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Planar-chiral cyclopalladated ferrocenyl amines and imines as enantioselective catalysts for allylic imidate rearrangements

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Abstract

A series of enantiopure cyclopalladated ferrocenyl amines and imines were synthesized and evaluated as catalysts for the [3,3]-rearrangement of allylic benzimidates to allylic benzamides. Yields and extent of enantioselection were found to be highly dependent upon the counter-ion, with a high of 78% yield and 73% ee being realized under optimum conditions. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Recent investigations in these laboratories have focused on the development of asymmetric catalysts for the addition of external (non-metal bound) nucleophiles to prochiral olefins.[1–3] Initial work in this area resulted in the first enantioselective catalyst for the rearrangement of allylic imidates to allylic amides (Scheme 1).[1,4,5] Tetraaminodipalladium complex **3** was found to catalyze the rearrangement of **1** (5 mol% **3**, CH_2Cl_2, 40°C, 48 h) in 69% yield providing **2** of 55% ee. The major side product was *N*-(4-trifluoromethylphenyl)benzamide, presumably a result of coordination of the imidate nitrogen to the cationic palladium, followed by ionization.

Subsequently, it was found that cyclopalladated benzylic amines are improved catalysts for this reaction.[2] In particular, cyclopalladated ferrocenyl complex **4** catalyzes the rearrangement of **1** to **2** (5 mol% **4**, CH_2Cl_2, 23°C, 21 h) in 97% yield and 61% ee. Two features of the structure of this improved catalyst warrant comment. First, the ferrocene provides an anionic ligand, resulting in a neutral complex (contrast to **3**). We postulate that this feature is responsible for suppression of the competing elimination reaction observed with **3**. Secondly, the ferrocene differentiates the two faces of the palladium square plane. This differentiation could be important for enantioselection since ligand substitution reactions at square planar palladium(II) complexes occur predominantly through associative processes.[6]

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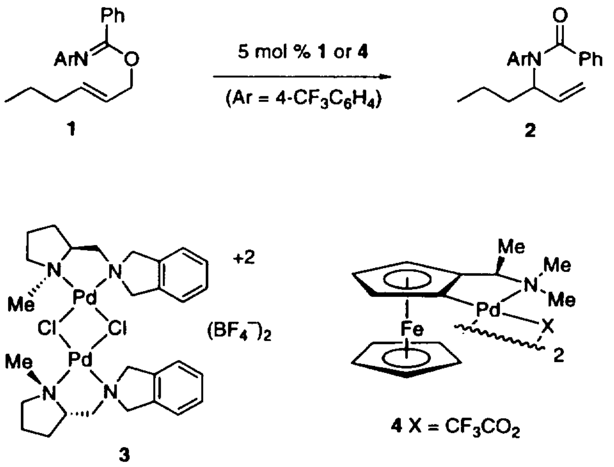


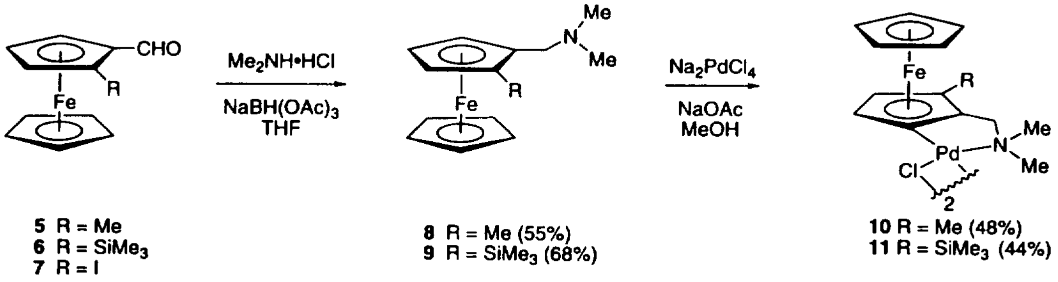
Scheme 1. Previous catalysts for the allylic imidate rearrangement

This report describes the synthesis of enantiopure cyclopalladated ferrocenyl amines and imines and the evaluation of these compounds as catalysts for the rearrangement of allylic imidates.

2. Cyclopalladated ferrocenyl amines

2.1. Synthesis of cyclopalladated amines

To allow for modular preparation of enantioenriched ferrocenyl amines and imine derivatives we chose to begin with chiral ferrocenyl aldehydes **5**–**7**, which are available in high enantiopurity by the method of Kagan.[7,8] Reductive amination of aldehydes **5** and **6** with dimethylamine hydrochloride and sodium triacetoxyborohydride in THF provided chiral ferrocenyl amines **8** and **9** in 55% and 68% yields, respectively (Scheme 2). Cyclopalladation of these amines under standard conditions yielded cyclopalladated amines **10** and **11**.[9,10] Attempted cyclopalladation of ferrocenyl amines bearing nitrogen substituents larger than methyl failed and resulted in decomposition of the ferrocene.



Scheme 2. Synthesis of cyclopalladated ferrocenyl amines

Crystals of **10** suitable for single-crystal X-ray analysis were obtained from benzene–hexanes; the result of this structural analysis is shown in Fig. 1. The crystal structure of **10** is unusual in that the two palladium square planes are co-planar; all other cyclopalladated ferrocene dimers in the Cambridge Crystallographic Database have a substantial dihedral angle between the two planes. This structure exhibits C_1-symmetry, with potential C_2-symmetry being broken by the differing conformations of the

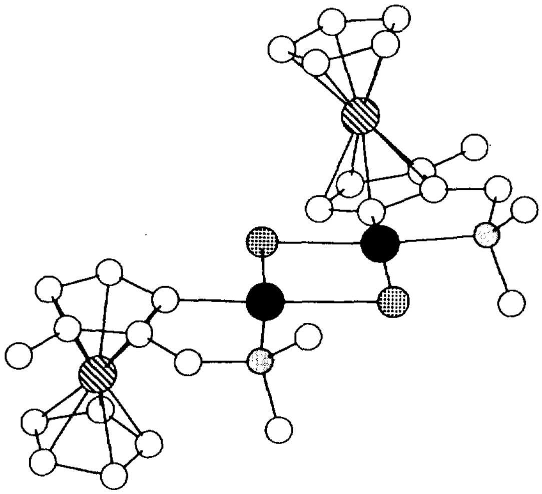


Fig. 1. Molecular structure of **10**

Table 1

Rearrangement of imidate **1** to amide **2** with cyclopalladated ferrocenyl amine catalysts[a]

Entry	catalyst or catalyst precursor	dehalogenating reagent	conditions		amide **2**		
			time	temp.	yield[b]	ee, %[e]	abs. config.
1	**10**	none	48 h	40 °C	34%[c]	49	*S*
2	**10**	$Ag(OCOCF_3)$	24 h	rt	47%[d]	37	*S*
3	**10**	$Tl(OCOCF_3)$	23 h	rt	73%[c]	40	*S*
4	**11**	none	48 h	rt	0%[c]	–	
5	**11**	$Tl(OCOCF_3)$	27 h	rt	80%[c]	17	*S*

[a] 0.1 mmol of **1**, 8 mol % catalyst, CH_2Cl_2.

[b] Yield of purified **2**.

[c] Remainder of material is **1**.

[d] Remainder of material are products of elimination.

[e] By HPLC analysis (Chiracel OD-H 10% *i*-PrOH–*n*-hexane).

two azapalladacyclopentene rings. The C_1-symmetric structure is apparently retained in solution, as evidenced by the complex ^{1}H NMR spectrum of **10**.

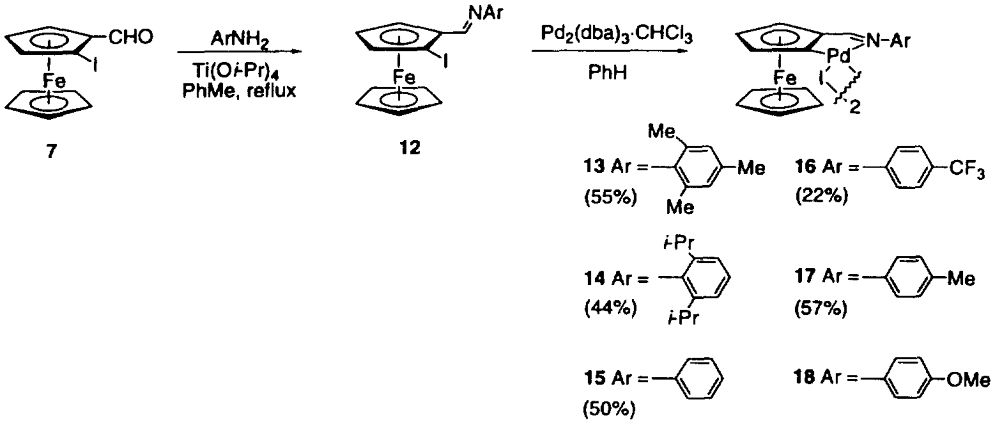
2.2. Evaluation of palladated ferrocenyl amines

Ferrocenyl amines **10** and **11** were evaluated as catalysts for the rearrangement of allylic imidate **1** to allylic benzamide **2** (Table 1). Entries 1 and 4 show that, in accordance with our previous observations,[1] chloro-bridged complexes are poor catalysts for this rearrangement. Exchange of the chloride for a more labile trifluoroacetate resulted in a species that was catalytically active. When $Ag(OCOCF_3)$ was employed to dechlorinate **10**, decomposition was apparent from both a color change and formation of a palladium mirror; not surprisingly, amide **2** was obtained in diminished yield and low enantiomeric excess (Table 1, entry 2). Use of $Tl(OCOCF_3)$ for anion exchange did not result in observable decomposition, and amide **2** was obtained in 73% yield and 40% ee (Table 1, entry 3) using the catalyst generated in this way. Changing the ferrocene 3-substituent from methyl to trimethylsilyl diminished the enantiomeric excess of the product (Table 1, entry 3 versus 5). Since these catalysts offered no advantage in terms of rate or enantioselection over catalyst **4**, cyclopalladated ferrocenyl amines were not pursued further.

3. Cyclopalladated ferrocenyl imines

3.1. Synthesis of planar chiral ferrocenyl imines

At the outset of this work, there was only one report of an enantiopure cyclopalladated ferrocenyl imine, in this case prepared by diastereoselective cyclopalladation of an imine derived from ferrocenecarboxaldehyde (or acetylferrocene) and (−)-*cis*-myrtanylamine.[11] Due to their greater stability, we were more interested in cyclopalladated ferrocenyl *N*-arylimines which had been prepared previously in racemic form by cyclopalladation with Na_2PdCl_4.[12] To avoid the cyclopalladation step (which we have found to lack generality) and also to be more modular, we chose to prepare the desired cyclopalladated ferrocenyl imines by the sequence illustrated in Scheme 3. Enantiopure iodoferrocenecarboxyaldehyde **7**[7] was condensed with an aniline under forcing conditions, to yield imines **12**.[13] Treatment of **12** with $Pd_2(dba)_3\cdot CHCl_3$ in benzene at 23°C yielded the desired ferrocenyl palladacycles. Depending upon the aryl group, the two steps from **7** to the iodide-bridged dimers **13**–**17** proceeded in 22–57% overall yield. These iodide-bridged dimers were readily purified by chromatography on silica gel. Curiously, the cyclopalladated imine **18** derived from *p*-anisidine and **7** was quite unstable, which precluded its purification and evaluation.



Scheme 3. Synthesis of cyclopalladated ferrocenyl imines

3.2. Evaluation of palladated imines

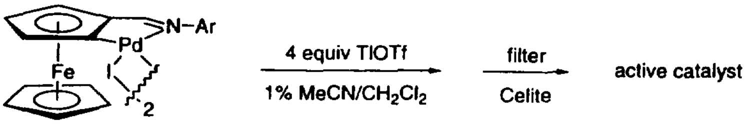
In contrast to the chloro-bridged amines, the iodide-bridged imine dimers **13**–**17** were not catalysts for the rearrangement of **1**. Significant effort was invested in dehalogenating these complexes with silver salts. Although catalytically active species could be formed, yields of **2** varied in irreproducible fashion (from 0–50%), with elimination accounting for the remainder of the material.[14] However, enantioselection for these dehalogenated catalysts was encouraging, with ees in the range of 60–70% often being observed. Unfortunately, we were unable to determine the source of the variability, or to

Table 2
Rearrangement of allylic imidates to allylic amides with cyclopalladated ferrocenyl imine catalysts[a]

entry	imidate	catalyst precursor	amide product		
			yield[b]	ee, %[d]	abs. config.
1	**1**	**13**	80%	46	*R*
2	**1**	**14**	94%	45	*R*
3	**1**	**15**	91%	49	*R*
4	**1**	**16**	83%	49	*R*
5	**1**	**17**	87%	47	*R*
6	**19**	**13**	57%	43	*R*[c]
7	**20**	**13**	45%	66	*S*[c]
8	**21**	**13**	78%	73	*S*[c]
9	**22**	**13**	complex mixture		

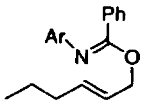
[a] 0.10 mmol of **1**, 11 mol% catalyst precursor, CH_2Cl_2, room temperature.
[b] Yield of purified product.
[c] Absolute configuration assigned by analogy.
[d] By HPLC analysis (Chiracel OD-H 10% *i*-PrOH–*n*-hexane).

crystallize products of dehalogenation despite screening a variety of silver salts. However, a reproducible method to generate active imine catalysts was developed using $Tl(OSO_2CF_3)$ (Eq. 1). Thus, reaction of the iodide-bridged dimers with 4 equiv. of $Tl(OSO_2CF_3)$ in CH_2Cl_2 containing 1% MeCN resulted in complete dehalogenation as assayed by ^1H NMR and TLC analysis. Removal of the resulting precipitate by filtration through Celite provided a solution of the active catalyst to which the allylic imidate was added. Using this procedure, imidate **1** rearranged cleanly to allylic benzamide **2**, generally within 8 h at room temperature. The data for these experiments are summarized in Table 2. Regardless of the aryl group (entries 1–5), ees varied from 45 to 49% indicating a remarkable insensitivity of enantioselection to the steric and electronic nature of the aryl substituent.

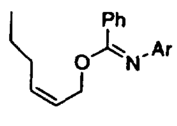


(1)

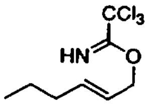
13–17



19 Ar = Ph



20 Ar = 4-$CF_3C_6H_4$
21 Ar = 4-$MeOC_6H_4$



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The effect of imidate structure was briefly surveyed. As previously observed with related amine catalysts,[2] the *N*-aryl substituent of the imidate had little effect on the course of the reaction (compare entries 1 with 6 and 7 with 8). The (Z)-allylic imidates **20** and **21** rearranged with slightly higher enantioselectivity to provide allylic benzamide products of the opposite absolute configuration (entries 7 and 8). Unfortunately, trichloroacetimidate **22** yielded a complex mixture of products when exposed to the catalyst derived from **13**.

4. Conclusion

A series of enantiopure cyclopalladated ferrocenyl imines were prepared for the first time. Cations derived from these iodide-bridged imine dimers are efficient catalysts for the [3,3]-rearrangement of allylic imidates to allylic amides. However, enantioselectivity with these catalysts was inferior to that of the palladated amine catalysts we reported earlier.[2] Efforts to further optimize cyclopalladated ferrocenes as catalysts for asymmetric activation of alkenes are continuing.

5. Experimental

5.1. *General*

General experimental details have been published elsewhere.[15] NMR spectra were recorded on either a General Electric QE300, Bruker DRX400 or DRX500 spectrometer. Methanol was distilled from Mg metal. Amines, hexanes, benzene, and acetonitrile were distilled from CaH_2. Enantiopure α-substituted ferrocenecarboxaldehydes were synthesized according to literature procedures.[7]

5.2. *(R)-α-(N,N-Dimethylaminomethyl)methylferrocene (8)*

Dimethylamine hydrochloride (915 mg, 11.3 mmol) and sodium triacetoxyborohydride (715 mg, 3.39 mmol) were added at rt to a solution of aldehyde **5**[7] (515 mg, 2.26 mmol) and THF (10 mL). The resulting suspension was stirred for 1 h, at which time another portion of sodium triacetoxyborohydride (ca. 200 mg) was added. After an additional hour, the reaction was diluted with CH_2Cl_2 (100 mL), washed with 1M NaOH (3×30 mL) and brine (1×30 mL). The organic phase was dried (K_2CO_3), filtered, concentrated and the residue was chromatographed (SiO_2, gradient elution with 50% EtOAc–hexanes followed by 50% EtOAc–hexanes containing 1% MeOH and 2% NEt_3) to yield 355 mg (55%) of **8** as a dark brown oil: ^1H NMR (300 MHz, C_6D_6) δ 3.98 (s, 1H, FcH), 3.35 (m, 7H, FcH), 3.30 (d, *J*=12.6 Hz, 1H, CH_2), 2.97 (d, *J*=12.6 Hz, 1H, CH_2), 2.05 (s, 6H, NMe_2), 1.85 (s, 3H, FcMe); ^{13}C NMR (75 MHz, C_6D_6) δ 83.8, 83.0, 69.0, 69.9, 69.5, 65.5, 57.5, 44.7, 13.2; FTIR (film) 3092, 1105, 800 cm^{-1}; $[\alpha]_D^{20}=-142$, $[\alpha]_{577}^{20}=-137$, $[\alpha]_{546}^{20}=-92$ (*c*=0.12, $CHCl_3$). Anal. calcd for $C_{14}H_{19}NFe$: C, 65.35; H, 7.45; N, 5.45. Found: C, 65.22; H, 7.39; N, 5.43.

5.3. *(S)-α-(N,N-Dimethylaminomethyl)trimethylsilylferrocene (9)*

68% yield of a dark brown oil: ^1H NMR (500 MHz, $CDCl_3$) δ 4.30 (s, 1H, FcH), 4.23 (s, 1H, FcH), 4.08 (s, 5H, FcH_5), 4.02 (s, 1H, FcH), 3.40 (d, *J*=13 Hz, 1H, CH_2), 3.01 (d, *J*=13 Hz, 1H, CH_2), 2.10 (s, 6H, NMe_2), 0.28 (s, 9H, $SiMe_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 90.0, 75.2, 73.4, 72.0, 69.5, 68.7, 59.6, 45.0, 0.3; FTIR (film) 3095, 2764, 1460, 1137, 836 cm^{-1}; $[\alpha]_{577}^{23}$=27.4 (*c*=0.07, $CHCl_3$). Anal. calcd for $C_{16}H_{25}NSiFe$: C, 60.93; H, 8.00; N, 4.44. Found: C, 61.07; H, 8.05; N, 4.35.

*5.4. (*R*)-Bis-μ-chloro-a,b-e,f-bis[2-(*N,N*-dimethylaminomethyl)-3-methyl(*C,N*)]dipalladium(II) (**10**)*

A mixture of Na_2PdCl_4 (403 mg, 1.16 mmol), $NaOAc{\cdot}3H_2O$ (157 mg, 1.16 mmol) and amine **8** (298 mg, 1.16 mmol) was stirred in MeOH (15 mL) at rt for 3 h. The resulting orange precipitate was collected by vacuum filtration on a fine frit. The solid was dissolved in CH_2Cl_2, filtered through Celite, and concentrated to give a dark-red solid, which was dissolved in dry PhH (20 mL), layered with dry hexanes (50 mL), and allowed to stand, with exclusion of air, for 1 week, yielding 153 mg of **10** as large, dark-red cubes. Concentration of the mother liquor and crystallization yielded another 70 mg (48% combined): mp 172–174°C (dec); ^{1}H NMR (500 MHz, C_6D_6) δ 4.56 (d, *J*=2 Hz, 1H, FcH), 4.49 (d, *J*=2 Hz, 1H, FcH), 4.27 (s, 5H, FcH_5), 4.19 (s, 5H, FcH_5), 3.86 (d, *J*=2 Hz, 1H, FcH), 3.82 (d, *J*=2 Hz, 1H, FcH), 3.20 (d, *J*=14 Hz, 1H, $FcCH_2$), 3.16 (d, *J*=14 Hz, 1H, $FcCH_2$), 2.65 (s, 3H, NMe), 2.60 (s, 3H, NMe), 2.52 (d, *J*=14 Hz, 1H, $FcCH_2$), 2.47 (d, *J*=14 Hz, 1H, $FcCH_2$), 2.39 (s, 3H, NMe), 2.32 (s, 3H, NMe), 1.76 (s, 3H, FcMe), 1.76 (s, 3H, FcMe); ^{13}C NMR (125 MHz, C_6D_6) δ 97.1, 96.6, 94.7, 94.6, 86.9, 76.7, 76.5, 71.0, 67.1, 66.8, 66.7, 65.5, 65.3, 53.2, 53.1, 52.8, 52.7, 14.5; FTIR (film) 3090, 1454, 1103, 809 cm^{-1}; $[\alpha]_D^{23}$=690, $[\alpha]_{577}^{23}$=749 (*c*=0.085, C_6H_6). Anal. calcd for $C_{28}H_{36}Cl_2N_2Fe_2Pd_2$: C, 42.25; H, 4.56; N, 3.52. Found: C, 42.09; H, 4.61; N, 3.47.

*5.5. (*R*)-Bis-μ-chloro-bis[2-(dimethylaminomethyl)-3-(trimethylsilyl)-*C,N*]dipalladium(II) (11)*

44% yield of a dark-red solid. An analytical sample was obtained by partial slow evaportation of an MeOH solution (13 mg/mL) to yield an orange powder: ^{1}H NMR (500 MHz, C_6D_6) δ 4.82 (d, *J*=2 Hz, 1H, FcH), 4.79 (d, *J*=2 Hz, 1H, FcH), 4.35 (s, FcH_5), 4.28 (s, FcH_5), 3.88 (d, *J*=2 Hz, 1H, FcH), 3.85 (d, *J*=2 Hz, 1H, FcH), 3.45 (d, *J*=13.8 Hz, 1H, Fc*C**H*$_2$), 3.40 (d, *J*=13.8 Hz, 1H, FcC*H*$_2$), 2.70 (d, *J*=13.8 Hz, 1H, FcC*H*$_2$), 2.63 (d, *J*=13.8 Hz, 1H, FcC*H*$_2$), 2.61 (s, 3H, NMe), 2.57 (s, 3H, NMe), 2.34 (s, 3H, NMe), 2.28 (s, 3H, NMe), 0.20 (s, 9H, $SiMe_3$); ^{13}C NMR (125 MHz, C_6D_6) δ 100.3, 99.7, 99.2, 71.3, 71.2, 70.6, 70.2, 69.7, 69.5, 68.3, 68.2, 64.6, 53.2, 52.8, 52.6, 0.17; FTIR (film) 3093, 1456, 1104, 837 cm^{-1}, $[\alpha]_D^{23}$=611, $[\alpha]_{577}^{23}$=675 (*c*=0.085, C_6D_6). Anal. calcd for $C_{32}H_{48}Cl_2N_2Fe_2Pd_2Si_2$: C, 42.20; H, 5.32; N, 3.08. Found: C, 42.06; H, 5.40; N, 3.07.

*5.6. (*S*)-Bis-μ-iodo-bis[ferrocenylmethyliden-2,4,6-trimethylaniline(*C,N*)]dipalladium(II) (13)*

A solution of aldehyde **7**[7] (767 mg, 2.6 mmol), 2,4,6-trimethylaniline (0.64 mL, 4.5 mmol), Ti(O*i*-Pr)$_4$ (1.3 mL, 4.5 mmol) and PhMe (10 mL) was heated at reflux for 3 h. The reaction was cooled to rt and citric acid (870 mg, 4.5 mmol) and water (80 μl, 4.5 mmol) were added, and the resulting mixture was stirred for 1 h. After removal of the precipitate by filtration, the mixture was diluted with 20% EtOAc–hexanes and washed with saturated $NaHCO_3$, brine, dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, elution with 2.5% to 5% EtOAc–hexane) to yield 650 mg of the imine which was carried on directly. Diagnostic data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H, N=CHFc), 6.90 (s, 2H, ArH), 5.08 (broad s, 1H, FcH), 4.72 (broad s, 1H, FcH), 4.58 (broad s, 1H, FcH), 4.25 (s, 5H, FcH_5), 2.29 (s, 3H, ArMe), 2.18 (s, 6H, ArMe); FTIR (film) 3090, 1626, 1478, 1203, 823 cm^{-1}.

This imine was combined with $Pd_2(dba)_3{\cdot}CHCl_3$ (810 mg, 0.78 mmol) in PhH (10 mL) and stirred overnight at rt. The resulting mixture was concentrated and the residue chromatographed (SiO_2, gradient elution with 30% to 50% CH_2Cl_2–hexanes) to give 700 mg (55%) of **13** as a red solid: ^{1}H NMR (500 MHz, C_6D_6) (2.5:1 mixture of isomers) major: δ 6.89 (s, 1H, N=CHFc), 6.81 (s, 1H, ArH), 6.70 (s, 1H, ArH), 4.92 (d, *J*=2.1 Hz, 1H, FcH), 4.26 (s, 5H, FcH_5), 4.01 (m, 4H, FcH), 2.48 (s, 3H, ArMe), 2.14 (s, 3H, ArMe), 2.08 (s, 3H, ArMe); minor: 6.87 (s, 1H, N=CHFc), 6.48 (s, 1H, ArH), 6.43 (s, 1H, ArH), 5.23 (d, *J*=2.1 Hz, 1H, FcH), 4.31 (s, 5H, FcH_5), 4.17 (t, *J*=2.3 Hz, 1H, FcH), 4.05 (d, *J*=2.1 Hz, 1H, FcH), 2.32 (s, 3H, ArMe), 2.03 (s, 3H, ArMe), 1.94 (s, 3H, ArMe); ^{13}C NMR (125 MHz, CD_2Cl_2) both isomers: δ 176.5, 176.2, 147.3, 145.9, 136.2, 136.16, 131.0, 129.8, 128.8, 128.7, 128.5, 109.0, 108.1, 88.9, 78.1, 78.0, 71.4, 71.0, 70.7, 67.03, 66.99, 21.0, 19.7, 19.6, 18.8; FTIR (film) 3092, 1451, 1564, 1320, 817 cm^{-1}. Anal. calcd for $C_{40}H_{40}I_2N_2Fe_2Pd_2$: C, 42.63; H, 3.58; N, 2.49. Found: C, 42.66; H, 3.55; N, 2.50.

5.7. (S)-Bis-μ-iodo-bis[ferrocenylmethyliden-2,6-diisopropylaniline(C,N)]dipalladium(II) ***(14)***

44% yield of a dark red solid. ^{1}H NMR (500 MHz, CD_2Cl_2) (1.4:1 mixture of isomers): δ 7.83 (s, 0.7H, N=CH), 7.80 (s, 0.3H, N=CH), 7.26–7.04 (m, 3H ArH), 5.02 (d, *J*=2.2 Hz, 0.3H, FcH), 4.85 (d, *J*=2.2 Hz, 0.7H, FcH), 4.55–4.38 (m, 7H, FcH), 3.57 (septet, *J*=6.9 Hz, 0.74H, CH), 3.40 (septet, *J*=6.9 Hz, 0.3 CH), 3.30 (septet, *J*=6.9 Hz, 0.7H, CH), 3.15 (septet, *J*=6.9 Hz, 0.3H, CH), 1.58 (d, *J*=6.9 Hz, 2H, Me), 1.40–1.25 (m, 7H, Me), 1.37 (d, *J*=6.9 Hz, 3H, Me), 1.33 (d, *J*=6.9 Hz, 3H, Me), 1.0 (d, *J*=6.9 Hz, 3H, Me), 1.05–0.96 (m, 3H, Me); ^{13}C NMR (125 MHz, CD_2Cl_2) both isomers: δ 175.8, 175.7, 147.0, 141.8, 141.4, 127.4, 127.2, 123.5, 123.4, 123.3, 123.1, 78.2, 78.0, 71.0, 70.9, 70.8, 67.1, 67.0, 28.4, 28.1, 25.3, 24.9, 23.4, 22.5; FTIR (film) 3084, 1562, 1327, 1107, 815 cm^{-1}. Anal. calcd for $C_{46}H_{52}N_2I_2Fe_2Pd_2$: C, 45.62; H, 4.33; N, 2.31. Found: C, 45.73; H, 4.43; N, 2.29.

5.8. (S)-Bis-μ-iodo-bis[ferrocenylmethylidenaniline(C,N)]dipalladium(II) ***(15)***

50% yield of a red solid: ^{1}H NMR (400 MHz, CD_2Cl_2) (1.4:1 mixture of isomers) δ 8.11 (s, 1H, N=CHFc), 7.47–7.16 (m, 5H, ArH), 5.11 (d, *J*=1.9 Hz, 0.42H, FcH), 4.98 (d, *J*=1.9 Hz, 0.59H, FcH), 4.59–4.44 (m, 7H, FcH); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 174.4, 174.3, 151.3, 150.1, 129.0, 128.7, 127.1, 127.0, 123.8, 123.8, 108.5, 88.8, 79.0, 78.7, 71.5, 71.4, 67.5, 67.4; FTIR (KBr) 3083, 1556, 1458, 1319, 1206 cm^{-1}. Anal. calcd for $C_{34}H_{28}I_2N_2Fe_2Pd_2$: C, 39.16; H, 2.71; N, 2.69. Found: C, 39.28; H, 2.65; N, 2.74.

5.9. (S)-Bis-μ-iodo-bis[ferrocenylmethyliden-4-trifluoromethylaniline(C,N)]dipalladium(II) ***(16)***

22% yield of a red solid: ^{1}H NMR (400 MHz, CD_2Cl_2) (1.3:1 mixture of isomers) δ 8.20 (s, 1H, N=CHFc), 7.72 (d, 1.2H, *J*=8.2 Hz, ArH), 7.63 (d, 0.30H, *J*=8.1 Hz, ArH), 7.43 (d, 1.4H, *J*=8.2 Hz, ArH), 7.31 (d, 0.60H, *J*=8.2 Hz, ArH), 5.19 (s, 0.43H, FcH), 5.07 (s, 0.57H, FcH), 4.64–4.48 (m, 7H, FcH); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 175.4, 126.3, 124.2, 88.5, 79.5, 79.3, 72.2, 71.6, 67.9; FTIR (KBr) 1610, 1559, 1321 cm^{-1}. Anal. calcd for $C_{36}H_{26}F_6I_2N_2Fe_2Pd_2$: C, 36.68; H, 2.22; N, 2.38. Found: C, 36.58; H, 2.22; N, 2.40.

5.10. (S)-Bis-μ-iodo-bis[ferrocenylmethyliden-4-methylaniline(C,N)]dipalladium(II) ***(17)***

57% of a red solid: ^{1}H NMR (400 MHz, CD_2Cl_2) (mixture of isomers) δ 8.07 (s, 1H, N=CHFc), 7.25–7.05 (m, 4H, ArH), 5.09 (s, 0.5H, FcH), 4.98 (s, 0.5H, FcH), 4.58–4.45 (m, 7H, FcH); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 173.6, 173.4, 148.4, 136.6, 136.5, 129.0, 128.8, 123.1, 122.9, 107.8, 107.4, 88.3, 78.3, 78.1, 71.2, 70.9, 70.8, 66.9, 66.8, 20.7, 20.6; FTIR (KBr) 3087, 2912, 1554, 1497, cm^{-1}. Anal. calcd for $C_{36}H_{32}I_2N_2Fe_2Pd_2$: C, 40.37; H, 3.01; N, 2.62. Found: C, 40.21; H, 3.09; N, 2.53.

6. Representative catalytic procedures

6.1. Table 1, entry 1

Complex **10** (6.8 mg, 0.0086 mmol) and imidate **1** (29 mg, 0.086 mmol) were combined in CH_2Cl_2 (1 mL) and heated at 40°C in a sealed tube for 48 h. The mixture was chromatographed (SiO_2, elution with 10% EtOAc–hexanes) to yield 10 mg (34%) of amide **2** as a colorless oil. HPLC analysis (Chiralpak AS column, 10% *i*-PrOH–*n*-C_6H_{14}) indicated an ee of 49%.

6.2. Table 1, entry 3

Complex **10** (6.8 mg, 0.0086 mmol) and thallium trifluoroacetate (6 mg, 0.019 mmol) were stirred vigorously in CH_2Cl_2 (0.5 mL) for 45 min. The solid was removed by filtration through Celite under N_2, and the filter was rinsed with CH_2Cl_2 (1 mL). Imidate **1** was added to the combined filtrates and the resulting solution was maintained at rt for 20 h. The final mixture was chromatographed (SiO_2, elution with 10% EtOAc–hexanes) to yield 22 mg (73%) of amide **2** as a colorless oil. HPLC analysis (Chiralpak AS column, 10% *i*-PrOH–*n*-C_6H_{14}) indicated an ee of 40%.

6.3. Table 2, entry 1

A mixture of TlOTf (12.5 mg, 0.035 mmol, weighed in a glove box), complex **13** (10.5 mg, 0.009 mmol) and CH_2Cl_2 containing 1% MeCN (1 mL) was stirred vigerously for 5 h. The resulting slurry was filtered through a 1 cm×2 cm pad of Celite under N_2. The pad was rinsed with CH_2Cl_2 (2 mL) and the resulting dark-purple solution was concentrated to approximately 1 mL under a stream of nitrogen. Imidate **2** (35 mg, 0.10 mmol) was added and the reaction was maintained at rt for 8 h. The mixture was then chromatographed (SiO_2, elution with CH_2Cl_2) to yield 28 mg (80%) of amide **2** as a colorless oil. HPLC analysis (Chiralpak AS column, 10% *i*-PrOH–*n*-C_6H_{14}) indicated an ee of 46%.

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