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Chiral iridium(I) bis(NHC) complexes as catalysts for asymmetric transfer hydrogenation

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The common use of NHC complexes in transition-metal mediated C–C coupling and metathesis reactions in recent decades has established *N*-heterocyclic carbenes as a new class of ligand for catalysis. The field of asymmetric catalysis with complexes bearing NHC-containing chiral ligands is dominated by mixed carbene/oxazoline or carbene/phosphane chelating ligands. In contrast, applications of complexes with chiral, chelating bis(NHC) ligands are rare. In the present work new chiral iridium(I) bis(NHC) complexes and their application in the asymmetric transfer hydrogenation of ketones are described. A series of chiral bis(azolium) salts have been prepared following a synthetic pathway, starting from L-valinol and the modular buildup allows the structural variation of the ligand precursors. The iridium complexes were formed via a one-pot transmetallation procedure. The prepared complexes were applied as catalysts in the asymmetric transfer hydrogenation of various prochiral ketones, affording the corresponding chiral alcohols in high yields and moderate to good enantioselectivities of up to 68%. The enantioselectivities of the catalysts were strongly affected by the various, terminal *N*-substituents of the chelating bis(NHC) ligands. The results presented in this work indicate the potential of bis-carbenes as stereodirecting ligands for asymmetric catalysis and are offering a base for further developments. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: chiral iridium(I)-NHC complexes; asymmetric transfer hydrogenation; ketones

Introduction

Since their discovery, stable *N*-heterocyclic carbenes (NHCs) have been the subject of intense interest, primarily as strong σ-donor ligands for transition metals. In comparison with phosphane complexes, NHC complexes display significant advantages, particularly their stability towards air, moisture and heat. Their common use in transition-metal mediated C–C coupling and metathesis reactions has established *N*-heterocyclic carbenes as a new class of ligand in catalysis beside phosphane and oxazoline ligands.[1–5]

The field of asymmetric catalysis with complexes bearing chiral NHC-containing ligands is dominated by chelating ligands with a carbene unit and a second coordinating group, such as phosphane or oxazoline.[6–9] Apart from the well-known bis(benzimidazolin-2-ylidene) palladium (II) and rhodium(III) complexes derived from BINAM, applications of chiral bis(NHC) complexes in asymmetric catalysis are notably rare.[10,11]

As recently demonstrated by Peris and Crabtree *et al*., rhodium (III) and iridium (III) complexes of achiral chelating bis(carbene) ligands are promising catalysts for the transfer hydrogenation of ketones using 2-propanol as hydrogen source and various amounts of KOH as cocatalyst.[12–14] Using benzophenone as the substrate and bis(imidazolin-2-ylidene) iridium (III) complexes as catalysts, Crabtree *et al*. observed turnover frequencies of up to 50 000 [h^{-1}].[12]

We recently reported the synthesis and structural characterization of Rh(I) and Ir(I) complexes bearing chiral bis(NHC) ligands derived from L-valinol.[15] In this article we wish to report the application of these iridium complexes as catalysts for the asymmetric transfer hydrogenation of prochiral ketones. For this purpose, chiral bis(NHC) ligands with various combinations of terminal *N*-substituents and their iridium(I) complexes were prepared. Moreover the synthetic pathway allowed us to prepare a bis(NHC) ligand and its iridium(I) complex combining two different azolin-2-ylidenes. The influence of the ligand shape on the catalytic activity and selectivity of the corresponding iridium(I) bis(NHC) complexes was determined.

Results and Discussion

Ligand and Complex Synthesis

As previously reported, the bis-imidazolium salts **3a–f** are accessible via a modular synthesis starting from L-valinol. The modular buildup of the ligand precursors makes it possible to introduce different substituents at the terminal nitrogen atoms in two steps using the chiral imidazolebromide **1** as a bifunctional synthon. The first reaction step was the alkylation of 1-R_1-imidazoles (R_1 = Me, *iso*-Pr and Ph) with **1** as alkylating agent. The resulting imidazolium salts **2a–c** were then treated with an excess of various electrophiles R_2Br (R_2 = *n*-Pr and *iso*-Pr) in acetonitrile or methyliodide in dichloromethane giving the bis-imidazolium salts **3a–f** in good yields (Scheme 1).[15] In a similar manner the mixed bis-azolium salt **5**, combining an imidazole and a benzimidazole unit, was obtained.

The iridium(I) complexes **6a–f** and **7** were prepared from the corresponding bis-imidazolium salts **3a–f**, silver(I) oxide

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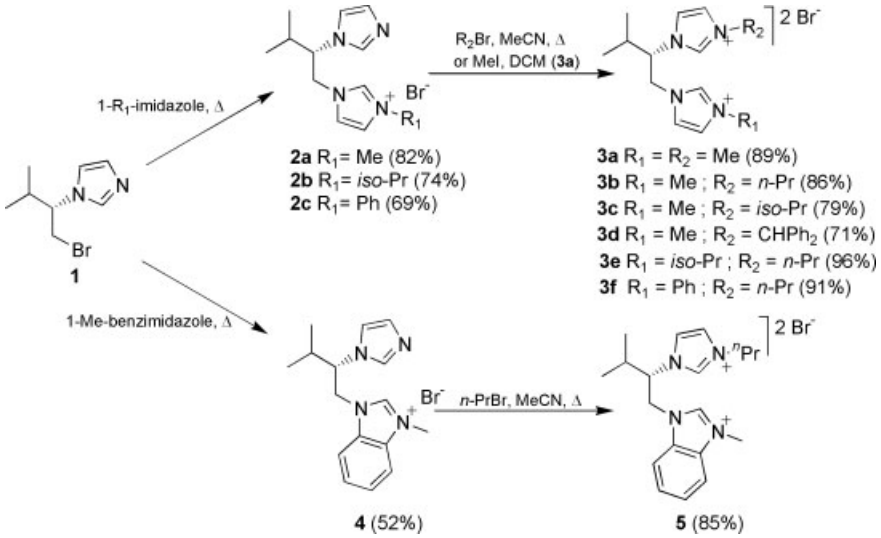
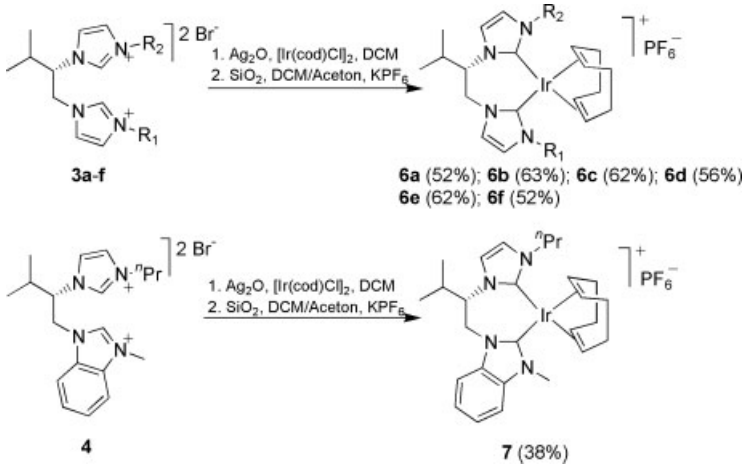


Scheme 1. Syntheses of ligand precursors.



Scheme 2. Complex syntheses by one-pot transmetallation.

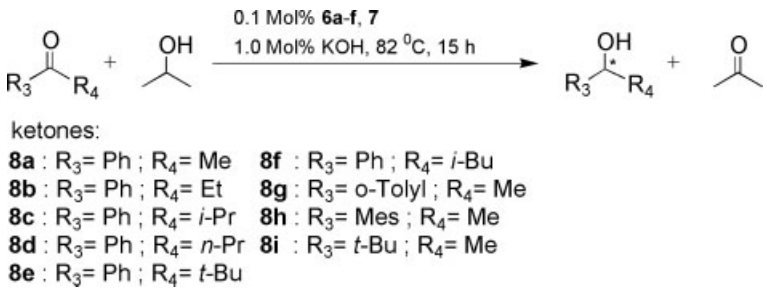
and $[Ir(cod)Cl]_2$ according to a one-pot transmetallation procedure developed by Mata *et al*.[12,16,17] All complexes were purified by gradient column chromatography on SiO_2 using dichloromethane–acetone mixtures as eluent and KPF_6 for anion exchange. The iridium(I) compounds **6a–f** were obtained as orange-red solids in 52–63% yield. Complex **7**, bearing an imidazolin-2-ylidene–benzimidazolin-2-ylidene ligand, was obtained in a lower yield of 38% (Scheme 2). The iridium complexes were obtained as mixtures of *exo* and *endo* stereoisomers, referring to the position of the backbone *iso*-propyl group relative to the coordination plane. Hence, the *iso*-propyl group of the *exo* isomer lies outside the C–Ir–C plane, while in the *endo* form it is oriented to the metal. The transmetallation reactions always gave excess *exo* isomers, ranging from 55% for **6a** to 94% for **6d**. The isomers were not separable by column chromatography, but crystals containing the *exo* isomers exclusively were obtained by layering concentrated THF–DCM solutions of complexes **6b–f** and **7** with cyclohexane.[15] Compound **6c** was also prepared as a 65 : 35 *exo*/*endo* mixture by increasing the reaction temperature during the transmetallation in acetonitrile to 80 °C. Complex **6a** did not crystallize and was obtained as a 55 : 45 *exo*/*endo* mixture after column chromatography.

All complexes were characterized by NMR spectroscopy, high-resolution mass spectrometry and elemental analysis. As previously reported, the structures of **6b** and **6c** were determined by single crystal X-ray crystallography (CCDC deposit numbers 696020 for **6b** and 696021 for **6c**). The ^{13}C NMR spectra of the iridium compounds **6a–f** show typical signals between 171 and 177 ppm for metallated carbene carbons.[16,18] In comparison, the signal of the metallated benzimidazolin-2-ylidene carbene carbon of complex **7** appears at 184 ppm. The amounts of *exo* and *endo* stereoisomers were determined by integration of their characteristic backbone proton signals in the ^1H NMR spectra.[15]

In addition to transfer hydrogenation, the prepared iridium(I) complexes were tested in further catalytic reactions and showed no activity in the hydrogenation of itaconic acid and 1-methylcyclohexene even at elevated hydrogen pressure. Only low activity with low to moderate enantioselection was observed in the hydrosilylation of prochiral ketones.

Asymmetric Transfer Hydrogenation

The iridium(I) complexes **6a–f** and **7** were used as catalysts for the asymmetric transfer hydrogenation of various ketones



Scheme 3. ATH of ketones.

with 2-propanol as solvent/hydrogen donor and 1 mol% KOH as cocatalyst (Scheme 3).[12,19] All reactions were heated for 15 h at 82 °C using ketone–catalyst–base ratios of 1000 : 1:10. It is well known that the catalyst–base ratio is essential to activate the catalysts for hydrogen transfer if no internal base is involved.[20,21] While rhodium–NHC catalysts basically require higher amounts of cocatalyst, iridium complexes are activated at lower base concentrations.[13] In the present case a catalyst–base ratio of 1 : 10 has been proven to be optimal.

The results of the catalytic transfer hydrogenations of acetophenone, propiophenone and α-methylpropiophenone are listed in Table 1. Generally all ketones were converted into the corresponding alcohols in high yields. To investigate the effect of various combinations of terminal *N*-substituents at the ligands on the enantioselectivity, all complexes were tested in ATH with different phenylalkylketones as substrates.

Starting with acetophenone, the obtained enantiomeric excesses of (*S*)-1-phenylethanol were low for all complexes. The highest *ee* value of 14% (*S*)-1-phenylethanol was achieved with complex **7** (entry 6, Table 1). Higher *ee* values of up to 42% (entry 9, table 1) were obtained using propiophenone as substrate, whereas the enantioselectivities of the catalysts were affected by the substitution patterns of the NHC-ligands. For α-methylpropiophenone as the substrate, the *ee* values of the corresponding product alcohol increased again for all catalysts.

Starting from the *N*-dimethyl substituted complex **6a**, the enantioselectivity was enhanced using ligands with sterically more demanding R_2 *N*-substituents, like *n*-propyl and particularly *iso*-propyl. However complex **6d** bearing the bulky diphenylmetyl group was generally less selective than complex **6c**. Changing the R_1 group from methyl to *iso*-propyl (**6e**, R_2 = *n*-Pr) or phenyl (**6f**, R_2 = *n*-Pr) resulted in lower *ee* values in asymmetric transfer hydrogenations of the ketones **8a–c**. The obtained *ee* values indicate that the combination of a small R_1 group with a branched R_2-alkyl group at the ligand, lead to enhanced catalyst selectivity. While most of the catalysts preferably generated the (*S*)-alcohols, the hydrogenation of α-methylpropiophenone with catalyst **6f** gave an excess of 21% (*R*)-1-phenyl-2-methylpropanol (entry 21, Table 1).

Similar yields and slightly lower enantiomeric excesses of the (*S*) product alcohols were obtained if a 65 : 35 *exo*/*endo* mixture of catalyst **6c** was used instead of enantiomerically pure **6c** (entries 9/10 and 17/18, Table 1). If the *exo*/*endo* mixture was applied, for example, to α-methylpropiophenone the *ee* value decreased from 55 to 49%. These results are indicating either a slightly different, but aligned stereoselectivity of both isomers or an opposite selectivity, associated with a lower activity of the *endo* isomer.

The most selective catalyst **6c** was then applied to other ketones with long or branched alkyl chains and bulky phenyl substituents. Additionally some catalytic runs were carried out at lower temperatures (entries 1 and 5, Table 2) or with an alternative cocatalyst (entry 2, Table 2).

The highest enantiomeric excess of 58% of the (*S*)-alcohol was obtained for the substrate *n*-butyrophenone (entry 3, table 2). The reduction of 2′,4′,6′-trimethylacetophenone (**8h**) bearing a very bulky phenylring with catalyst **6c** gave a marginally lower *ee* value of 57% of the (*R*)-enantiomer (entry 8, Table 2). Alkylphenylketones with sterically demanding alkylgroups like *tert*-butyl in **8e** or *iso*-butyl in **8f** were hydrogenated to the corresponding alcohols with *ee* values of 54 and 28% (entries 4 and 6, Table 2). Alkylketones

Table 1. ATH of ketones catalyzed by **6a–f** and **7**[a]

Entry	Catalyst	R_1/R_2	Conversion[b] (%)	*ee*[c] (%) (config.)[d]
		Substrate: ***8a***		
1	**6a**[e]	Me/Me	85	6 (*R*)
2	**6b**	Me/*n*-Pr	97	0
3	**6c**	Me/*iso*-Pr	>99	11 (*S*)
4	**6d**	Me/$CHPh_2$	>99	7 (*S*)
5	**6d**	Ph/*n*-Pr	>99	7 (*R*)
6	**7**	Me/*n*-Pr	98	14 (*S*)
		Substrate: ***8b***		
7	**6a**[e]	Me/Me	>99	20 (*S*)
8	**6b**	Me/*n*-Pr	>99	12 (*S*)
9	**6c**	Me/*iso*-Pr	97	42 (*S*)
10	**6c**[f]	Me/*iso*-Pr	98	40 (S)
11	**6d**	Me/$CHPh_2$	94	36 (*S*)
12	**6e**	*n*-Pr/*iso*-Pr	90	8 (*S*)
13	**6f**	Ph/*n*-Pr	99	6 (*S*)
14	**7**	Me/*n*-Pr	91	20 (*S*)
		Substrate: ***8c***		
15	**6a**[e]	Me/Me	98	24 (*S*)
16	**6b**	Me/*n*-Pr	98	44 (*S*)
17	**6c**	Me/*iso*-Pr	>99	55 (*S*)
18	**6c**[f]	Me/*iso*-Pr	>99	49 (S)
19	**6d**	Me/$CHPh_2$	95	37 (*S*)
20	**6e**	*n*-Pr/*iso*-Pr	78	13 (*S*)
21	**6f**	Ph/*n*-Pr	>99	21 (*R*)
22	**7**	Me/*n*-Pr	91	25 (*S*)

[a] Reaction conditions: 10 ml 2-propanol, 2.0 mmol ketone, temperature = 82 °C, time 15 h, ketone–catalyst–KOH = 1000 : 1 : 10, catalysts were applied in pure *exo* form, unless otherwise stated. [b] Conversion was determined by GC. [c] Measured by GC using chiral columns. [d] Determined by comparison of the sign of optical rotation to literature values. [e] Applied as 55 : 45 mixture of *exo*/*endo* isomers. [f] 65 : 35 mixture of *exo*/*endo* isomers.

Table 2. ATH of various ketones catalyzed by **6c**[a]

Catalyst: **6c** (R_1 = Me/R_2 = *iso*-Pr)				
Entry	Ketone	Conversion[b] (%)	*ee*[c] (%) (configuration)[d]	TON
1[e]	**8b**	<5	–	–
2[f]	**8b**	92	42 (*S*)	920
3	**8d**	82	58 (*S*)	820
4	**8e**	83	54 (*S*)	830
5[g]	**8e**	15	53 (*S*)	150
6	**8f**	>99	28 (*S*)	1000
7	**8g**	92	30 (*S*)	920
8	**8h**	93	57 (*R*)	930
10	**8i**	46	21 (*S*)	460

[a] Reaction conditions: 10 ml 2-propanol, 2.0 mmol ketone, temperature = 82 °C, time 15 h, ketone–catalyst–KOH = 1000 : 1 : 10, unless otherwise stated, catalyst **6c** was applied as pure *exo* isomer. [b] Conversion was determined by GC. [c] Measured by GC using chiral columns. [d] Determined by comparison of the sign of optical rotation to literature values. [e] Reaction temperature 60 °C. [f] Base: *t*-BuOK. [g] Reaction temperature: 70 °C.

Table 3. ATH of various ketones catalyzed by **6f**[a]

Catalyst: **6f** (R_1 = Ph/R_2 = *n*-Pr)				
Entry	Ketone	Conversion[b] (%)	*ee*[c] (%) (configuration)[d]	TON
1	**8d**	98	22 (*S*)	980
2	**8e**	67	10 (*S*)	670
3	**8g**	>99	10 (*R*)	1000
4	**8h**	82	68 (*R*)	820
5[e]	**8h**	79	64 (*R*)	790
6[f]	**8h**	75	63 (*R*)	750
7	**8i**	97	31 (*S*)	970

[a] Reaction conditions: 10 ml 2-propanol, 2.0 mmol ketone, temperature = 82 °C, time 15 h, ketone–catalyst–KOH = 1000 : 1 : 10, unless otherwise stated, catalyst **6f** was applied as pure *exo* isomer. [b] Conversion was determined by GC. [c] Measured by GC using chiral columns. [d] Determined by comparison of the sign of optical rotation to literature values. [e] Base: K_2CO_3. [f] Base: Cs_2CO_3.

like pinacolone were generally reduced in lower yields (entry 10, Table 2). In summary the selectivity of catalyst **6c** strongly depends on the substrate and ketones with long, unbranched alkyl chains or bulky phenylrings yielded the highest *ee* values. Low conversions of 5 and 15% were obtained, if the reaction temperatures were decreased from 82 to 60 and 70 °C, while the *ee* values were affected only marginally (entries 1 and 5, Table 2). Similar *ee* and conversion were observed when the base was changed from KOH to *tert*-BuOK (entry 2, Table 2).

The results of the transfer hydrogenations of various ketones using catalyst **6f** (R_1 = Ph; R_2 = *n*-Pr) are listed in Table 3. Alkylphenylketones like butyrophenone or 2,2-dimethylpropiophenone were transferred into the corresponding alcohols with only low *ee* values. Interestingly, the highest *ee* value within this work of 68% was obtained when catalyst **6f** was applied to ketone **8h**, bearing a bulky, trimethylsubstituted phenylring (entry 4, Table 3). The configurations of the product alcohols changed from (*S*) to (*R*) if ketones with short alkyl chains and methylated phenyl rings like **8g,h** were used. Presumably the bulky phenyl ring now dominates the enantiofacial selectivity, while for the other alkylphenylketones the long or branched alkylchains are determining the formation of (*S*)-alcohols.

The use of alkalicarbonates K_2CO_3 and Cs_2CO_3 as alternative cocatalysts gave slightly lower *ee* values of 64 and 63% in comparison to potassium hydroxide (entries 5 and 6, Table 3).[22]

Conclusions

In conclusion we have synthesized a series of new chiral iridium(I)–bis(NHC) complexes. The versatile synthetic pathway makes it possible to vary the terminal *N*-substituents at both imidazole rings separately. In this way, the chiral environment of the iridium center can be formed specifically. Furthermore we described the synthesis of a mixed imidazolin-2-ylidene–benzimidazolin-2-ylidene chelating ligand and its iridium complex.

The obtained iridium(I) complexes were then used as catalysts for asymmetric transfer hydrogenations of prochiral ketones and showed high activities under the described reaction conditions. Lower yields and *ee* values were observed if the reaction temperature was decreased. To determine how the enantioselectivity is affected by the substrates and different combinations of terminal *N*-substituents at the imidazolin-2-ylidene units, various catalyst/ketone pairs have been tested in ATH. The highest enantioselectivties, within this work, of 58 and 68% *ee* were obtained by catalysts, bearing methyl-/*iso*-propyl and methyl-/phenyl-*N*-substituents. These results were obtained using alkylphenylketones with long alkylchains or methylated phenyl rings as substrates. Currently efforts are in progress to improve the activity of the complexes for other catalytic reactions as well as the enantioselectivity.

Experimental

General Remarks

NMR spectra were recorded on a Bruker DRX-400 spectrometer, with $CDCl_3$, CD_3OD and D_2O as solvents. Elemental analyses were carried out in a Vario EL analyzer. Electron impact (EI+) and Fast Atom Bombardment (FAB+) mass spectra were recorded on a Finnigan MAT, TSQ 70 instrument, using 3-nitrobenzyl alcohol as matrix. Electrospray mass spectra were recorded on a Bruker Daltonics APEX II FT-ICR instrument using CH_3OH as solvent and nitrogen as drying and nebulizing gas. Melting points are uncorrected and were determined on a Mel-Temp Z15 apparatus. Chiral GC was performed on a Chrompack 438A with chiral columns from Macherey-Nagel (FS-Lipodex E, 50 m, 0.25 mm diameter) and Chrompack (FS-Cyclodex beta-I/P, 60 m, 0.25 mm diameter). Optical rotations of chiral alcohols were determined on a Knauer, Polar-M polarimeter. Imidazolebromide **1** was prepared from L-valinol (97% *ee*, Sigma-Aldrich) according to our previously reported procedure.[15] All other reagents are commercially available and were used as received.

Preparation of 2a

A mixture of **1** (495 mg, 2.28 mmol) and 1-methylimidazole (936 mg, 11.4 mmol) was stirred at 50 °C for 72 h. After cooling to ambient temperature, diethyl ether (20 ml) was added, while stirring to dissolve excess 1-methylimidazole. The ether was removed via syringe and the colorless, oily precipitate was washed

two more times with diethyl ether and dried *in vacuo*. The oil was then dissolved in $CHCl_3$ (10 ml) and extracted in water (2 × 8 ml). After removal of the water under reduced pressure, the resulting solid was washed with diethyl ether (2 × 15 ml) and dried *in vacuo*, giving **2a** as a hygroscopic, white solid. Yield: 556 mg (82%). MS (FAB): *m/z* 219 (100%). MS (HRESI+): calcd for $C_{12}H_{19}N_4$, 219.16042; found, 219.16042. ^{1}H NMR (CD_3OD, 400 MHz): δ 8.93 (s, 1H, NC*H*N), 7.77 (s, 1H, NC*H*N), 7.54 (t, $^3J_{HH}$ = 1.6 Hz, 1H, CH_{imid}), 7.47 (brs, 1H, CH_{imid}), 7.42 (t, $^3J_{HH}$ = 1.7 Hz, 1H, CH_{imid}), 7.08 (brs, 1H, CH_{imid}), 4.98–4.81 (m, 2H, NCH_2CH), 4.60 (qd, $^3J_{HH}$ = 3.4 Hz, 1H, CH_2CHN), 3.90 (s, 3H, NCH_3), 2.35 [m, 1H, $CHCH(CH_3)_2$], 1.20 [d, $^3J_{HH}$ = 6.7 Hz, 3H, $CHCH(CH_3)_2$], 0.86 [d, $^3J_{HH}$ = 6.7 Hz, 3H, $CHCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (CD_3OD, 100 MHz): δ 139.06, 138.40 (NCN), 129.89, 124.99, 123.88, 119.21 (CH_{imid}), 65.41 (CH_2CHN), 52.93 (NCH_2CH), 36.83 (NCH_3), 32.79 [$CHCH(CH_3)_2$], 20.03, 19.43 [$CH(CH_3)_2$].

Preparation of 2b

The same procedure as for **2a** was carried out by stirring imidazole-bromide **1** (230 mg, 1.1 mmol) and 1-*iso*-propylimidazole (473 mg, 4.5 mmol) at 60 °C for 48 h. Compound **2b** was obtained as a hygroscopic white solid. Yield: 267 mg (74%). MS (FAB): 247 (100%). MS (HRESI+): calcd for $C_{14}H_{23}N_4$, 247.19172; found, 247.19171. ^{1}H NMR (CD_3OD, 400 MHz): δ 9.06 [s, 1H, NC*H*N $CH(CH_3)_2$], 7.75 (bs, 2H, NC*H*N), 7.57 (s, 1H, CH_{imid}), 7.51 (bs, 1H, CH_{imid}), 7.07 (s, 1H, CH_{imid}), 4.95–4.80 (m, 2H, $CHCH_2N$), 4.64–4.55 (m, 1H, CH_2CHN), 4.38 [m, 1H, $NCH(CH_3)_2$], 2.44–2.33 [m, 1H, $CHCH(CH_3)_2$], 1.51 [d, $^3J_{HH}$ = 6.7 Hz, 6H, $NCH(CH_3)_2$], 1.21 [d, $^3J_{HH}$ = 6.7 Hz, 3H, $CHCH(CH_3)_2$], 0.87 [d, $^3J_{HH}$ = 6.7 Hz, 3H, $CHCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (CD_3OD, 100 MHz): δ 136.38 [$NCHNCH(CH_3)_2$], 129.10 (NCHN), 123.98, 122.14, 121.97, 119.40 (CH_{imid}), 65.88 (CH_2CHN), 54.78 [$NCH(CH_3)_2$], 52.96 (NCH_2CH), 32.67 [$CHCH(CH_3)_2$], 23.14, 22.91 [$NCH(CH_3)_2$], 19.85, 19.50 [$CH(CH_3)_2$].

Preparation of 2c

The same procedure as for **2a** was used by stirring imidazole-bromide **1** (173 mg, 0.8 mmol) and 1-phenylimidazole (473 mg, 4.5 mmol) at 65 °C for 72 h. The title compound **2c** was obtained as hygroscopic white solid. Yield: 198 mg (69%). MS (FAB): 281 (100%).MS (HRESI+): calcd for $C_{17}H_{21}N_4$, 281.17607; found, 281.17630. ^{1}H NMR (D_2O, 400 MHz): δ 8.91 (s, 1H, $NCHNC_{Phenyl}$), 7.72 (s, 1H, NC*H*N), 7.52 (s, 1H, CH_{imid}), 7.48 (m, 4H, C_6H_5, CH_{imid}), 7.36 (m, 3H, C_6H_5, CH_{imid}), 7.12 (br s, 1H, CH_{imid}), 4.96–4.80 (m, 2H, $CHCH_2N$), 4.44 (m, 1H, NCH_2CH), 2.23 [m, 1H, $CHCH(CH_3)_2$], 1.09 [d, $^3J_{HH}$ = 6.6 Hz, 3H, $CHCH(CH_3)_2$], 0.74 [d, $^3J_{HH}$ = 6.6 Hz, 3H, $CHCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (D_2O, 100 MHz): δ 136.91 ($NCHNC_{Phenyl}$), 136.05 (NC_{Phenyl}), 131.60 (C_6H_5), 129.89 (NCHN), 128.96, 124.75 (CH_{imid}), 123.36 (C_6H_5), 122.95 (CH_{imid}), 122.37 (C_6H_5), 119.23 (CH_{imid}), 65.44 (CH_2CHN), 53.46 (NCH_2CH), 32.81 [$CHCH(CH_3)_2$], 19.95, 19.56 [$CH(CH_3)_2$].

Preparation of 3a

To a solution of **2a** (132 mg, 0.44 mmol) in dichloromethane (3 ml), methyliodide (0.5 ml) was added in one portion. The clear solution was then stirred for 18 h at ambient temperature. After all volatiles were removed under reduced pressure, the remaining white solid was redissolved in dichloromethane and added dropwise to diethylether while stirring. The resulting white precipitate was washed several times with ether and dried *in vacuo* to give the title compound **3a** as very hygroscopic, white powder. Yield: 172 mg (89%). MS (FAB): *m/z* 313 $[M - Br]^+$ (40%). ^{1}H NMR (CD_3OD, 400 MHz): δ 9.17, 9.03 (s, 2H, NC*H*N), 7.83, 7.61 (s, 2H, CH_{imid}), 7.48 (m, 2H, CH_{imid}), 4.98–4.87 (m, 3H, $CHCH_2N$), 3.89, 3.85 (s, 6H, NCH_3), 2.39–2.31 [m, 1H, $CHCH(CH_3)_2$], 1.12 [d, $^3J_{HH}$ = 6.7 Hz, 3H, $CH(CH_3)_2$], 0.83 [d, $^3J_{HH}$ = 6.7 Hz, 3H, $CH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (CD_3OD, 100 MHz): δ 138.73 (NCHN), 138.18 (NCHN), 126.33, 125.71, 123.77, 122.51 (CH_{imid}), 67.86 (CH_2CHN), 51.89 (NCH_2CH), 37.71, 37.52 (NCH_3), 32.44 [$CHCH(CH_3)_2$], 19.77, 19.04 [$CH(CH_3)_2$].

Compound 3b

Hygroscopic white solid; Yield: 200 mg (86%) MS (FAB), *m/z* 341 (40%). ^{1}H NMR (CD_3OD, 400 MHz): δ 9.32 (s, 1H, NC*H*N), 9.08 (s, 1H, NC*H*N), 7.91 (d, $^3J_{HH}$ = 1.8 Hz, 1H, CH_{imid}), 7.75 (d, $^3J_{HH}$ = 1.7 Hz 1H, CH_{imid}), 7.52 (d, $^3J_{HH}$ = 1.7 Hz, 1H, CH_{imid}), 7.50 (d, $^3J_{HH}$ = 1.8 Hz, 1H, CH_{imid}), 5.00–4.85 (m, 3H, CH_2CHN, NCH_2CH), 4.18 (t, $^3J_{HH}$ = 7.1 Hz, 2H, NCH_2CH_2), 3.88 (s, 3H, NCH_3), 2.38 [m, 1H, $CHCH(CH_3)_2$], 1.87 (sext, $^3J_{HH}$ = 3.6 Hz, 2H, NCH_2CH_2), 1.17 [d, $^3J_{HH}$ = 6.7 Hz, 3H, $CHCH(CH_3)_2$], 1.06 [m, 6H, CH_2CH_3, $CHCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (CD_3OD, 100 MHz): δ 138.91, 137.82 (NCN), 125.76, 125.29, 123.91, 122.70 (CH_{imid}), 68.27 (CH_2CHN), 52.96 (NCH_2CH), 51.96 (NCH_2CH_2), 37.19 (NCH_3), 32.53 [$CHCH(CH_3)_2$], 24.45 (NCH_2CH_2), 19.75, 19.11 [$CH(CH_3)_2$], 11.00 (CH_2CH_3).

Compound 3c

Hygroscopic, white solid; Yield: 190 mg (79%) MS (FAB), *m/z* 341 (30%). ^{1}H NMR (CD_3OD, 400 MHz): δ 9.41 (s, 1H, NC*H*N), 9.09 (s, 1H, NC*H*N), 7.90 (d, $^3J_{HH}$ = 1.8 Hz, 1H, CH_{imid}), 7.82 (brs, 1H, CH_{imid}), 7.49 (d, $^3J_{HH}$ = 1.8 Hz, 1H, CH_{imid}), 7.44 (brs, 1H, CH_{imid}), 4.95 (t, $^3J_{HH}$ = 4.8 Hz, 2H, NCH_2CH), 4.87 (m, 1H, CH_2CHN), 4.65 [m, 1H, $NCH(CH_3)_2$], 3.85 (s, 1H, NCH_3), 2.36 [m, 1H, $CHCH(CH_3)_2$], 1.48 [d, $^3J_{HH}$ = 6.7 Hz, 6H, $NCH(CH_3)_2$], 1.13 [d, $^3J_{HH}$ = 6.6 Hz, 3H, $CHCH(CH_3)_2$], 0.82 [d, $^3J_{HH}$ = 6.7 Hz, 3H, $CHCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (CD_3OD, 100 MHz): δ 138.85, 136.40 (NCN), 125.54, 123.75, 123.38, 122.78 (CH_{imid}), 68.21 (CH_2CHN), 55.23 [$NCH(CH_3)_2$], 51.88 (NCH_2CH), 37.19 (NCH_3), 32.31 [$CHCH(CH_3)_2$], 23.22, 23.13 [$NCH(CH_3)_2$], 19.69, 19.15 [$CH(CH_3)_2$].

Preparation of 3d

An acetonitrile solution of **2a** (83 mg, 0.28 mmol) and bromodiphenylmethane (178 mg, 0.72 mmol) was heated at reflux temperature for 18 h. After all volatiles were removed under reduced pressure, the remaining solid was dissolved in dichloromethane and extracted in water (2 × 5 ml). The water was removed under reduced pressure. The resulting white solid was then washed with ether and dried *in vacuo* to give **3d** as hygroscopic, white solid. Yield: 109 mg (71%). MS (FAB): *m/z* 465 $[M - Br]^+$ (20%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.63, 8.24 (s, 2H, NC*H*N), 7.37–7.31 (m, 8H, C_6H_5), 7.25–7.19 (m, 2H, CH_{imid}), 7.14 (m, 2H, C_6H_5), 7.08 (m, 2H, CH_{imid}), 5.82–5.64 [m, 3H, $CHCH_2N$, $NCH(C_6H_5)_2$], 4.91 (m, 1H, CH_2CHN), 3.85 (s, 3H, NCH_3), 2.41 [m, 1H, $CHCH(CH_3)_2$], 1.10 [d, $^3J_{HH}$ = 6.5 Hz, 3H, $CH(CH_3)_2$], 0.86 [d, $^3J_{HH}$ = 6.4 Hz, 3H, $CH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 137.72, 137.08 (NCN), 136.20, 136.06 ($C_{Phenyl,quart.}$), 129.46 (C_6H_5), 129.38 (C_6H_5), 128.30 (C_6H_5), 128.20 (C_6H_5), 127.78 (C_6H_5), 123.79, 123.56, 123.14, 121.53 (CH_{imid}), 67.02 [$NCH(C_6H_5)_2$], 65.84 (CH_2CHN), 50.11 (NCH_2CH), 37.03 (NCH_3), 31.49 [$CHCH(CH_3)_2$], 19.45, 18.66 [$CH(CH_3)_2$].

Preparation of 3e

Following the procedure described for **3d**, reaction between **2b** (165 mg, 0.50 mmol) and 1-bromopropane (0.4 ml) gave the title compound **3e** as hygroscopic white solid. Yield: 187 mg (84%). MS (FAB): *m/z* 369 $[M - Br]^+$ (20%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.02 (s, 1H, NC*H*N), 9.91 (s, 1H, NC*H*N), 8.37, 8.12, 7.40, 7.33 (s, 4H, CH_{imid}), 5.61–5.53 (m, 2H, NCH_2CH), 4.79 (m, 1H, CH_2CHN), 4.57 [m, 1H, $NCH(CH_3)_2$], 4.28–4.23 (m, 2H, NCH_2CH_2), 2.35 [m, 1H, $CHCH(CH_3)_2$], 1.83 (m, 2H, NCH_2CH_2), 1.48 [d, $^3J_{HH}$ = 6.5 Hz, 6H, $NCH(CH_3)_2$] 1.12 [d, $^3J_{HH}$ = 6.4 Hz, 3H, $CHCH(CH_3)_2$], 0.84–0.78 [m, 6H, $CHCH(CH_3)_2$, CH_2CH_3]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 136.46, 135.78 (NCN), 123.96, 123.33, 122.47, 120.31 (CH_{imid}), 65.42 (CH_2CHN), 53.74 [$NCH(CH_3)_2$], 51.74 ($CHCH_2N$), 50.19 (NCH_2CH_2), 31.69 [$CHCH(CH_3)_2$], 23.38 (NCH_2CH_2), 22.93, 22.66 [$NCH(CH_3)_2$], 19.78, 19.18 [$CHCH(CH_3)_2$], 10.49 (CH_2CH_3).

Preparation of 3f

Following the procedure described for **3d**, reaction between **2c** (120 mg, 0.34 mmol) and 1-bromopropane (0.3 ml) gave the title compound **3f** as hygroscopic white solid. Yield: 147 mg (91%). MS (FAB): *m/z* 403 $[M - Br]^+$ (70%). ^{1}H NMR (CD_3OD, 400 MHz): δ 9.73, 9.35 (s, 2H, NC*H*N), 8.01, 7.92, 7.72, 7.53 (s, 4H, CH_{imid}), 7.67 (m, 2H, C_6H_5), 7.59–7.48 (m, 3H, C_6H_5), 5.08–4.92 (m, 3H, $NCHCH_2$, $NCHCH_2$), 4.13 (t, $^3J_{HH}$ = 7.1 Hz, 2H, NCH_2CH_2), 2.38 [m, 1H, $CHCH(CH_3)_2$], 1.79 (m, 2H, NCH_2CH_2), 1.16 [d, $^3J_{HH}$ = 6.6 Hz, 3H, $CHCH(CH_3)_2$], 0.84 [d, $^3J_{HH}$ = 6.6 Hz, 3H, $CHCH(CH_3)_2$], 0.76 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_3OD, 100 MHz): δ 137.78, 137.33 (NCHN), 131.56 (C_6H_5), 125.13, 124.70, 123.52 (CH_{imid}), 123.70, 123.42 (C_6H_5), 122.69 (CH_{imid}), 67.94 (CH_2CHN), 52.80 (NCH_2CH), 52.32 (NCH_2CH_2), 32.52 [$CHCH(CH_3)_2$], 24.30 (CH_2CH_3), 19.64, 18.97 [$CH(CH_3)_2$], 10.85 (CH_2CH_3).

Preparation of 4

Following the procedure described for **2a**, reaction between **1** (120 mg, 0.34 mmol) and 1-methylbenzimidazole (462 mg, 3.5 mmol), the title compound **4** was obtained as a hygroscopic white solid. Yield: 195 mg (52%). MS (FAB): *m/z* 269 (100%). MS (HRESI+): calcd for $C_{16}H_{21}N_4$, 269.36524; found, 269.36483. ^{1}H NMR (CD_3OD, 400 MHz): δ 8.48 (s, 1H, NC*H*NCH_3), 7.96 (s, 1H, NC*H*N), 7.83 (s, 1H, CH_{imid}), 7.69–7.52 (m, 2H, $CH_{Benzimid.}$), 7.36–7.31 (m, 2H, $CH_{Benzimid.}$) 7.05 (s, 1H, CH_{imid}), 5.13–4.98 (m, 2H, $CHCH_2N$), 4.62 (td, $^3J_{HH}$ = 4.2 Hz, 20.0 Hz, 1H, CH_2CHN), 4.01 (s, 3H, NCH_3), 2.31 [m, 1H, $CHCH(CH_3)_2$], 1.21 [d, $^3J_{HH}$ = 6.7 Hz, 3H, $CHCH(CH_3)_2$], 0.79 [d, $^3J_{HH}$ = 6.7 Hz 3H, $CHCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (CD_3OD, 100 MHz): δ 140.70 ($NCHNCH_3$), 136.21, 133.54 ($CH_{quart.\ Benzimid.}$), 128.95 (NCHN), 127.03 (CH_{imid}), 123.04, 123.44 ($CH_{Benzimid.}$), 117.93 (CH_{imid}), 112.81, 111.52 ($CH_{Benzimid.}$), 63.32 (CH_2CHN), 49.34 (NCH_2CH), 32.82 (NCH_3), 30.49 [$CHCH(CH_3)_2$], 18.71, 18.16 [$CH(CH_3)_2$].

Preparation of 5

Following the procedure described for **3d**, reaction between **4** (95 mg, 0.27 mmol) and 1-bromopropane (0.5 ml) gave the title compound **5** as a hygroscopic white solid. Yield: 107 mg (85%). MS (FAB): *m/z* 395 $[M - Br]^+$ (10%); 259, 261 (80%). ^{1}H NMR (D_2O, 400 MHz): δ 9.21, 8.71 (s, 2H, NC*H*N), 7.81–7.58 (m, 5H, CH_{imid}, $CH_{Benzimid.}$), 7.50 (s, 1H, CH_{imid}), 5.29–5.02 (m, 3H, $CHCH_2N$, $NCHCH_2$), 4.37 (t, $^3J_{HH}$ = 7.0 Hz, NCH_2CH_2), 4.02 (s, 3H, NCH_3), 2.50 [m, 1H, $CHCH(CH_3)_2$], 1.48 (m, 2H, NCH_2CH_2), 1.26 [d, $^3J_{HH}$ = 6.3 Hz, 3H, $CHCH(CH_3)_2$], 0.85 [d, $^3J_{HH}$ = 6.5 Hz 3H, $CHCH(CH_3)_2$], 0.47 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (D_2O, 100 MHz): δ 141.78, 141.20 (NCHN), 135.47, 131.72 ($CH_{quart.Benzimid.}$), 127.69, 126.80 ($CH_{Benzimid.}$), 124.22, 120.71 (CH_{imid}), 113.67, 111.93 ($CH_{Benzimid.}$), 66.94 (CH_2CHN), 51.40 (NCH_2CH_2), 48.70 (NCH_2CH), 33.04 (NCH_3), 30.41 [$CHCH(CH_3)_2$], 22.70 (NCH_2CH_2), 18.66, 18.15 [$CH(CH_3)_2$], 9.58 (CH_2CH_3).

Complex Synthesis: General Procedure

Silver(I) oxide (0.70 mmol) was added to a dichloromethane (15 ml) solution of bis imidazolium salts (0.35 mmol) and stirred in the dark at room temperature for 2.5 h under argon. Then $[Ir(COD)Cl]_2$ (0.17 mmol) was added to the gray suspension in one portion, under formation of a white precipitate. To complete the reaction, the mixture was stirred in the dark at room temperature for 14 h. To remove insoluble silver salts, the suspension was filtered through celite and the resulting orange-red solution was concentrated under reduced pressure. The crude solid was then purified by gradient column chromatography (SiO_2, first CH_2Cl_2; CH_2Cl_2–acetone 2:1; then CH_2Cl_2–acetone 1:1 with 2 equiv. KPF_6). Analytically pure material was obtained by a second flash column chromatography, with CH_2Cl_2–acetone 4:1 as elutant. The title compounds were obtained as orange-red solids.

Compound 6a

Complex **6a** was obtained as 55:45 mixture of *exo* and *endo* stereoisomers.Yield: 120 mg (52%). M.p.: 155–156 °C; MS (HRESI+): calcd for $C_{21}H_{32}IrN_4$, 533.22574; found, 533.22520. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.98 (d, $^3J_{HH}$ = 2.0 Hz, 1H, CH_{imid}), 6.88 (d, $^3J_{HH}$ = 1.9 Hz, 1H, CH_{imid}), 6.81 (d, $^3J_{HH}$ = 2.0 Hz, 1H, CH_{imid}), 6.77 (d, $^3J_{HH}$ = 1.9 Hz, 1H, CH_{imid}), 6.43 (td, $^3J_{HH}$ = 4.6 Hz, 11.5 Hz, 1H, CH_2CHN), 4.45–3.91 (m, 6H, $CHCH_2N$, CH_{COD}), 3.84 (s, 1H, NCH_3), 3.57 (s, 1H, NCH_3), 2.39–1.80 (m, $CHCH(CH_3)_2$, $CH_{2,COD}$), 1.16 [d, $^3J_{HH}$ = 6.5 Hz, 3H, $CH(CH_3)_2$], 0.97 [d, $^3J_{HH}$ = 6.4 Hz, 3H, $CH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 176.74, 173.87 (IrC), 124.43, 123.19, 122.04, 117.44 (CH_{imid}), 78.04, 75.43, 74.24, 73.57 (CH_{COD}), 63.95 (CH_2CHN), 52.47 (NCH_2CH), 39.21, 36.82 (NCH_3), 32.52, 32.04, 30.28, 29.32 ($CH_{2\ COD}$), 29.98 [$CHCH(CH_3)_2$], 20.84, 19.82 [$CH(CH_3)_2$]. Anal. calcd for $C_{21}H_{32}F_6IrN_4P$ (678.47), C, 37.18; H, 4.75; N, 8.26; found, C, 37.70; H, 4.59; N, 8.37.

Compound 6b

Diastereomerically pure (100% *exo*), crystalline material was obtained by layering a THF–CH_2Cl_2 (3:1) solution of **6b** with cyclohexane. Yield: 152 mg (63%). M.p.: 159 °C, 209 °C dec.; MS (HRESI+): calcd for $C_{23}H_{36}IrN_4$, 561.25638; found, 561.25631. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.02 (d, $^3J_{HH}$ = 2.0 Hz, 1H, CH_{imid}), 6.90 (d, $^3J_{HH}$ = 1.9 Hz, 1H, CH_{imid}), 6.81 (d, $^3J_{HH}$ = 2.0 Hz, 1H, CH_{imid}), 6.78 (d, $^3J_{HH}$ = 2.0 Hz, 1H, CH_{imid}), 6.49 (td, J_{HH} = 4.3 Hz, 12.5 Hz, 1H, CH_2CHN), 4.38 (td, J_{HH} = 2.8 Hz, 7.2 Hz 1H, $CHCH_2N$), 4.31–4.25 (m, 2H, CH_{COD}), 4.08 (m, 1H, $CHCH_2N$), 3.99–3.87 (m, 2H, CH_{COD}),3.83 (s, 3H, NCH_3), 3.79 (td, J_{HH} = 3.4 Hz, 7.2 Hz, 2H, NCH_2CH_2), 2.42–1.78 [m, 9H, $CH_{2,COD}$, $CHCH(CH_3)_2$], 1.67 (sext, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2CH_2), 1.16 [d, $^3J_{HH}$ = 6.5 Hz, 1H, $CH(CH_3)_2$], 0.97 [d, $^3J_{HH}$ = 6.4 Hz, 3H, $CH(CH_3)_2$], 0.69 (t, $^3J_{HH}$ = 7.4 Hz, 1H, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 176.06, 173.35 (IrC), 124.59, 121.87, 121.65, 117.53 (CH_{imid}), 77.86, 74.30, 74.23, 72.56 (CH_{COD}), 64.34 (CH_2CHN), 52.54 (NCH_2CH_2),51.42 (NCH_2CH), 39.31 (NCH_3), 32.67 [$CHCH(CH_3)_2$], 32.64, 30.18, 29.89, 29.32 ($CH_{2\ COD}$),

24.46 (NCH_2CH_2), 20.82, 19.88 [$CH(CH_3)_2$], 10.58 (CH_2CH_3). Anal. calcd for $C_{23}H_{36}F_6IrN_4P$ (705.74), C, 39.14; H, 5.14; N, 7.94; found, C, 39.17; H, 5.19; N, 8.02.

Compound 6c

Diastereomerically pure (100% *exo*), crystalline material was obtained by layering a THF–CH_2Cl_2 (1 : 1) solution of **6c** with cyclohexane. Yield: 143 mg (62%).

A 65 : 35 *exo*/*endo* mixture of complex **6c** was obtained by heating the transmetallation reaction in acetonitrile to 80 °C for 5 h. Then the general purification procedure was used. M.p.: 151 °C, 205 °C dec.; MS (HRESI+): calcd for $C_{23}H_{36}IrN_4$, 559.25404; found, 559.25396. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.03 (d, $^3J_{HH}$ = 2.1 Hz, 1H, CH_{imid}), 6.89 (d, $^3J_{HH}$ = 2.0 Hz, 1H, CH_{imid}), 6.81 (m, 2H, CH_{imid}), 6.41 (td, $^3J_{HH}$ = 4.6 Hz, 10.9 Hz, 1H, CH_2CHN), 4.54 [vsep, $^3J_{HH}$ = 6.8 Hz, 1H, $NCH(CH_3)_2$], 4.26 (m, 3H, CH_{COD}, NCH_2), 4.09–3.92 (m, 3H, CH_{COD}, NCH_2), 3.84 (s, 3H, NCH_3), 2.39–2.20 [m, 3H, $CH_{2\ COD}$, $CHCH(CH_3)_2$], 2.09 (m, 3H, $CH_{2\ COD}$), 1.87 (m, 3H, $CH_{2\ COD}$), 1.35 [d, $^3J_{HH}$ = 6.8 Hz, 3H, $NCH(CH_3)_2$], 1.17 [d, $^3J_{HH}$ = 6.5 Hz, 3H, $NCH(CH_3)_2$], 1.10 [d, $^3J_{HH}$ = 6.8 Hz, 3H, $CHCH(CH_3)_2$], 0.98 [d, $^3J_{HH}$ = 6.4 Hz, 3H, $CHCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 175.47, 173.61 (IrC), 124.72, 121.67, 118.17, 117.49 (CH_{imid}), 77.82, 74.63, 74.34, 73.34 (CH_{COD}), 64.29 (CH_2CHN), 52.59 [$NCH(CH_3)_2$], 52.08 (NCH_2CH), 39.12 (NCH_3), 32.12 [$CHCH(CH_3)_2$], 32.09, 30.67, 30.39, 29.34 ($CH_{2\ COD}$), 23.58, 23.32 [$NCH(CH_3)_2$], 20.87, 19.82 [$CH(CH_3)_2$]. Anal. calcd for $C_{23}H_{36}F_6IrN_4P$ (705.74), C, 39.14; H, 5.14; N, 7.94; found, C, 38.82; H, 5.03; N, 8.06.

Compound 6d

Diastereomerically pure (100% *exo*), crystalline material was obtained by layering a THF–CH_2Cl_2 (10 : 1) solution of **6d** with cyclohexane. Yield: 143 mg (56%).M.p.: 169–171 °C (Zers.). MS (HRESI+): calcd for $C_{33}H_{40}IrN_4$, 683.28534; found, 683.28606. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31–7.16 (m, 6H, C_6H_5), 7.11 (d, $^3J_{HH}$ = 2.1 Hz, 1H, CH_{imid}), 6.98 (m, 3H, CH_{imid}, C_6H_5), 6.79 [s, 1H, $NCH(C_6H_5)_2$], 6.63 (d, $^3J_{HH}$ = 1.9 Hz, 1H, CH_{imid}), 6.58 (d, $^3J_{HH}$ = 2.1 Hz, 1H, CH_{imid}), 6.50 (td, $^3J_{HH}$ = 4.9 Hz, 11.3 Hz, 1H, CH_2CHN), 6.41 (m, 2H, C_6H_5) 4.48, 4.29 (m, 2H, $CHCH_2N$), 4.24 (m, 1H, CH_{COD}), 4.37–4.20 (m, 4H, NCH_2CH_2, CH_{COD}), 3.99 (m, 2H, CH_{COD}), 2.98 (s, 3H, NCH_3), 2.80 (m, 1H, CH_{COD}), 2.41 [m, 1H, $CHCH(CH_3)_2$], 2.06–1.91 (m, 4H, $CH_{2\ COD}$), 1.78–1.67 (m, 4H, $CH_{2\ COD}$), 1.19 [d, $^3J_{HH}$ = 6.5 Hz, 1H, $CH(CH_3)_2$], 1.01 [d, $^3J_{HH}$ = 6.4 Hz, 3H, $CH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 177.41, 171.64 (IrC), 138.18, 137.54 ($C_{Phenyl,\ quart.}$), 128.17 (C_6H_5), 127.95 (C_6H_5), 127.66 (C_6H_5), 127.21 (C_6H_5), 125.59 (C_6H_5), 123.87, 120.61, 119.88, 117.11 (CH_{imid}), 77.86, 73.83, 73.22, 73.01 (CH_{COD}), 65.73 [$NCH(C_6H_5)_2$], 63.57 (CH_2CHN), 51.60 (NCH_2CH), 37.09 (NCH_3), 31.48, 31.31, 29.41, 29.07 ($CH_{2\ COD}$), 28.19 [$CHCH(CH_3)_2$], 19.93, 18.84 [$CH(CH_3)_2$]. Anal. calcd for $C_{33}H_{40}F_6IrN_4P$ (829.88), C, 47.76; H, 4.86; N, 6.75; found, C, 48.14; H, 4.73; N, 6.90.

Compound 6e

Yield: 122 mg (62%). M.p.: 151–152 °C, 200 °C dec. MS (HRESI+): calcd for $C_{25}H_{40}IrN_4$, 587.28534; found, 587.28581. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.06 (d, $^3J_{HH}$ = 2.1 Hz, 1H, CH_{imid}), 6.96 (d, $^3J_{HH}$ = 2.0 Hz, 1H, CH_{imid}), 6.82 (d, $^3J_{HH}$ = 2.2 Hz, 1H, CH_{imid}), 6.80 (d, $^3J_{HH}$ = 2.1 Hz, 1H, CH_{imid}), 6.49 (td, $^3J_{HH}$ = 4.3 Hz, 11.5 Hz, 1H, CH_2CHN), 5.12 [sep, $^3J_{HH}$ = 6.8 Hz, 1H, $NCH(CH_3)_2$], 4.35–4.27 (m, 2H, NCH_2CH, CH_{COD}), 4.15–4.08 (m, 2H, NCH_2CH, CH_{COD}), 3.89–3.81 (m, 3H, NCH_2CH_2, CH_{COD}), 3.68-3.61 (m, 1H, NCH_2CH_2), 2.44–2.30 (m, 2H, $CH_{2\ COD}$), 2.24–1.58 [m, 9H, $CHCH(CH_3)_2$, NCH_2CH_2, $CH_{2\ COD}$], 1.40 [d, $^3J_{HH}$ = 6.8 Hz, 3H, $NCH(CH_3)_2$], 1.20 [d, $^3J_{HH}$ = 6.7 Hz, 3H, $NCH(CH_3)_2$], 1.16 [d, $^3J_{HH}$ = 6.5 Hz, 1H, $CH(CH_3)_2$], 0.96 [d, $^3J_{HH}$ = 6.4 Hz, 3H, $CH(CH_3)_2$], 0.86 (t, $^3J_{HH}$ = 7.4 Hz, 1H, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 175.75, 172.15 (IrC), 125.39, 121.20, 117.92, 116.52 (CH_{imid}), 78.10, 73.97, 73.85, 72.40 (CH_{COD}), 64.05 (CH_2CHN), 54.21 [$NC(CH_3)_2$], 52.32 (NCH_2CH_2), 51.41 (NCH_2CH), 32.91, 32.76, 29.96, 29.76 ($CH_{2\ COD}$), 29.32 [$CHCH(CH_3)_2$], 24.76 [$NCH(CH_3)_2$], 24.40 (NCH_2CH_2), 23.72 [$NCH(CH_3)_2$], 20.83, 19.88 [$CH(CH_3)_2$], 10.91 (CH_2CH_3). Anal. calcd for $C_{25}H_{40}F_6IrN_4P$ (733.79), C, 40.87; H, 5.45; N, 7.63; found, C, 40.59; H, 5.49; N, 7.27.

Compound 6f

Yield: 105 mg (64%). M.p.: 146–147 °C, 185 °C dec. MS (HRESI+): calcd for $C_{28}H_{38}IrN_4$, 621.26969; found, 621.27053. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (m, 2H, C_6H_5), 7.43 (m, 3H, C_6H_5), 7.14 (d, $^3J_{HH}$ = 2.1 Hz, 1H, CH_{imid}), 7.12 (d, $^3J_{HH}$ = 2.1 Hz, 1H, CH_{imid}), 7.07 (d, $^3J_{HH}$ = 2.0 Hz, 1H, CH_{imid}), 6.92 (d, $^3J_{HH}$ = 2.1 Hz, 1H, CH_{imid}), 6.65 (td, $^3J_{HH}$ = 4.0 Hz, 11.4 Hz 1H, CH_2CHN), 4.48–4.29 (m, 2H, $CHCH_2N$), 4.24 (m, 1H, CH_{COD}), 4.11–3.93 (m, 3H, NCH_2CH_2, CH_{COD}), 2.80 (m, 1H, CH_{COD}), 2.41 [m, 1H, $CHCH(CH_3)_2$], 2.06–1.91 (m, 4H, $CH_{2\ COD}$), 1.78–1.67 (m, 4H, $CH_{2\ COD}$), 1.45 (m, 2H NCH_2CH_2), 1.20 [d, $^3J_{HH}$ = 6.5 Hz, 1H, $CH(CH_3)_2$], 0.98 [d, $^3J_{HH}$ = 6.4 Hz, 3H, $CH(CH_3)_2$], 0.89 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 175.11, 172.74 (IrC), 140.24 (NC_{Phenyl}), 129.01 (2C, C_6H_5), 128.90 (1C, C_6H_5), 124.17 (2C, C_6H_5), 125.29, 121.83, 121.02, 118.11 (CH_{imid}), 78.31, 75.06, 74.46, 72.59 (CH_{COD}), 64.37 (CH_2CHN), 53.06 (NCH_2CH_2), 51.33 (NCH_2CH), 39.31 (NCH_2CH_2), 32.02 [$CHCH(CH_3)_2$], 32.02, 30.66, 29.71, 29.18 ($CH_{2\ COD}$), 24.46 (NCH_2CH_2), 20.78, 20.00 [$CH(CH_3)_2$], 10.83 (CH_2CH_3). Anal. calcd for $C_{28}H_{38}F_6IrN_4P$ (767.81), C, 43.80; H, 4.99; N, 7.30; found, C, 44.08; H, 4.60; N, 7.44.

Compound 7

Yield: 49 mg (38%). M.p.: 157–159 °C, 187 °C dec. MS (HRESI+): calcd for $C_{27}H_{38}IrN_4$, 609.26969; found, 609.26960. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (m, 1H, $CH_{Benzimid.}$), 7.25–7.19 (m, 3H, $CH_{Benzimid.}$), 7.09 (d, $^3J_{HH}$ = 2.0 Hz, 1H, CH_{imid}), 6.79 (m, 1H, CH_2CHN), 6.75 (d, $^3J_{HH}$ = 2.0 Hz, 1H, CH_{imid}), 4.59 (m, 1H, CH_{COD}), 4.36 (m, 2H, NCH_2CH_2), 4.26 (m, 2H, CH_{COD}), 4.09 (s, 3H, NCH_3), 3.92 (m, 1H, CH_{COD}), 3.78 (td, J_{HH} = 3.0 Hz, 7.3 Hz, 2H, NCH_2CH), 2.57 [m, 1H, $CHCH(CH_3)_2$], 2.42–2.03 (m, 5H, $CH_{2\ COD}$), 1.94–1.85 (m, 3H, $CH_{2\ COD}$), 1.65 (sext, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2CH_2), 1.27 [d, $^3J_{HH}$ = 6.5 Hz, 3H, $NCH(CH_3)_2$], 1.02 [d, $^3J_{HH}$ = 6.4 Hz, 3H, $CHCH(CH_3)_2$], 0.68 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 184.33 ($IrC_{Benzimid.}$), 174.54 (IrC), 135.84, 134.37 ($C_{quart.,Benzimid.}$), 123.96, 123.92 ($CH_{Benzimid.}$), 121.94, 117.75 (CH_{imid}), 110.70, 109.87 ($CH_{Benzimid.}$), 78.44, 77.21, 76.38, 73.52 (CH_{COD}), 64.48 (CH_2CHN), 51.49 (NCH_2CH), 49.40 (NCH_2CH_2), 36.84 (NCH_3), 32.66, 32.50 ($CH_{2\ COD}$), 30.13 [$CHCH(CH_3)_2$], 29.94, 29.15 ($CH_{2\ COD}$), 24.51 (NCH_2CH_2), 20.91, 20.25 [$CH(CH_3)_2$], 10.68 ($NCH_2CH_2CH_3$). Anal. calcd for $C_{27}H_{38}F_6IrN_4P$ (755.80), C, 42.91; H, 5.07; N, 7.41; found, C, 41.98; H, 4.90; N, 7.34.

General Prodedure for Transfer Hydrogenations

A solution of the catalyst (0.002 mmol), KOH (0.02 mmol) and the ketone (2.0 mmol) in 2-propanol (10 ml) was heated under

argon in a Schlenktube at 82 °C for 15 h. After cooling to ambient temperature, water was added to the reaction mixture and extracted with ether (2 × 10 ml). The organic phase was dried over Mg_2SO_4 and filtered through celite. After removing all volatiles under reduced pressure, the product alcohols were obtained as oils. Turnovers and enantiomeric excesses were determined by GC with chiral columns (see General Remarks). Absolute configurations of the product alcohols were determined by comparing the retention times of the products with enantiomerically pure samples (1-phenylethanol, 1-phenylpropanol) or by comparing the sense of optical rotations of the product samples with literature values.

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