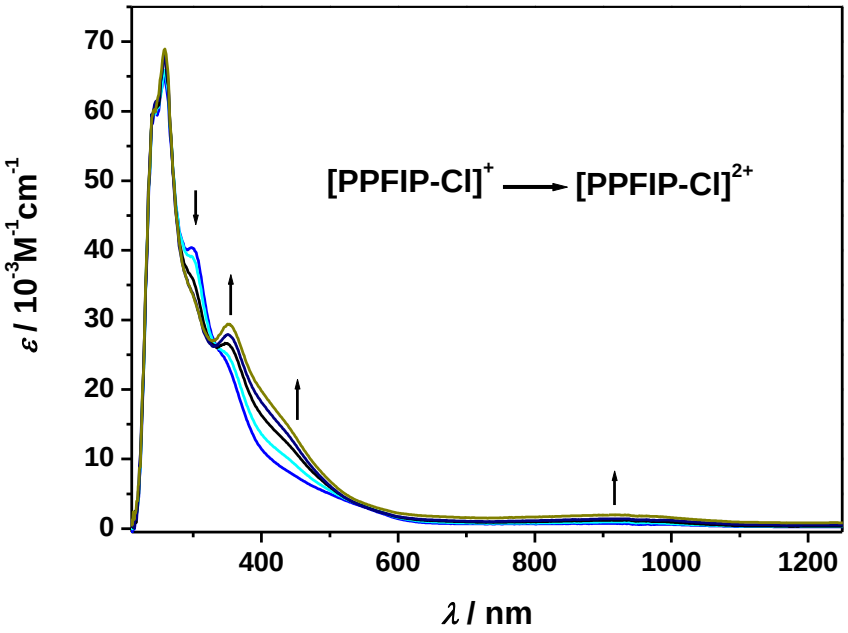
PPFI



UV-vis-NIR Spectroscopy

Chemical oxidation of **PPFIP-Cl** with one (top) and two (bottom) equivalents of thianthrenium tetrafluoroborate:

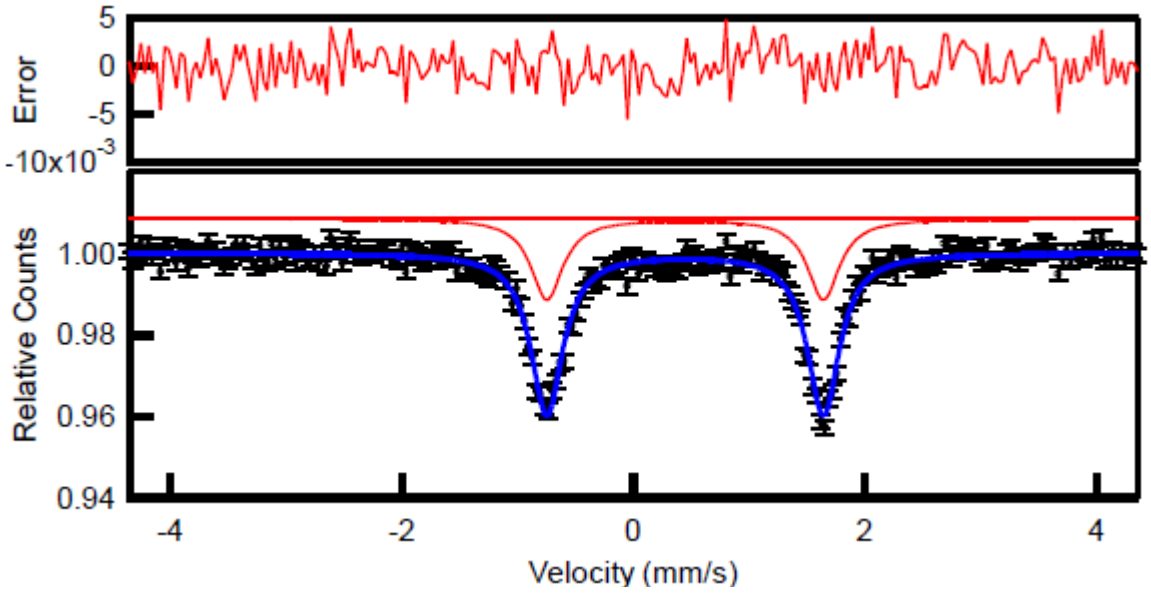




Mössbauer Experiments

Mössbauer spectra of the precatalyst PPFIP-Cl at 40K

The α-Fe-foil consists an isomer shift of –0.110 mm/s referenced to the source. The calculated values of the fit correspond with the source and should be corrected.



\Nr. channels (folded) = 256

Velocity scale: = triangular

Fitting quality Chi2 = 1.07265

Model: = thin-absorber

Maximum velocity = –4.356

Folding point = 512.512

Fitting chi2 = 0.500000

Variable fit	Start	Final	Error
BKG	300374.833333	300404.091039	± 43.4041
BK1	0.00000000	0.000000	± 0.000000
BK2	0.000000	0.000000	± 0.000000
BK3	0.000000	0.000000	± 0.000000
BK4	0.000000	0.000000	± 0.000000
PHS	0.000000	0.000000	± 0.000000
MIX	0.000000	0.000000	± 0.000000
GFR	-0.571423	-0.571423	± 0.000000

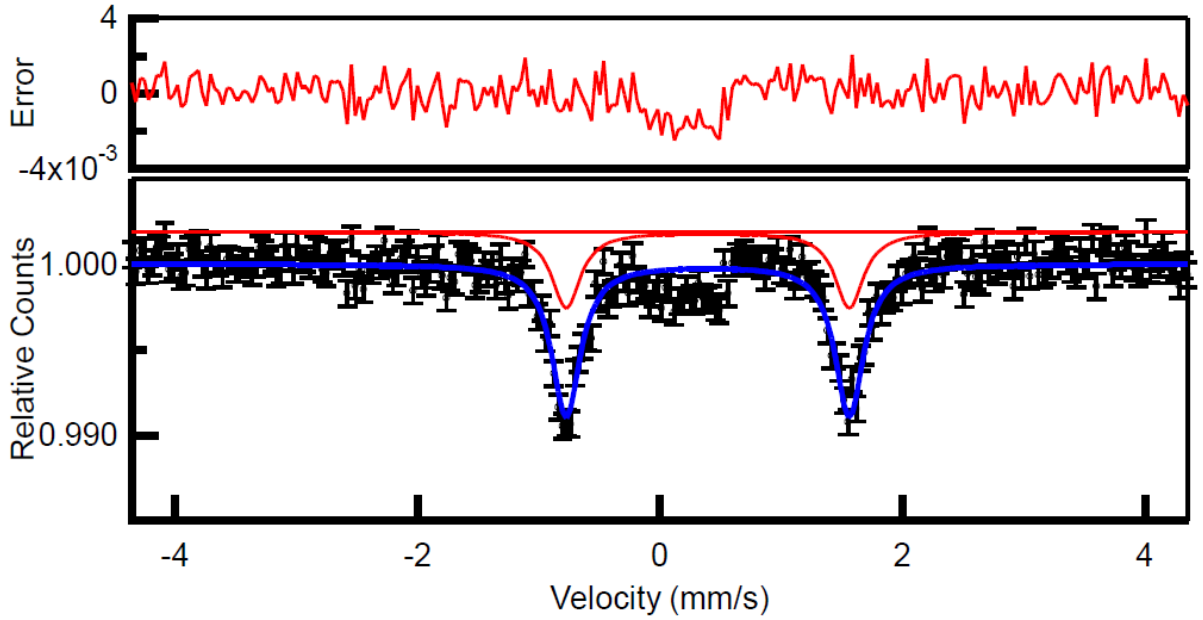
QMR	1.000000	1.000000	± 0.000000
AKS	0.000000	0.000000	± 0.000000
Fso	0.000000	0.000000	± 0.000000
Tab	0.000000	0.000000	± 0.000000
Wso	0.097000	0.097000	± 0.000000

Subspectrum: 1 Type: doublet

Variable fit	Start	Final	Error
ARE	0.020947	0.020947	± 0.000424
WID	0.331728	0.331729	± 0.008469
ISO	0.448721	0.448721	± 0.002694
QUA	2.389152	2.389152	± 0.005367
A12	1.000000	1.000000	± 0.000000
W12	1.000000	1.000000	± 0.000000

Mössbauer spectra of the precatalyst PPFIP-Cl at room temperature

The α-Fe-foil consists an isomer shift of –0.110 mm/s referenced to the source. The calculated values of the fit correspond with the source and should be corrected.



\Nr. channels (folded) = 256

Velocity scale: = triangular

Fitting quality Chi2 = 1.40452

Model: = thin-absorber

Maximum velocity = –4.356

Folding point = 512.025

Fitting chi2 = 0.500000

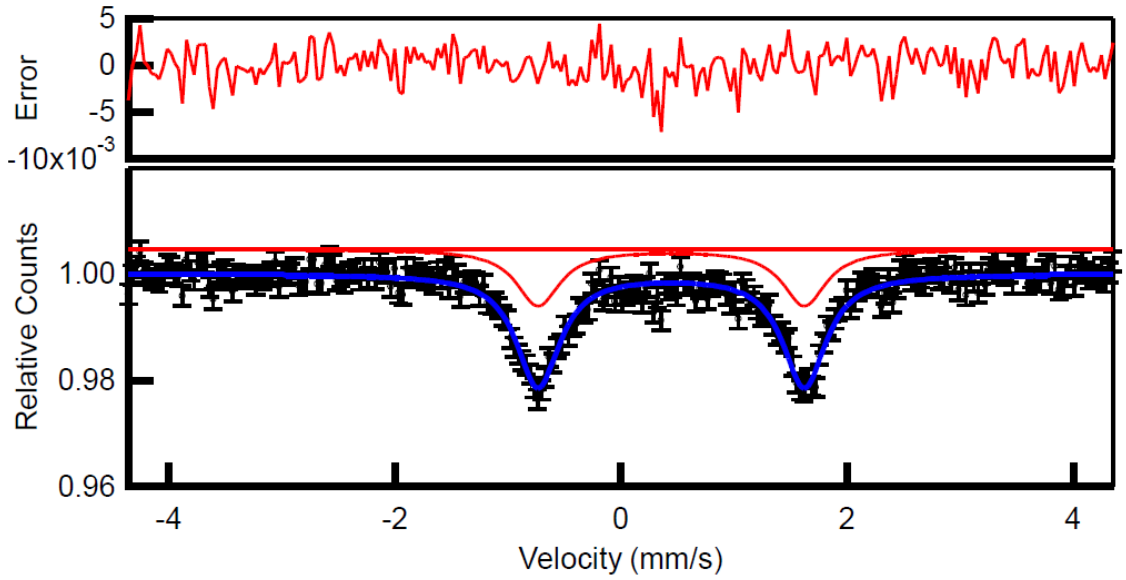
Variable fit	Start	Final	Error
BKG	1779735.333333	1779932.205359	± 102.1321
BK1	0.00000000	0.000000	± 0.000000
BK2	0.000000	0.000000	± 0.000000
BK3	0.000000	0.000000	± 0.000000
BK4	0.000000	0.000000	± 0.000000
PHS	0.000000	0.000000	± 0.000000
MIX	0.000000	0.000000	± 0.000000
GFR	-0.571423	-0.571423	± 0.000000
QMR	1.000000	1.000000	± 0.000000
AKS	0.000000	0.000000	± 0.000000
Fso	0.000000	0.000000	± 0.000000
Tab	0.000000	0.000000	± 0.000000
Wso	0.097000	0.097000	± 0.000000

Subspectrum: 1 Type: doublet

Variable fit	Start	Final	Error
ARE	0.003986	0.003988	± 0.000157
WID	0.281434	0.281605	± 0.014312
ISO	0.396789	0.396543	± 0.004567
QUA	2.337404	2.337180	± 0.009165
A12	1.000000	1.000000	± 0.000000
W12	1.000000	1.000000	± 0.000000

Mössbauer spectra of the Pd^{III}-complex 2 at 40K

The α-Fe-foil consists an isomer shift of –0.110 mm/s referenced to the source. The calculated values of the fit correspond with the source and should be corrected.



\Nr. channels (folded) = 256

Velocity scale: = triangular

Fitting quality Chi2 = 0.945446

Model: = thin-absorber

Maximum velocity = –4.356

Folding point = 512.767

Fitting chi2 = 0.500000

Variable fit	Start	Final	Error
BKG	288059.500000	287947.963506	± 45.9787
BK1	0.00000000	0.000000	± 0.000000
BK2	0.000000	0.000000	± 0.000000
BK3	0.000000	0.000000	± 0.000000
BK4	0.000000	0.000000	± 0.000000
PHS	0.000000	0.000000	± 0.000000
MIX	0.000000	0.000000	± 0.000000
GFR	-0.571423	-0.571423	± 0.000000
QMR	1.000000	1.000000	± 0.000000
AKS	0.000000	0.000000	± 0.000000

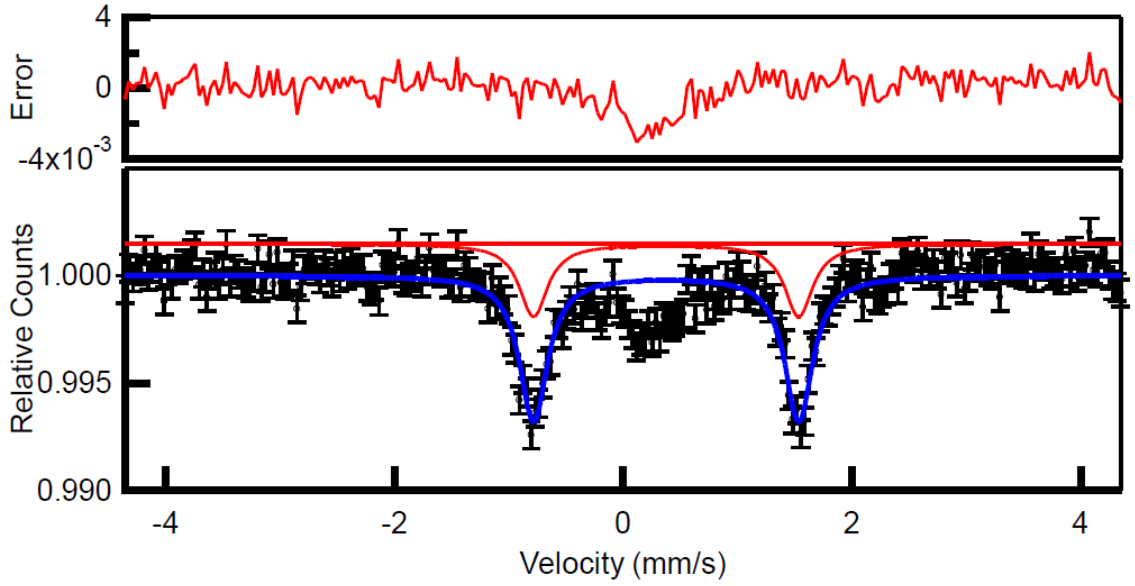
Fso	0.000000	0.000000	± 0.000000
Tab	0.000000	0.000000	± 0.000000
Wso	0.097000	0.097000	± 0.000000

Subspectrum: 1 Type: doublet

Variable fit	Start	Final	Error
ARE	0.015752	0.015752	± 0.000545
WID	0.464689	0.464689	± 0.019412
ISO	0.446644	0.446644	± 0.006114
QUA	2.356514	2.356514	± 0.011970
A12	1.000000	1.000000	± 0.000000
W12	1.000000	1.000000	± 0.000000

Mössbauer spectra of the Pd^{III}-complex 2 at room temperature

The α-Fe-foil consists an isomer shift of –0.110 mm/s referenced to the source. The calculated values of the fit correspond with the source and should be corrected.



\Nr. channels (folded) = 256

Velocity scale: = triangular

Fitting quality Chi2 = 1.86413

Model: = thin-absorber

Maximum velocity = -4.356

Folding point = 512.501

Fitting chi2 = 0.500000

Variable fit	Start	Final	Error
BKG	2450252.666667	2450383.434098	± 120.8081
BK1	0.00000000	0.000000	± 0.000000
BK2	0.000000	0.000000	± 0.000000
BK3	0.000000	0.000000	± 0.000000
BK4	0.000000	0.000000	± 0.000000
PHS	0.000000	0.000000	± 0.000000
MIX	0.000000	0.000000	± 0.000000
GFR	-0.571423	-0.571423	± 0.000000
QMR	1.000000	1.000000	± 0.000000
AKS	0.000000	0.000000	± 0.000000
Fso	0.000000	0.000000	± 0.000000
Tab	0.000000	0.000000	± 0.000000
Wso	0.097000	0.097000	± 0.000000

Subspectrum: 1 Type: doublet

Variable fit	Start	Final	Error
ARE	0.003183	0.003183	± 0.000138
WID	0.294389	0.294751	± 0.016289
ISO	0.378150	0.378150	± 0.005249
QUA	2.320044	2.320044	± 0.010461
A12	1.000000	1.000000	± 0.000000
W12	1.000000	1.000000	± 0.000000

Determination of Metal Amounts in the Activated Catalyst 1 and 2

Pd-, Fe- and Ag-amounts by ICP-OES

Pd- (340.458 nm), Fe- (259.941 nm) and Ag-amounts (328.068 nm) were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). Samples (concentrations between 1 and 5 mg/L metal) were prepared by dissolution of the organic substance (**1** and **2**) in conc. HNO_3 (5 mL, 20 h, 80 °C). After cooling to room temperature the mixture was filtrated and diluted with demineralized water to 25.00 mL. Standardization was carried out with Pd-, Fe- and Ag-standard solutions.

The results of the metal-amount determination in Table 2 display that no or only traces of Ag are left in the activated complexes **1** and **2**.

Table 2: Pd-, Fe- and Ag-amounts of complex 1 and 2.

#	Acitivated Catalyst	Pd (wt%) found/calc.	Fe (wt%) found/calc.	Ag (wt%) found	molar ratio Pd:Fe:Ag
1	Complex **1**	11.85/11.73	6.42/6.16	*bld*	1:1.02:-
2	Complex **2**	8.30/8.36	4.45/4.39	0.25	1:1.03:0.03

bld.: below limit of detection.

Ag- and Cl-amounts in the formed AgCl/Ag precipitate

The precipitate formed during the activation of complex **2** with AgO_2CCF_3 (4 equiv) was analyzed by microanalysis (for Cl) and EDX (for Ag and Cl). The reaction mixture of the activation step was centrifugated after 24 h and the red-brown liquid was removed by decantation. The precipitate was two times washed with DCM and dried in vacuo.

Microanalysis found 18.91 wt% Cl (corresponding to a AgCl/Ag ratio of 1:0.41; expected for pure AgCl: 24.74 wt%; for a mixture of AgCl/Ag (1:1): 14.11 wt%). EDX measurements gave a Ag content of 81.33 wt% and a Cl content of 18.67 wt%.

References

[1] Weiss, M. E.; Fischer, D. F.; Xin, Z.-q.; Jautze, S.; Schweizer, W. B.; Peters, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 5694.

[2] Fischer, D. F.; Barakat, A.; Xin, Z.-q.; Weiss, M. E.; Peters, R. *Chem. Eur. J.* **2009**, *15*, 8722.

[3] Boduszek, B.; Shine, H. J. *J. Org. Chem.* **1988**, *53*, 5142.

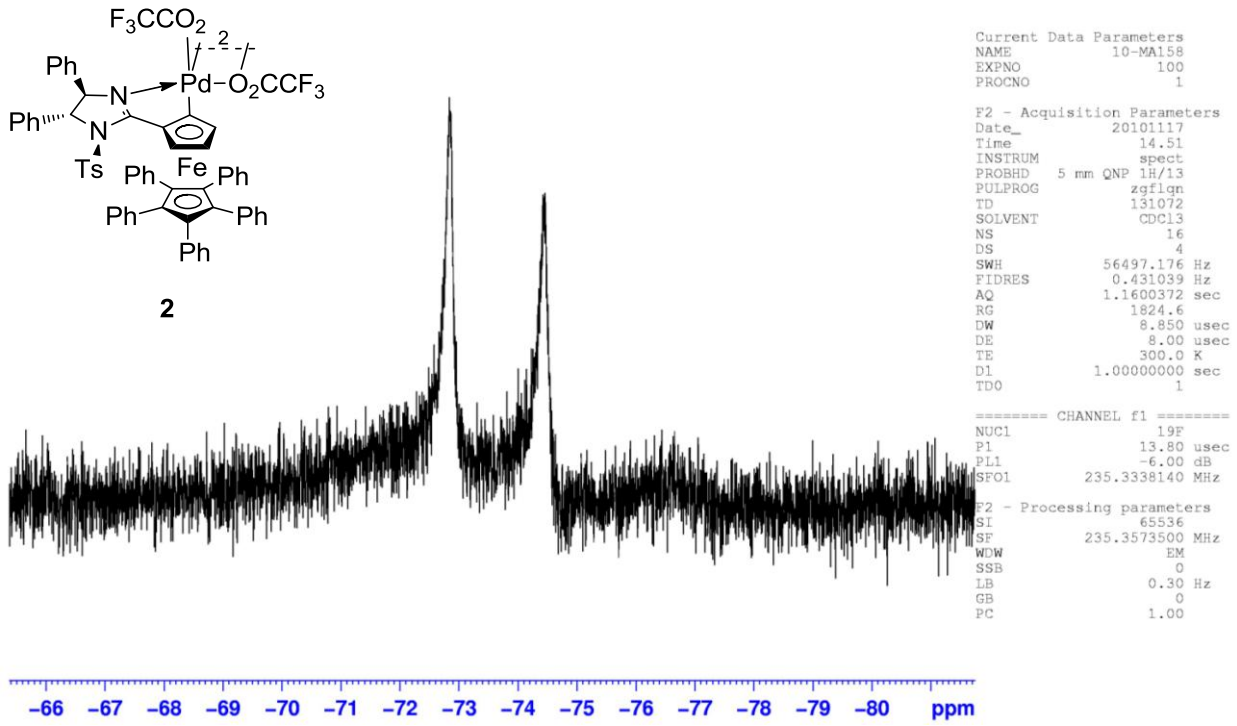
[4] (a) Atkins, T.K.; Richman, J. E.; Oettle, W. F. *Org. Synth.* **1978**, *58*, 68; (b) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc* **1974**, *96*, 2268.

[5] McAuley, A.; Whitecombe, T. W. *Inorg. Chem.* **1988**, *27*, 3090.

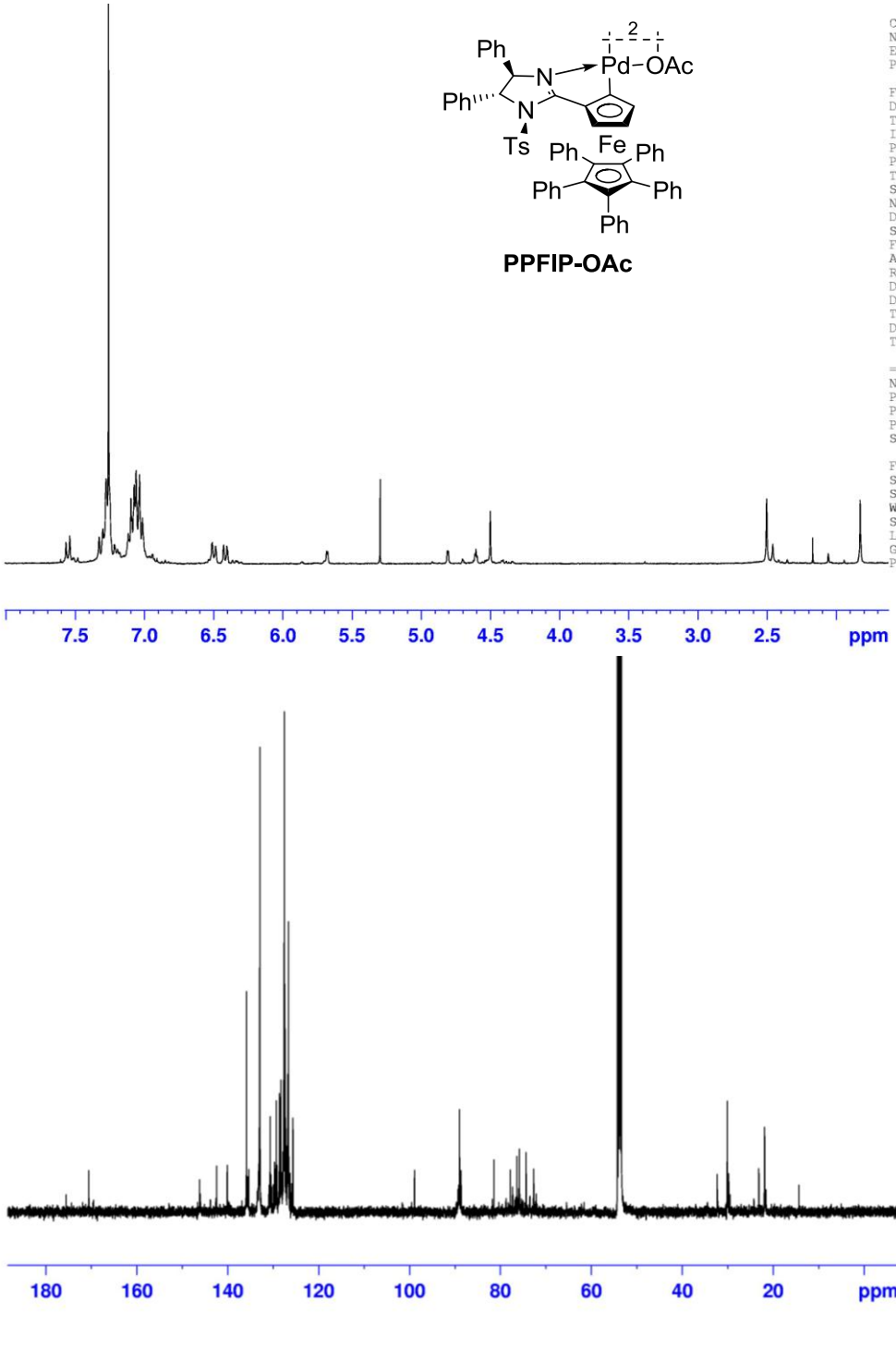
[6] L. E. Overman, C. E. Owen, M. M. Pavan, C. J. Richards, *Org. Lett.* **2003**, *5*, 1809.

NMR spectra

Bis[trifluoroacetato]bis(μ-trifluoroacetato-κO:κO')bis[(*1S*$_p$)-2-[(*4R*,*5R*)-4,5-dihydro-1-[(4-methylphenyl)sulfonyl]-4,5-diphenyl-1H-imidazol-2-yl-κN3]-1',2',3',4',5'-pentaphenylferrocenyl-κC]di-palladium(III) (2)



Bis(μ-acetato-κO:κO')bis[(*1S*$_p$)-2-[(*4R*,*5R*)-4,5-dihydro-1-[(4-methyl-phenyl)sulfonyl]-4,5-diphenyl-1H-imidazol-2-yl-κN3]-1',2',3',4',5'-penta-phenylferrocenyl-κC]di-palladium(II) (PPFIP-OAc)




```
Current Data Parameters
NAME                  10-MA149
EXPNO                      160
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20101109
Time                     13.14
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      32768
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  6188.119 Hz
FIDRES               0.188846 Hz
AQ                   2.6477044 sec
RG                         645
DW                      80.800 usec
DE                       8.00 usec
TE                      296.0 K
D1                   1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                       11.05 usec
PL1                      -2.00 dB
PL1W               37.02396774 W
SFO1              300.1318534 MHz

F2 - Processing parameters
SI                       16384
SF                300.1300065 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

```
Current Data Parameters
NAME                  10-MA149
EXPNO                      161
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20110624
Time                     6.57
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CD2Cl2
NS                         5120
DS                            4
SWH                  32894.738 Hz
FIDRES               0.501934 Hz
AQ                   0.9961972 sec
RG                          3250
DW                      15.200 usec
DE                       10.00 usec
TE                      296.8 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                       10.40 usec
PL1                       1.50 dB
PL1W               51.74793243 W
SFO1              125.7761482 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                   100.00 usec
PL2                       1.00 dB
PL12                     18.79 dB
PL13                     21.00 dB
PL2W               19.75309753 W
PL12W               0.32857543 W
PL13W               0.19753097 W
SFO2              500.1550006 MHz

F2 - Processing parameters
SI                       32768
SF                125.7635217 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

(3,5-Di-*tert*-butylsemiquinone-κO:O')-[(*1S*$_p$)-2-[(*4R*,*5R*)-4,5-dihydro-1-[(4-methylphenyl)sulfonyl]-4,5-diphenyl-1H-imidazol-2-yl-κN3]-1',2',3',4',5'-pentaphenylferrocenyl-κC]-palladium(II) (5)