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Modular Synthesis of a New Type of Chiral Bis(carbene) Ligand from L-Valinol and Iridium(I) and Rhodium(I) Complexes Thereof

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New, chiral bis(imidazol-2-ylidene) ligands, and their rhodium(I) and iridium(I) complexes, have been prepared by a simple six-step synthesis starting from commercially available enantiomerically pure L-valinol. The stepwise introduction of the imidazoles makes it possible to create chiral bis(NHC) complexes with different substituents at the terminal nitrogen atoms. Formation of Ir^I and Rh^I complexes by a one-pot transmetallation reaction gives the *endo* and *exo* stereoisomers in different ratios, depending on the metal and the reaction conditions. Diastereomerically pure material was obtained by crystallisation.

Introduction

Since their discovery, stable N-heterocyclic carbenes (NHCs) have been the subject of intense interest, primarily as ligands for transition metals. NHC complexes display significant advantages in comparison with phosphane complexes, particularly their stability towards air, moisture and heat.[1–3] Their use in transition-metal-mediated C–C coupling and metathesis reactions has established N-heterocyclic carbenes as a new class of ligands alongside traditional phosphane and amine ligands.[3–6] The field of asymmetric catalysis with NHC-containing ligands is dominated by mixed ligands with a carbene unit and a second coordinating group, such as a phosphane or oxazoline.[7–12] These unsymmetrical ligands illustrate the fact that C_2 symmetry is not a necessary criterion for efficient enantioselectivity in asymmetric catalysis.

Applications of bis(N-heterocyclic carbene) complexes in asymmetric catalysis, however, are rare, and we are only aware of one example with good to excellent *ee* values that has been reported in the literature by Shi et al. for the hydrosilylation of prochiral ketones.[13] Further potential applications of chiral bis(NHC) complexes are transfer hydrogenations of prochiral ketones. Recent reports by Crabtree, Peris and co-workers have indicated the high activity of [bis(NHC)]rhodium and -iridium complexes in hydrogen-transfer reactions.[14,15]

Most of the existing routes to chiral bidentate NHC ligands use condensation reactions or alkylation of *N*-substituted imidazoles with a suitable precursor.[13,16,17] This precursor must either have two amino functions for the condensation, or two leaving groups if the precursor acts as an alkylating agent.[18] Another method, published by Douthwaite et al., uses a base-induced 1,3-cycloaddition to form imidazoles.[19]

In the early 1990s, Itoh, Pfaltz and others demonstrated that valinol-based chiral ligands are useful for asymmetric catalysis.[20–23] They used valinol and other β-amino alcohols as building blocks for chiral oxazolines, which were then combined with pyridines, phosphanes and, more recently, by Herrmann and Gade with carbenes.[7,24–26] Beside oxazolines, valinol has also been used to prepare chiral phosphanes and alkoxy-NHC ligands.[24,27,28]

In this article we report a synthetic strategy that offers a basis for a great number of different chiral bis(NHC) ligands and their unsymmetrical rhodium and iridium complexes, inspired by the well-established concept of C_1-symmetrical enantioselective catalysts. Our aim was to find a simple synthesis for chiral chelating N-heterocyclic carbene ligand precursors derived from readily available, enantiomerically pure amino acids or their corresponding chiral β-amino alcohols.

Apart from the choice of starting material, this synthetic pathway should offer further possibilities for ligand modification. The stepwise introduction of the imidazole units by combining two different methods allows unsymmetrical substitution of the terminal nitrogen atoms at both imidazole rings. Starting with bromide **3**, it should be possible to introduce other nucleophilic coordinating units like phosphanes or amines into the ligand precursor. With regard to a catalytic application of the rhodium and iridium complexes, the modular synthesis of the ligand offers several possibilities for adjusting the catalytic activity and selectivity.

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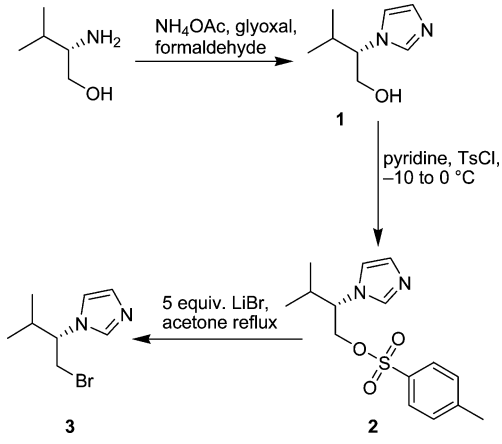
Results and Discussion

Synthesis of Ligand Precursors

Starting from commercially available, enantiomerically pure L-valinol, the first imidazole was introduced according to a method of Saigo et al. by a condensation reaction with ammonium acetate, glyoxal and formaldehyde in moderate yields.[29]

To make the alcohol a good leaving group, compound **2** was converted into the tosylate according to a conventional method by treatment with *p*-tosyl chloride and pyridine at –10 to 0 °C in a maximum isolated yield of 81%. Attempts to tosylate the alcohol with tosyl chloride in thf/water/sodium hydroxide gave the product in lower yields along with a higher amount of by-products.

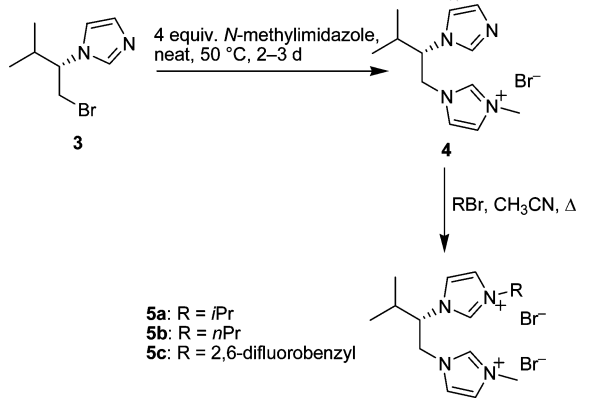
With regard to complex synthesis by transmetallation with silver(I) oxide, tosylate **2** was converted into the bromide under Finkelstein conditions by treatment with lithium bromide in acetone (Scheme 1).[30] Direct methods to convert the alcohol into the bromide, such as an Appel reaction or treatment with thionyl bromide, were not successful.[31] The major side reactions observed for compounds **2** and **3** were elimination of TsOH or HBr and intermolecular dimerisation or polymerisation. To avoid these reactions, all conversions were carried out at low temperatures or in dilute solution.



Scheme 1. Synthesis of the chiral imidazole bromide **3**.

With imidazole bromide **3** as starting point, it was possible to obtain chiral ligand precursors with different substituents in two steps (Scheme 2). The first step was the alkylation of 1-methylimidazole with **3** as alkylating agent. Generally, all *N*-monoalkylated imidazoles, even those with sterically demanding substituents, can be used in this reaction.[32]

The correct choice of reaction conditions proved to be of great importance to achieve acceptable yields of **4**. The best result (82%) was obtained without solvent, with an excess of 1-methylimidazole at 50 °C, and a reaction time of 3 d. The excess 1-methylimidazole was necessary to prevent intermolecular alkylation of imidazole bromides. Conversions in toluene as solvent at 95–105 °C and reaction times of approximately 12 h were also partially successful but



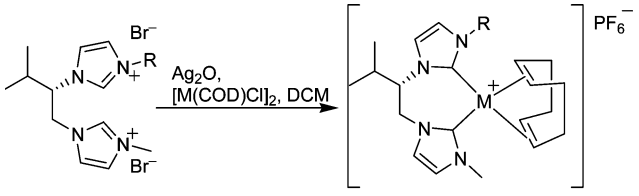
Scheme 2. Preparation of the bis(imidazolium) salts **5a**–**c**.

gave lower yields and more by-products. Compound **4** is a hygroscopic, air-stable, white solid that shows characteristic ^{1}H NMR signals at δ = 8.9 ppm (in $CDCl_3$) and ^{13}C NMR signals at δ = 139.0 ppm for the NCHN proton and carbon atom of the imidazolium salts, respectively. The bis(imidazolium) salts were prepared by S_N2 displacement of bromide from the electrophiles RBr (R = *n*Pr, *i*Pr and 2,6-difluorobenzyl) by the remaining imidazole nitrogen atom of **4**. However, only electrophiles with bromine in a primary, benzylic or at least secondary position provided good yields.[32] The reactions were carried out in acetonitrile at reflux temperature and gave the bis(imidazolium) salts **5a**–**c** in >78% yield.[16,19] All compounds obtained are hygroscopic, white solids, which are soluble in water, methanol, dichloromethane and acetonitrile but insoluble in diethyl ether and hexane. The ^{1}H and ^{13}C NMR spectra of compounds **5a**–**c** show the typical signals of bis(imidazolium) salts in the range δ = 9.1–9.4 ppm for the NCHN protons and δ = 136.4–138.9 ppm for the corresponding carbon atoms, in CD_3OD or D_2O as solvent.[33] Further characteristic NMR signals for compounds **1**–**5** are the separate signals for the diastereotopic methyl groups at $\delta \approx 19$ ppm in the ^{13}C NMR spectra and two doublets at $\delta \approx 0.9$ ppm in the ^{1}H NMR spectrum. The ^{1}H NMR signals of the diastereotopic methylene protons are separated as well.

Preparation and Stereochemistry of the Complexes

All iridium(I) and rhodium(I) complexes of **5a**–**c** were prepared from the bis(imidazolium) bromides by treatment with silver(I) oxide and $[MCl(cod)]_2$ in dichloromethane according to the method of Mata et al. under slightly different conditions (Scheme 3).[33] To avoid the previously observed formation of dimetallated species, especially at this linker length, all complex syntheses were carried out as one-pot reactions with 2 equiv. of silver(I) oxide. Whereas the iridium complexes were prepared by stirring the reaction mixtures overnight at ambient temperature, the reactions with rhodium were conducted at reflux temperature for 2 h and then with stirring at ambient temperature for 3 h. All complexes were purified by gradient column chromatography on silica gel, with dichloromethane/acetone as eluent and

KPF_6 for anion exchange, to give the rhodium(I) (**6a**,**b**) and iridium(I) (**7a**,**b**) complexes in 58–68% yield.[33,34] An additional aspect of complexation was the formation of two diastereomers, which were not separable by column chromatography. The reaction between $[IrCl(cod)]_2$, Ag_2O and **5a** or **5b** gave the *exo* isomer as the major product, where the backbone isopropyl group lies out of the coordination plane, as depicted in Figure 2 (vide infra). After column chromatography, complex **7a** was obtained with an *exo*/*endo* ratio of 96:4, whereas **7b** was obtained as a 92:8 mixture under the conditions described above. To investigate the stability of the complexes and the stereoisomers, complex **7a** was dissolved in $[D_6]$dmso and heated in an NMR tube at 85 °C. No decomposition of the complex was observed after 3 d at this temperature, but the *exo*/*endo* ratio decreased from 96:4 to 85:15. The reaction between **5a** and $[IrCl(cod)]_2$ was also carried out in refluxing dichloromethane and gave **7a** as a 65:35 *exo*/*endo* mixture.



5a: R = *i*Pr
5b: R = *n*Pr
5c: R = 2,6-difluorobenzyl

6a: M = Rh, R = *i*Pr
6b: M = Rh, R = 2,6-difluorobenzyl
7a: M = Ir, R = *i*Pr
7b: M = Ir, R = *n*Pr

Scheme 3. Synthesis of complexes **6a**,**b** and **7a**,**b**. DCM = dichloromethane.

The opposite diastereoselectivity was observed for the reaction between $[RhCl(cod)]_2$, Ag_2O and bis(imidazolium) salts **5a** and **5c**, with the *endo* stereoisomers of **6a** and **6b** being the major products (*exo*/*endo* ratios of 15:85 and 20:80). As shown in Figure 1 (vide infra), the isopropyl group in the *endo* isomer is oriented in the coordination plane. Complex **6a** was heated in an NMR tube at 85 °C in $[D_6]$dmso for 2 d like the iridium compound **7a** and showed complete decomposition. Only slow decomposition and no alteration of the *exo*/*endo* ratio was observed at 50 °C.

In summary, the small *exo*/*endo* preference is primarily related to the metal, although the factors determining this ratio are not obvious. At higher temperatures, the iridium complex **7a** generally tends to give lower *exo* values, which is indicative of a kinetically controlled formation of the *exo* complex under the reaction conditions described. A rapid isomerisation to the products of thermodynamic equilibrium is prevented by the kinetic stability of the resulting complexes even in hot, coordinating solvents like dimethyl sulfoxide. Another possible reason for the *exo* preference of iridium could be weak agostic interactions between the backbone C–H and the metal centre, although the data we have do not corroborate this hypothesis.

Diastereomerically pure material was obtained by crystallisation for both iridium complexes (*exo*) and the rhodium complex **6a** (*endo*). Attempts to crystallise **6b** always gave a yellow oily precipitate and crystals. Whereas the crystals were a 1:1 mixture of *endo*/*exo* stereoisomers, the oil contained only the *endo* form.

The described complexes were tested in catalysis and showed no activity in the hydrogenation of ithaconic acid and low activity, with poor enantioselectivity, in the hydrosilylation of prochiral ketones. Promising preliminary results with *ee* values of up to 60% have been obtained in transfer hydrogenations of phenyl ketones by using 2-propanol as hydrogen source. These results indicate that the activity and enantioselectivity of the tested complexes depend on the ligand architecture, the metal and the ketones, but presumably not on the *exo*/*endo* ratio.

All complexes were characterised by NMR spectroscopy, high-resolution mass spectrometry, elemental analysis and some by single-crystal X-ray diffractometry. Due to the lack of symmetry, ^{13}C NMR spectra of the iridium and rhodium complexes show a signal for each carbon atom. Thus, the spectra for the rhodium compounds display two characteristic doublets at $\delta \approx 179$ ppm, with typical Rh–C coupling constants of 52 Hz, for the metallated carbene carbon atoms, and four doublets for the vinylic carbon atoms of the cod ring with coupling constants ranging from 7.7 to 8.2 Hz.[33,35] The diastereotopic methyl groups appear as two signals between $\delta = 18$ and 20 ppm. The spectra of the iridium complexes are very similar to the rhodium ones, except for the absence of metal–carbon coupling and a high-field shift by ca. 15 ppm for the vinylic cod signals.[34] The existence of two stereoisomers is indicated by a double set of signals with intensities that correspond to the *exo*/*endo* ratios. The ^1H NMR shifts of the backbone protons are characteristic for the *exo* and *endo* isomers. Thus, the signal for the single proton at the chiral carbon atom appears as a triplet of doublets at $\delta = 6.5$ ppm for the *exo* isomer, whereas the diastereotopic protons of the adjacent methylene group give rise to a signal located in the range $\delta = 4.1$–4.5 ppm, beneath the signals of the vinylic cod protons. The chemical shifts of the three relevant backbone protons are inverted for the *endo* isomer. Thus, the signal for the methylene proton oriented towards the metal atom appears as a doublet of doublets at $\delta = 6.0$ ppm, whereas the signals for the second methylene proton and for the proton at the chiral carbon atom are in the range $\delta = 4.1$–4.7 ppm.

Crystal Structures of 6a and 7a

Crystals of **6a** and **7a** suitable for X-ray diffraction were obtained by layering a concentrated thf (**6a**) or thf/CH_2Cl_2 (**7a**) solution with cyclohexane. The molecular structures shows that the geometry about the rhodium and iridium atom is distorted square-planar, with C–M–C bite angles of 80.6° for the rhodium complex and 79.8° for the iridium complex. The $M–C_{carbene}$ bond lengths are between 2.015 and 2.068 Å, as expected for (NHC)rhodium(I) and -iridium(I) compounds.[33,34,36,37] The seven-membered rings formed by the ligands and the metal atoms adopt boat-like

conformations, as known for cycloheptane, with the backbone isopropyl group in either the *endo* (Figure 1) or *exo* position (Figure 2).

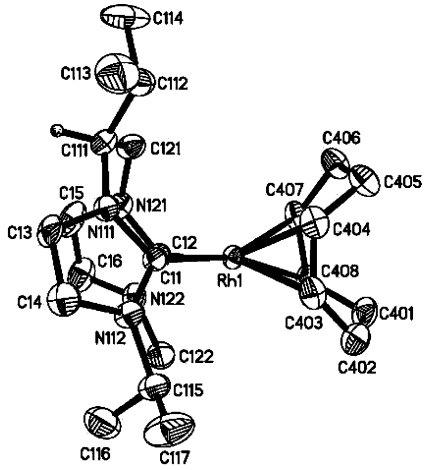


Figure 1. ORTEP diagram of **6a** (thermal ellipsoids at the 50% probability level). Hydrogen atoms [except H at C(111)] and the counterion (PF_6^-) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh(1)–C(11) 2.035(3), Rh(1)–C(12) 2.026(8), Rh(1)–C(403) 2.204(5), Rh(1)–C(404) 2.218(4), Rh(1)–C(407) 2.173(3), Rh(1)–C(408) 2.202(6), Rh(1)–C(121) 3.174(14), Rh(1)–C(111) 3.561(16), Rh(1)–C(122) 3.620(6), Rh(1)–C(115) 3.448(7); C(11)–Rh(1)–C(12) 80.62(12), C(407)–Rh(1)–C(404) 81.17(11), C(408)–Rh(1)–C(403) 81.20(11).

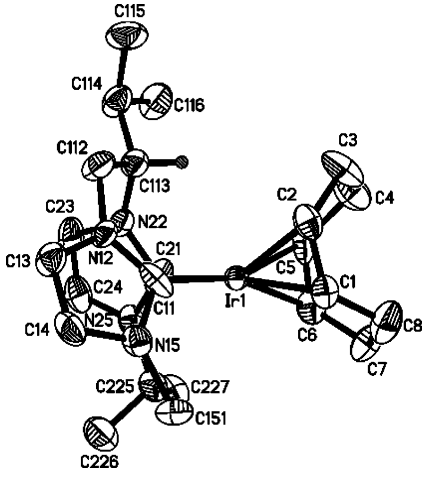


Figure 2. ORTEP diagram of **7a** (thermal ellipsoids at the 50% probability level). Hydrogen atoms [except H at C(113)] and the counterion (PF_6^-) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–C(11) 2.068(4), Ir(1)–C(21) 2.015(6), Ir(1)–C(1) 2.204(3), Ir(1)–C(2) 2.147(4), Ir(1)–C(5) 2.186(5), Ir(1)–C(6) 2.197(4), Ir(1)–C(112) 3.552(14), Ir(1)–C(113) 3.112(13), Ir(1)–C(151) 3.442(7), Ir(1)–C(225) 3.628(8); C(11)–Ir(1)–C(21) 79.76(10), C(5)–Ir(1)–C(2) 80.95 (10), C(6)–Ir(1)–C(1) 81.19 (11).

A comparison of the distances between the metal atom and the backbone carbon atoms of both stereoisomers shows that these carbon atoms change their positions relative to the metal atom. For the *endo* isomer **6a** the distance between the bridging methylene carbon atom and the metal atom is 3.17 Å, and that between the asymmetric carbon atom and the metal atom is 3.56 Å; for the *exo* isomer **7a** the M–C distances are 3.11 Å for the asymmetric carbon atom and 3.55 Å for the methylene carbon atom. The distances between the metal atom and the methyl/isopropyl carbon atoms at the imidazole nitrogen atoms are also affected by the stereoisomers of the chelate ring. Thus, whereas the isopropyl carbon atom is ca. 0.2 Å closer to the Rh centre than the methyl carbon atom in the structure of **6a**, the positions in the structure of **7a** are inverted.

Conclusions

We have demonstrated that chiral bis(NHC) ligand precursors are accessible from chiral amino alcohols by a five-step synthesis. This synthetic pathway makes it possible to use a large number of enantiomerically pure amino acids as the starting point for further preparations of chiral, chelating NHC complexes. The modular build-up of the ligand offers several opportunities for its modification, including the introduction of different substituents at the terminal nitrogen atoms of the imidazole rings or, possibly, the introduction of other coordinating groups instead of the second imidazole. Furthermore, we have shown that a one-pot transmetallation procedure is also applicable to this kind of ligand, with formation of two stable diastereomers. Diastereomerically pure complexes were obtained by crystallisation. Preliminary results for the transfer hydrogenation of prochiral ketones indicate a potential application for the described complexes. Our future investigations will focus on diastereoselective complex synthesis and the catalytic activity and stereoselectivity of the prepared iridium and rhodium complexes and their dependence on variations in the substitution pattern of the ligand.

Experimental Section

General Remarks: NMR spectra were recorded with a Bruker DRX-400 spectrometer, with $CDCl_3$, CD_3OD or D_2O as solvent. Elemental analyses were performed with a VARIO EL analyzer. Electron impact (EI+) and fast atom bombardment (FAB^+) mass spectra were recorded with a Finnigan MAT, TSQ 70 instrument by using 3-nitrobenzyl alcohol as matrix. Electrospray mass spectra were recorded with a Bruker Daltonics APEX II FT-ICR instrument by using CH_3OH as solvent and nitrogen as drying and nebulizing gas. Imidazole **1** was prepared from L-valinol (97% *ee*, Sigma-Aldrich) according to a literature procedure.[29] All other reagents were commercially available and were used as received.

(2*S*)-2-(1-Imidazolyl)-3-methylbutyl 4-Methylbenzenesulfonate (2): A pyridine (20 mL) solution of **1** (3.6 g, 23.4 mmol) was cooled to –10 °C in an ice/NaCl bath. *p*-Tosyl chloride (4.9 g, 25.7 mmol) was added in one portion, then the solution was stirred at –10 °C for 1 h and at 0 °C for a further 4 h. Water (50 mL) was then added dropwise, and the resulting mixture was extracted with CH_2Cl_2 (3×100 mL). The combined organic extracts were dried with Na_2SO_4, and all volatiles were removed under reduced pressure to give **2** as a pale-yellow oil. Yield: 5.8 g (81%). MS (EI): *m*/*z* (%) =

308 (70). MS (HREI$^+$): calcd. for $C_{15}H_{20}N_2O_3S$ 308.1194; found 308.1183. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.65 (m, 2 H, SCC*H*CH), 7.49 (s, 1 H, NC*H*N), 7.31 (m, 2 H, SCCHC*H*CCH$_3$), 7.02 (s, 1 H, NCHC*H*N), 6.86 (s, 1 H, NC*H*CHN), 4.29 (d, $^3J_{H,H}$ = 5.2 Hz, 2 H, OCH_2CH), 3.92 [m, 1 H, CH$_2$ C*H*CH(CH$_3$)$_2$], 2.43 (s, 3 H, C$_6$H$_4$CH_3), 2.13 [m, 1 H, CHC*H*(CH$_3$)$_2$], 0.98 [d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH(CH_3)$_2$], 0.65 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 145.21 (*C*SO$_3$), 136.70 (N*C*HN), 132.06 (CH*C*CH$_3$), 129.93 (CH*C*HCCH$_3$), 129.24 (SC*C*HCH), 127.72 (NCH*C*HN), 117.22 (N*C*HCHN), 69.37 (O*C*H$_2$CH), 62.76 (CH$_2$*C*HCH), 26.81 [CH*C*H(CH$_3$)$_2$], 21.51 (C*C*H$_3$), 19.47, 18.92 [CH(*C*H$_3$)$_2$] ppm.

1-[(1*S*)-1-(Bromomethyl)-2-methylpropyl]imidazole (3): A mixture of **2** (5.8 g, 18.8 mmol) and lithium bromide (4.9 g, 56.4 mmol) was stirred in refluxing acetone (60 mL) for 5 h. After cooling to ambient temperature, the formed precipitate was removed by filtration, and the volatiles were removed under reduced pressure. Water (100 mL) was added to the residue to remove excess LiBr, and the mixture was extracted with $CHCl_3$ (3 × 80 mL). The organic extracts were combined, washed with brine and dried with Na_2SO_4. After filtration, all volatiles were removed under reduced pressure. The crude product was then purified by gradient column chromatography [SiO_2; first CH_2Cl_2/acetone (1:1), then acetone] to give **3** as a colourless oil. Yield: 3.5 g (85%). MS (EI): *m*/*z* (%) = 216 (60). MS (HREI$^+$): calcd. for $C_8H_{13}BrN_2$ 216.0262; found 216.0254. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.46 (s, 1 H, NC*H*N), 7.03 (s, 1 H, NCHC*H*N), 6.91 (s, 1 H, NC*H*CHN), 3.86 (m, 1 H, CH$_2$C*H*N), 3.69 (m, 2 H, CHCH_2Br), 2.11 [m, 1 H, CHC*H*(CH$_3$)$_2$], 0.96 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CHCH(CH_3)$_2$], 0.72 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CHCH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 136.75 (N*C*HN), 129.11 (CH$_{imid}$), 116.82 (CH$_{imid}$), 64.79 (CH$_2$*C*HN), 34.15 (CH*C*H$_2$Br), 32.04 [CH*C*H (CH$_3$)$_2$], 19.43, 18.62 [CH(*C*H$_3$)$_2$] ppm.

1-[(2*S*)-2-(1-Imidazolyl)-3-methylbutyl]-3-methylimidazolium Bromide (4): A mixture of **3** (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, whilst stirring, to dissolve excess 1-methylimidazole. The diethyl ether fraction was then removed with a syringe and the colourless, 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 into 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 to give **4** as a hygroscopic, white solid. Yield: 556 mg (82%). MS (FA): *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, 1 H, NC*H*N), 7.77 (s, 1 H, NC*H*N), 7.54 (t, $^3J_{H,H}$ = 1.6 Hz, 1 H, CH$_{imid}$), 7.47 (br. s, 1 H, CH$_{imid}$), 7.42 (t, $^3J_{H,H}$ = 1.7 Hz, 1 H, CH$_{imid}$), 7.08 (br. s, 1 H, CH$_{imid}$), 4.98–4.81 (m, 2 H, NCH_2CH), 4.60 (qd, $^3J_{H,H}$ = 3.4 Hz, 1 H, CH$_2$C*H*N), 3.90 (s, 3 H, NCH_3), 2.35 [m, 1 H, CHC*H*(CH$_3$)$_2$], 1.20 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CHCH(CH_3)$_2$], 0.86 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CHCH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (CD_3OD, 100 MHz): δ = 139.06, 138.40 (N*C*N), 129.89, 124.99, 123.88, 119.21 (CH$_{imid}$), 65.41 (CH$_2$*C*HN), 52.93 (N*C*H$_2$CH), 36.83 (N*C*H$_3$), 32.79 [CH*C*H(CH$_3$)$_2$], 20.03, 19.43 [CH(*C*H$_3$)$_2$] ppm.

3-Isopropyl-1-{(1*S*)-2-methyl-1-[(3-methylimidazolium)methyl]propyl}imidazolium Dibromide (5a): An acetonitrile solution (5 mL) of **4** (170 mg, 0.57 mmol) and 2-bromopropane (1 mL), was stirred under argon at reflux temperature for 48 h. After removal of all volatiles under reduced pressure, the remaining solid was dissolved in dichloromethane and extracted into water (2 × 5 mL). The water was removed under reduced pressure, and the resulting white solid was washed with diethyl ether (2 × 10 mL) and dried in vacuo to give **5a** as a very hygroscopic, white solid. Yield: 190 mg (79%). MS (FA): *m*/*z* (%) = 341 (30). ^{1}H NMR (CD_3OD, 400 MHz): δ = 9.41 (s, 1 H, NC*H*N), 9.09 (s, 1 H, NC*H*N), 7.90 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, CH$_{imid}$), 7.82 (br. s, 1 H, CH$_{imid}$), 7.49 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, CH$_{imid}$), 7.44 (br. s, 1 H, CH$_{imid}$), 4.95 (t, $^3J_{H,H}$ = 4.8 Hz, 2 H, NCH_2CH), 4.87 (m, 1 H, CH$_2$C*H*N), 4.65 [m, 1 H, N*C*H(CH$_3$)$_2$], 3.85 (s, 1 H, NCH_3), 2.36 [m, 1 H, CHC*H*(CH$_3$)$_2$], 1.48 [d, $^3J_{H,H}$ = 6.7 Hz, 6 H, CHCH(CH_3)$_2$], 1.13 [d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CHCH(CH_3)$_2$], 0.82 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CHCH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (CD_3OD, 100 MHz): δ = 138.85, 136.40 (N*C*N), 125.54, 123.75, 123.38, 122.78 (CH$_{imid}$), 68.21 (CH$_2$*C*HN), 55.23 [N*C*H(CH$_3$)$_2$], 51.88 (N*C*H$_2$CH), 37.19 (N*C*H$_3$), 32.31 [CH*C*H(CH$_3$)$_2$], 23.22, 23.13 [NCH(*C*H$_3$)$_2$], 19.69, 19.15 [CH(*C*H$_3$)$_2$] ppm.

1-{(1*S*)-2-Methyl-1-[(3-methyl-1-imidazolium)methyl]propyl}-3-propylimidazolium Dibromide (5b): An acetonitrile solution (3 mL) of **4** (165 mg, 0.55 mmol) and 1-bromopropane (1 mL) was stirred at reflux temperature under argon for 20 h. The volatiles were then removed under reduced pressure, and the resulting solid was dissolved in dichloromethane and added dropwise to diethyl ether, with stirring, to give a white, fluffy precipitate. This precipitate was washed with diethyl ether (2 × 10 mL) and dried in vacuo to give **5b** as a hygroscopic, white powder. Yield: 200 mg (86%). MS (FA): *m*/*z* (%) = 341 (40). ^{1}H NMR (CD_3OD, 400 MHz): δ = 9.32 (s, 1 H, NC*H*N), 9.08 (s, 1 H, NC*H*N), 7.91 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, CH$_{imid}$), 7.75 (d, $^3J_{H,H}$ = 1.7 Hz 1 H, CH$_{imid}$), 7.52 (d, $^3J_{H,H}$ = 1.7 Hz, 1 H, CH$_{imid}$), 7.50 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, CH$_{imid}$), 5.00–4.85 (m, 3 H, CH$_2$C*H*N, NCH_2CH), 4.18 (t, $^3J_{H,H}$ = 7.1 Hz, 2 H, NCH_2CH$_2$), 3.88 (s, 3 H, NCH_3), 2.38 [m, 1 H, CHC*H*(CH$_3$)$_2$], 1.87 (sext, $^3J_{H,H}$ = 3.6 Hz, 2 H, NCH$_2$CH_2), 1.17 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CHCH(CH_3)$_2$], 1.06 [m, 6 H, CH$_2$CH_3, CHCH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (CD_3OD, 100 MHz): δ = 138.91, 137.82 (N*C*N), 125.76, 125.29, 123.91, 122.70 (CH$_{imid}$), 68.27 (CH$_2$*C*HN), 52.96 (N*C*H$_2$CH), 51.96 (N*C*H$_2$CH$_2$), 37.19 (N*C*H$_3$), 32.53 [CH*C*H(CH$_3$)$_2$], 24.45 (NCH$_2$*C*H$_2$), 19.75, 19.11 [CH(*C*H$_3$)$_2$], 11.00 (CH$_2$*C*H$_3$) ppm.

3-(2,6-Difluorobenzyl)-1-{(1*S*)-2-methyl-1-[(3-methylimidazolium)-methyl]propyl}imidazolium Dibromide (5c): 2,6-Difluorobenzyl bromide (207 mg, 1.0 mmol) was added to a solution of **4** (146 mg, 0.49 mmol) in acetonitrile in one portion, and the mixture was heated at reflux temperature for 17 h. The same procedure used to give **5b** was applied to give **5c** as a white, hygroscopic solid. Yield: 192 mg (78%). MS (FA$^+$): *m*/*z* (%) = 425 (25). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.04, 9.66 (s, 2 H, NC*H*N), 8.37, 8.07 (s, 1 H, CH_{imid}), 7.43 (m, 1 H, CH_{phenyl}), 7.27, 7.18 (s, 1 H, CH_{imid}), 6.97 (m, 2 H, CH_{phenyl}), 5.51 [q, $^4J_{H,F}$ = 13.6 Hz, 2 H, N*C*H$_2$C(CF)$_2$], 5.85 (m, 1 H, NCH$_2$C*H*N), 4.85–4.56 (m, 2 H, NCHCH_2N), 3.88 (s, 3 H, NCH_3), 2.41 [m, 1 H, CHC*H*(CH$_3$)$_2$], 1.11 [d, $^3J_{H,H}$ = 6.5 Hz, 3 H, CHCH(CH_3)$_2$], 0.84 [d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CHCH(CH_3)$_2$] ppm. ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz): δ = –115.69, –115.52 ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 162.33 (d, $^1J_{C,F}$ = 5.9 Hz, *C*F), 152.82 (d, $^1J_{C,F}$ = 6.3 Hz, *C*F), 137.35, 137.04 (N*C*HN), 132.67 (t, $^2J_{C,F}$ = 10.9 Hz, *C*H$_{phenyl}$), 123.82, 122.32, 121.93, 120.55 (*C*H$_{imid}$), 112.22 (m, 2 C, *C*H$_{phenyl}$), 109.46 (t, $^2J_{C,F}$ = 18.8 Hz, *C*$_{q\ phenyl}$), 65.89 (CH$_2$*C*HN), 50.13 (N*C*H$_2$CH), 41.59 [NCH$_2$C(CF)$_2$] 36.74 (N*C*H$_3$), 31.44 [CH*C*H(CH$_3$)$_2$], 19.09, 18.26 [CH(*C*H$_3$)$_2$] ppm.

(η^4-1,5-Cyclooctadiene)(3-isopropyl-1-{(1*S*)-2-methyl-1-[(3-methylimidazol-2-ylidene)methyl]propyl}imidazol-2-ylidene)rhodium(I)

Hexafluorophosphate (6a): Silver(I) oxide (130 mg, 0.56 mmol) was added to a dichloromethane (12 mL) solution of **5a** (120 mg, 0.28 mmol), and the mixture was stirred under argon at ambient temperature for 2 h. $[Rh(cod)Cl]_2$ (69 mg, 0.14 mmol) was added to the resulting grey suspension in one portion to give a white precipitate. To complete the reaction, the mixture was stirred in the dark under argon at reflux temperature for 2 h and at room temperature for a further 3 h. The suspension was filtered through Celite to remove insoluble silver salts and the resulting yellow 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) and 2 equiv. KPF_6]. A second flash chromatography with CH_2Cl_2/acetone (4:1) as eluent gave the title compound as an analytically pure, yellow powder. Crystals were obtained by layering a thf solution of **6a** with cyclohexane. Yield: 118 mg (68%). M.p. 115 °C (dec. at 165 °C). MS (HRESI$^+$): calcd. for $C_{23}H_{36}N_4Rh$ 471.19895; found 471.19907. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.10 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, CH_{imid}), 6.79 (d, $^3J_{H,H}$ = 1.9 Hz, 1 H, CH_{imid}), 6.76 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, CH_{imid}), 6.65 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, CH_{imid}), 5.94 (dd, $J_{H,H}$ = 11.4, 14.1 Hz, 1 H, NCH_2CH), 5.27 [m, 1 H, NCH(CH$_3$)$_2$], 4.66–4.34 (m, 5 H, NCH_2CH, CH_{cod}), 4.11 [m, 1 H, NCHCH(CH$_3$)$_2$], 3.61 (s, 3 H, NCH$_3$), 2.51–2.04 [m, 9 H, CHCH(CH$_3$)$_2$, C$H_{2\,cod}$], 1.39 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, NCH(CH_3)$_2$], 1.25 [d, $^3J_{H,H}$ = 6.6 Hz, 3 H, NCH(CH_3)$_2$], 1.12 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CHCH(CH_3)$_2$], 0.88 [d, $^3J_{H,H}$ = 6.7 Hz 3 H, CHCH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 180.54 (d, $^1J_{C,Rh}$ = 52.3 Hz, Rh*C*), 176.86 (d, $^1J_{C,Rh}$ = 51.5 Hz, Rh*C*), 126.33, 122.37, 122.00, 115.72 (*C*H$_{imid}$), 91.06 (d, $^1J_{C,Rh}$ = 7.9 Hz, CH$_{cod}$), 88.51 (d, $^1J_{C,Rh}$ = 7.7 Hz, CH$_{cod}$), 88.0 (d, $^1J_{C,Rh}$ = 8.2 Hz, CH$_{cod}$), 86.54 (d, $^1J_{C,Rh}$ = 7.8 Hz, CH$_{cod}$), 65.04 (CH$_2$*C*HN), 54.16 [N*C*H(CH$_3$)$_2$], 50.21 (N*C*H$_2$CHN), 36.74 (N*C*H$_3$), 35.28 [CH*C*H(CH$_3$)$_2$], 31.37, 31.25, 29.66, 29.22 (CH$_{2\,cod}$), 24.14, 23.43 [NCH(*C*H$_3$)$_2$], 19.78, 18.57 [CHCH(*C*H$_3$)$_2$] ppm. $C_{25}H_{40}F_6N_4PRh$ (616.43): calcd. C 44.81, H 5.89, N 9.09; found C 44.52, H 5.61, N 8.93.

(η^4-1,5-Cyclooctadiene)[3-(2,6-difluorobenzyl)-1-{(1*S*)-2-methyl-1-[(3-methylimidazol-2-ylidene)methyl]propyl}imidazol-2-ylidene)-rhodium(I) Hexafluorophosphate (6b): The same procedure was used as for **6a**. The reaction between **5c** (230 mg, 0.45 mmol), silver(I) oxide (209 mg, 0.90 mmol) and $[Rh(cod)Cl]_2$ (118 mg, 0.24 mmol) in dichloromethane (15 mL) gave the title compound **6b** as a yellow powder. Crystalline material was obtained by layering a thf/CH_2Cl_2 (7:1) solution of **6b** with cyclohexane. Yield: 184 mg (58%). M.p. 127 °C (dec. at 195 °C). MS (HRESI$^+$): calcd. for $C_{27}H_{34}F_2N_4Rh$ 555.18011; found 555.17968. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.34 (m, 1 H, CFCHC*H*), 7.15 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, CH_{imid}), 6.92 (m, 2 H, CFC*H*), 6.78 (d, $^3J_{H,H}$ = 1.9 Hz, 1 H, CH_{imid}), 6.65 (d, $^3J_{H,H}$ = 1.7 Hz, 1 H, CH_{imid}), 6.50 (d, $^3J_{H,H}$ = 1.7 Hz, 1 H, CH_{imid}), 6.03 (dd, $J_{H,H}$ = 11.6, 14.1 Hz, 1 H, CH_2CHN), 5.85, 5.35 [d, $^4J_{H,F}$ = 14.0 Hz, 2 H, CH_2C(CF)$_2$], 4.73–4.20 (m, 6 H, NCHCH_2N, CH$_{cod}$), 3.62 (s, 3 H, NCH_3), 2.58–1.95 [m, 9 H, CHCH(CH$_3$)$_2$, CH$_{2\,cod}$], 1.13 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH(CH_3)$_2$], 0.93 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 179.77 (d, $^1J_{C,Rh}$ = 52.1 Hz, Rh*C*), 179.12 (d, $^1J_{C,Rh}$ = 52.1 Hz, Rh*C*), 162.65 (d, $^1J_{C,F}$ = 7.0 Hz, CH*C*F), 160.16 (d, $^1J_{C,F}$ = 7.1 Hz, CH*C*F),131.64 (t, $^3J_{C,F}$ = 10.5 Hz, CFCH*C*H), 125.08, 122.18, 122.09, 118.82 (*C*H$_{imid}$), 112.08 (t, $^2J_{C,F}$ = 12.3 Hz, CF*C*H), 111.08 (t, $^2J_{C,F}$ = 18.4 Hz, CF*C*), 91.51 (d, $^1J_{C,Rh}$ = 8.1 Hz, CH$_{cod}$), 88.62 (d, $^1J_{C,Rh}$ = 8.2 Hz, CH$_{cod}$), 88.02 (d, $^1J_{C,Rh}$ = 7.7 Hz, CH$_{cod}$), 87.33 (d, $^1J_{C,Rh}$ = 7.9 Hz, CH$_{cod}$), 65.33 (CH$_2$*C*HN), 49.88 (N*C*H$_2$CH), 44.09 (N*C*H$_2$C), 35.17 (N*C*H$_3$), 31.72, 31.61, 29.39, 29.09 (CH$_{2\,cod}$), 19.67, 18.42 [CH(*C*H$_3$)$_2$] ppm. $C_{27}H_{34}F_8N_4PRh$ (705.74): calcd. C 46.30, H 4.89, N 8.00; found C 46.00, H 5.13, N 7.70.

(η^4-1,5-Cyclooctadiene)(3-isopropyl-1-{(1*S*)-2-methyl-1-[(3-methylimidazol-2-ylidene)methyl]propyl}imidazol-2-ylidene)iridium(I) Hexafluorophosphate (7a): Silver(I) oxide (162 mg, 0.70 mmol) was added to a dichloromethane (15 mL) solution of **5a** (140 mg, 0.33 mmol), and the mixture was stirred in the dark at room temperature under argon for 2.5 h. $[Ir(cod)Cl]_2$ (101 mg, 0.15 mmol) was then added to the grey suspension in one portion to give a white precipitate. To complete the reaction, the mixture was stirred in the dark at room temperature for 14 h. The suspension was filtered through Celite to remove insoluble silver salts, 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) and 2 equiv. KPF_6]. Analytically pure material was obtained by a second flash column chromatography with CH_2Cl_2/acetone (7:1) as eluent to give the title compound as an orange-red solid. Crystalline material was obtained by layering a thf/CH_2Cl_2 (1:1) solution of **7a** with cyclohexane. Yield: 143 mg (62%). M.p. 151 °C (dec. at 205 °C). 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, $^3J_{H,H}$ = 2.1 Hz, 1 H, CH_{imid}), 6.89 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, CH_{imid}), 6.81 (m, 2 H, CH_{imid}), 6.41 (td, $^3J_{H,H}$ = 4.6, 10.9 Hz, 1 H, CH$_2$C*H*N), 4.54 [vsept, $^3J_{H,H}$ = 6.8 Hz, 1 H, NCH(CH$_3$)$_2$], 4.26 (m, 3 H, CH$_{cod}$, NCH_2), 4.09–3.92 (m, 3 H, CH$_{cod}$, NCH_2), 3.84 (s, 3 H, NCH$_3$), 2.39–2.20 [m, 3 H, CH$_{2\,cod}$, CHCH(CH$_3$)$_2$], 2.09 (m, 3 H, CH$_{2\,cod}$), 1.87 (m, 3 H, CH$_{2\,cod}$), 1.35 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, NCH(CH_3)$_2$], 1.17 [d, $^3J_{H,H}$ = 6.5 Hz, 3 H, NCH(CH_3)$_2$], 1.10 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CHCH(CH_3)$_2$], 0.98 [d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CHCH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 175.47, 173.61 (Ir*C*), 124.72, 121.67, 118.17, 117.49 (*C*H$_{imid}$), 77.82, 74.63, 74.34, 73.34 (CH$_{cod}$), 64.29 (CH$_2$*C*HN), 52.59 [N*C*H(CH$_3$)$_2$], 52.08 (N*C*H$_2$CH), 39.12 (N*C*H$_3$), 32.12 [CH*C*H(CH$_3$)$_2$], 32.09, 30.67, 30.39, 29.34 (CH$_{2\,cod}$), 23.58, 23.32 [NCH(*C*H$_3$)$_2$], 20.87, 19.82 [CH(*C*H$_3$)$_2$] ppm. $C_{23}H_{36}F_6IrN_4P$ (705.74): calcd. C 39.14, H 5.14, N 7.94; found C 38.82, H 5.03, N 8.06.

(η^4-1,5-Cyclooctadiene)(1-{(1*S*)-2-methyl-1-[(3-methylimidazol-2-ylidene)methyl]propyl}-3-propylimidazol-2-ylidene)iridium(I) Hexafluorophosphate (7b): The same procedure was used as for **7a**. Reaction between **5b** (145 mg, 0.34 mmol), silver(I) oxide (162 mg, 0.70 mmol) and $[Ir(cod)Cl]_2$ (108 mg, 0.16 mmol) in dichloromethane (15 mL) gave **7b** as an orange-red solid. Crystalline material was obtained by layering a thf/CH_2Cl_2 (3:1) solution of **7b** with cyclohexane. Yield: 152 mg (63%). M.p. 159 °C (dec. at 209 °C). 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, $^3J_{H,H}$ = 2.0 Hz, 1 H, CH_{imid}), 6.90 (d, $^3J_{H,H}$ = 1.9 Hz, 1 H, CH_{imid}), 6.81 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, CH_{imid}), 6.78 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, CH_{imid}), 6.49 (td, $J_{H,H}$ = 4.3, 12.5 Hz, 1 H, CH$_2$C*H*N), 4.38 (td, $J_{H,H}$ = 2.8, 7.2 Hz 1 H, CHCH_2N), 4.31–4.25 (m, 2 H, CH$_{cod}$), 4.08 (m, 1 H, CHCH_2N), 3.99–3.87 (m, 2 H, CH$_{cod}$), 3.83 (s, 3 H, NCH$_3$), 3.79 (td, $J_{H,H}$ = 3.4, 7.2 Hz, 2 H, NCH_2CH$_2$), 2.42–1.78 [m, 9 H, CH$_{2\,cod}$, CHCH(CH$_3$)$_2$], 1.67 (sext, $^3J_{H,H}$ = 7.3 Hz, 2 H, NCH$_2$CH_2), 1.16 [d, $^3J_{H,H}$ = 6.5 Hz, 1 H, CH(CH_3)$_2$], 0.97 [d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH(CH_3)$_2$], 0.69 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, 3 H, CH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 176.06, 173.35 (Ir*C*), 124.59, 121.87, 121.65, 117.53 (*C*H$_{imid}$), 77.86, 74.30, 74.23, 72.56 (CH$_{cod}$), 64.34 (CH$_2$*C*HN), 52.54 (N*C*H$_2$CH$_2$), 51.42 (N*C*H$_2$CH), 39.31 (N*C*H$_3$), 32.67 [CH*C*H(CH$_3$)$_2$], 32.64, 30.18, 29.89, 29.32 (CH$_{2\,cod}$), 24.46 (NCH$_2$*C*H$_2$), 20.82, 19.88 [CH-

Table 1. Crystallographic data.

	6a	**7a**
Empirical formula	$C_{23}H_{36}F_6N_4PRh{\cdot}C_4H_8O$	$C_{23}H_{36}F_6IrN_4P$
Formula mass	688.54	705.73
T [K]	173	173
λ [Å]	0.71073	0.71073
Crystal system	triclinic	orthorhombic
Space group	$P1$	$P2_12_12_1$
a [Å]	9.7115(8)	10.2580(6)
b [Å]	11.8538(10)	13.2530(8)
c [Å]	14.8137(12)	19.2342(14)
α [°]	94.839(7)	90
β [°]	92.479(7)	90
γ [°]	112.774(6)	90
V [Å^3]	1561.4(2)	2614.9(3)
Z	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.465	1.793
μ [mm^{-1}]	0.661	5.229
F(000)	712	1392
θ range for data collection	3.44–29.30	3.07–26.80
Index ranges	$-13 \le h \le 13$	$-12 \le h \le 12$
	$-16 \le k \le 16$	$-16 \le k \le 16$
	$-20 \le l \le 20$	$-24 \le l \le 24$
Reflections collected	27159	36294
Independent reflections	15322	5549
	[R(int) = 0.0509]	[R(int) = 0.0947]
Refinement method	full matrix least-squares on F^2	
Data/restraints/parameters	15322/3/721	5549/0/311
Goodness of fit on F^2	1.101	1.071
Absolute structure factor	–0.02(2)	–0.018(13)
Final R indices [$I \ge 2\sigma(I)$]	R_1 = 0.0466, wR_2 = 0.1076	R_1 = 0.0402, wR_2 = 0.0818
R indices (all data)	R_1 = 0.0545, wR_2 = 0.1127	R_1 = 0.0461, wR_2 = 0.0840
Largest difference peak/hole [e Å^{-3}]	+0.982/–0.830	+1.810/–1.618

(CH_3)$_2$], 10.58 (CH_2CH_3) ppm. $C_{23}H_{36}F_6IrN_4P$ (705.74): calcd. C 39.14, H 5.14, N 7.94; found C 39.17, H 5.19, N 8.02.

X-ray Diffraction Studies: Data were collected with a Stoe IPDS 2T diffractometer (Mo-K_α radiation) and processed by using Stoe's X-AREA[38] and the WinGX[39] suite of programs. The structures were solved by direct methods and expanded with Fourier techniques using SHELXS and SHELXL.[40,41] Numerical absorption correction based on crystal-shape optimisation was applied with X-Red and X-Shape.[42,43] Graphical illustrations and calculations were performed with the SHELXTL 5.1 package. Further details can be found in Table 1. CCDC-696022 (**6a**) and -696021 (**7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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