

Four-coordinate Complexes of Bis(1-diphenylphosphinoindenyl)iron(II)

Julian J. Adams, Owen J. Curnow* and Glen M. Fern

Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand

Received...

Dedicated to Professor D. Michael P. Mingos in recognition of his outstanding contributions to
inorganic chemistry

* Corresponding author. Fax: +64 3 364 2110; E-mail: owen.curnow@canterbury.ac.nz

Abstract

Palladium, platinum and rhodium complexes of *rac*- and *meso*-bis(1-diphenylphosphinoindenyl)iron(II) (**1**) are reported. Both *rac* and *meso* isomers of {bis(1-diphenylphosphinoindenyl)iron(II)}palladium dichloride (*rac*- and *meso*-**2**) were characterized by X-ray crystallography along with the *rac* isomer of the Pt analogue (*rac*-**3**). NMR analysis of the rhodium complex [{bis(1-diphenylphosphinoindenyl)iron(II)}(cyclooctadiene)rhodium(I)] tetraphenylborate suggests a similar structure in solution. Coupling reactions of *n*- and *sec*-BuCl with bromobenzene in THF are catalysed by *rac*-**2** and found to be similar to (PPh₃)₂PdCl₂ but poorer than (dppf)PdCl₂ in diethyl ether.

Keywords: Phosphine complex, Ferrocene, X-ray Structure, Indenyl, Group 10, Rhodium

1. Introduction

Ferrocenylphosphines continue to be intensively investigated for their utility in homogeneous catalysis; chiral derivatives are of particular interest for asymmetric catalysis [1]. The introduction of a chiral substituent to a ferrocene core or the use of heterotopic, planar chiral ligands is usually

used to create the chirality. Compounds containing two planar chiral units may exhibit *rac* and *meso* isomers. We have reported the preparation of the diindenyl analogue of 1,1'-bis(diphenylphosphino)ferrocene (dppf), [(1-PPh₂-η⁵-C₉H₆)₂Fe] (**1**), and the characterization of its *rac* and *meso* isomers by X-ray crystallographic studies of their tetracarbonylmolybdenum complexes in which the *meso* isomer exhibited significant structural distortions resulting from steric interactions [2]. Further studies on **1** have shown that this indenyl ferrocene undergoes a facile isomerization in THF from the *meso* isomer to the *rac* isomer at ambient temperatures [3] and a number of studies all point to a mechanism involving THF coordination, indenyl ring-slippage, and indenide dechelation with phosphine coordination to give a zwitterionic intermediate (Scheme 1). To further understand the factors influencing this unprecedented ferrocene isomerization process, a number of derivatives were reported [4].

Ferrocenylphosphines are widely employed in the formation of polymetallic complexes. Of these, 1,1'-bis(diphenylphosphino)ferrocene (dppf) is the most studied. As a ligand, dppf is capable of coordination to a variety of transition metals, with examples of group 5 metalates [5], carbonyl complexes of groups 6, 7, and 8 [6], and halo complexes of the late transition metals being known [7,8]. The success of dppf as a ligand has been attributed to the different ways the diphosphine can coordinate to a metal centre, with unidentate, chelate, and bridging coordination modes possible [9]. The flexibility of the ferrocenyl core along with the ability of the phosphorus atoms to deviate from coplanarity with the cyclopentadienyl rings makes dppf highly adaptable to the individual requirements of the different metals.

Bimetallic complexes of dppf are known to catalyze a wide variety of organic transformations [10]. Palladium and nickel complexes of dppf are effective catalysts for the cross-coupling of organic moieties [11], while rhodium, ruthenium, and palladium complexes are efficient at the hydrogenation of olefins [12,13]. Platinum complexes of dppf have been employed as catalysts for the hydrosilylation of olefins [14]. Derivatives of dppf containing chiral functionalities have found use in asymmetric catalysis [15]. The related bis(1-(diphenylphosphino)tetrahydroindenyl)iron(II) has been reported along with the characterization of molybdenum, rhodium, and iridium complexes [16]. It is anticipated that palladium complexes of **1** would also be able to catalyze organic transformations, with the *C*₂ symmetric *rac* isomer providing interesting possibilities in the field of asymmetric catalysis. In this paper we report on some Pd and Pt complexes of **1**, as well as a Rh complex, and assess a Pd complex of *rac*-**1** as a catalyst for the cross coupling of alkyl Grignards reagents with aryl bromides.

2. Results and Discussion

2.1 Synthesis and characterization of the complexes

Treatment of bisnitrile complexes of palladium and platinum with the appropriate isomer of the diphosphine complex **1** were found to give the desired heterobimetallic complexes *rac*- and *meso*-bis(1-diphenylphosphinoindenyl)iron(II)-*cis*-dichloropalladium(II) (*rac*- and *meso*-**2**, respectively) and *rac*-bis(1-diphenylphosphinoindenyl)iron(II)-*cis*-dichloroplatinum(II) (*rac*-**3**) (Scheme 2). Syntheses of **2** starting from various ratios of *rac*- and *meso*-**1** were found to give the same ratio of *rac*- and *meso*-**2** compounds, as shown by ³¹P-NMR spectroscopy: *rac*-**2** exhibits a single resonance at 35.79 ppm in CDCl₃ whereas *meso*-**2** exhibits a single resonance at 33.94 ppm. As with the isomers of **1** [3], the *rac* isomer is observed downfield of the *meso* isomer.

The ¹H-NMR spectrum of *rac*-**2** consists of an aromatic multiplet centred at 6.93 ppm and singlets at 2.53 and 4.70 ppm for the indenyl protons H2 and H3, respectively. For *meso*-**2**, the indenyl protons H2 and H3 were found at 3.95 and 4.65 ppm, respectively. These chemical shifts are markedly different from those observed for the parent ferrocenes (Table 1), with the resonances for the indenyl protons H2 and H3 shifted upfield for *rac*-**2** and downfield for *meso*-**2** (relative to *rac*- and *meso*-**1**, respectively). These changes in chemical shifts, which are considerably greater than observed for the analogous dppf complex, are indicative of significant conformational changes that have occurred upon coordination of the phosphorus atoms to the palladium. As a result, the resonances for the indenyl proton H3 of both *rac*- and *meso*-**2** now occur at similar chemical shifts. These observations will be discussed further with respect to the X-ray structural studies. ¹³C-NMR spectral assignments were based on the spectra of *rac*- and *meso*-**1**.

The platinum analogue of *rac*-**2**, *rac*-**3**, was prepared similarly from *rac*-**1** and (PhCN)₂PtCl₂. The proton resonances for H2 and H3 appear in positions similar to those observed for *rac*-**2**, an indication that the conformation of the two complexes in solution is similar. The ¹³C{¹H}-NMR spectrum of *rac*-**3** is consistent with the formation of the diphosphine-platinum complex. In general, the carbon resonances are shifted upfield relative to *rac*-**1**. The ³¹P{¹H}-NMR spectrum of *rac*-**3** consists of a singlet at 12.65 ppm flanked by two satellites due to coupling with the ¹⁹⁵Pt nucleus. The magnitude of the coupling, ¹J_{PtP} = 3818 Hz, is indicative of the phosphine being *trans* to a chloro ligand and is similar to that observed for (dppf)PtCl₂ (3765 Hz) [18].

[(Cyclooctadiene)(*rac*-bis(1-diphenylphosphinoindenyl)iron(II))rhodium(I)]tetraphenylborate (*rac*-**4**) was synthesized by the reaction of *rac*-**1** with [Rh(COD)₂]BF₄ followed by the addition of NaBPh₄ (Scheme 3). Complex *rac*-**4** was isolated in good yield (84%) as a yellow powder.

Although the reaction was attempted with two equivalents of *rac-1*, only a single COD was displaced from the rhodium by the diphosphine. Chaloner et al. has reported that the addition of two equivalents of 1,1'-bis(diisopropylphosphino)ferrocene (disopff) to $[\text{Rh}(\text{NBD})_2]\text{BF}_4$ led to the exclusive formation of $[\text{Rh}(\text{NBD})(\text{disopff})]\text{BF}_4$ [19]. Subsequent treatment of $[\text{Rh}(\text{NBD})(\text{disopff})]\text{BF}_4$ with a ten-fold excess of dppf produced, exclusively, $[\text{Rh}(\text{NBD})(\text{dppf})]\text{BF}_4$. It was suggested that large distortions in the geometry about the rhodium, caused by the bulkiness of the diphosphine ligands, was responsible for the inability of the second diphosphine to displace the remaining NBD ligand [13,20]. It is anticipated that *rac-4* will suffer from similar steric demands, making substitution of the second COD ligand more difficult. Interestingly, the homoleptic species $[\text{M}(\text{dppf})_2]\text{BF}_4$ (M = Rh, Ir) has been prepared via a different route and it was found that the geometry around the iridium atom was severely distorted from square planar [21].

The NMR spectra of *rac-4* are consistent with the displacement of a single cyclooctadiene from the rhodium precursor. The ^1H -NMR spectrum consists of an aromatic multiplet centred at 7.31 ppm and two singlets 2.81 and 4.96 ppm for H2 and H3, respectively. The resonances for the CH_2 and CH protons of the cyclooctadiene occur at 2.56 and 4.37 ppm, respectively. The resonances for H2 and H3 are upfield of those for *rac-1*, similar to what was observed for *rac-2* and *rac-3*. This suggests that the indenyl ligands in *rac-4* are adopting a conformation similar to that of the palladium and platinum complexes, with H2 positioned over the benzo ring. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of *rac-4* consists of a doublet at 29.1 ppm, with a rhodium-phosphorus coupling constant of 150 Hz. The values for the chemical shift and coupling constant are similar to those previously seen for analogous rhodium-dppf complexes [22,23].

2.2 X-ray structural analyses

In order to investigate the structural effects of the benzo substituents, *rac-2*, *meso-2*, and *rac-3* were characterized by X-ray crystallography. Crystallographic and refinement data are given in Table 2 and selected distances and angles are given in Table 3.

Complexes *rac-2* and *rac-3* are isomorphous: they crystallize in the monoclinic space group $\text{P}2_1/\text{n}$, with one complete molecule being in the asymmetric unit. The ligand conformations are essentially the same. Fig. 1 shows the molecules with the atomic labeling schemes and Fig. 2 shows the views down the M-Fe axes. As expected, the indenyl ligands are coordinated to the iron atom via their five-membered rings in an η^5 -fashion. In order for both phosphine moieties to

coordinate to the metal, the indenyl ligands adopt a conformation in which the rotation angle (RA), 172.5° and 172.3°, respectively, is considerably greater than the π -offset conformation observed in *rac-1* (RA = 20.8°) [4]. This conformation places each indenyl proton H2 near the centre of the six-membered ring of the other indenyl ligand and accounts for the upfield shift of these protons in the ¹H-NMR spectrum: 2.53 and 2.42 ppm, respectively, for *rac-2* and **3**. The conformations of the phenyl rings in the two complexes (illustrated best in Fig. 2) are very similar. In each case, there is an indenyl ligand in which one phenyl group is approximately perpendicular to the C₅ ring plane (angle between the C11-P1-C30 plane and the C₅ plane = 87.2° and 85.7° for *rac-2* and *rac-3*, respectively) and the other is close to the C₅ plane and oriented towards the Fe atom (angle between the C11-P1-C40 plane and the C₅ plane = 14.0° and 12.9° for *rac-2* and *rac-3*, respectively). The other indenyl ligand has one phenyl close to the C₅ plane, but oriented away from the Fe atom (angle between the C21-P2-C50 plane and the C₅ plane = 17.6° and 19.2° for *rac-2* and *rac-3*, respectively) while the other phenyl group is at about 50° to the C₅ plane (angle between the C21-P2-C60 plane and the C₅ plane = 50.0° and 49.2° for *rac-2* and *rac-3*, respectively). The phenyl groups close to the C₅ plane are oriented away from their ligand's benzo ring and away from each other. This minimises the benzo-phenyl and phenyl-phenyl steric interactions.

The palladium and platinum atoms adopt a distorted square planar geometry similar to that observed previously for other diphosphine palladium and platinum complexes [17,23]. P2 is significantly displaced from the MCl₂ plane by ca 0.3 Å, whereas P1 is approximately in the MCl₂ plane.

The X-ray structural analysis of *meso-2* shows one independent molecule in the asymmetric unit. Fig. 3 shows the molecule with the atomic labeling scheme and Fig. 4 shows the view down the Pd-Fe axis. The molecular structure of *meso-2* is surprisingly similar to that of *rac-2*: even the conformations adopted by the phenyl groups, best observed by comparing Figs 2 and 4, are very similar despite the presence of a benzo group near the C50–55 phenyl group. The biggest difference seems to be that P2 is pushed slightly out of the C₅ plane away from the Fe atom by 0.049 Å, rather than towards the Fe atom as in *rac-2*. The similarity between *rac-* and *meso-2* is in stark contrast to the Mo(CO)₄ analogues, *rac-* and *meso*-[Fe(C₉H₆PPh₂)Mo(CO)₄], in which the axial CO groups in the *meso* isomer force the P atom out of the plane by 0.230 Å, whereas the CO groups in the *rac* Mo(CO)₄ isomer give rise to only a small deviation of the P atoms from the C₅ planes: 0.048 Å away from the Fe atom [2].

2.3 Cyclic voltammetry

Cyclic voltammetry of *rac-2* and *rac-3* both showed a single reversible redox process: ΔE_p and I_a/I_c were found to change only slightly with scan rate and were similar to ferrocene as an internal standard. The oxidation of the ferrocenyl moiety of *rac-2* occurs at 260 mV vs Fc/Fc⁺, a potential 320 mV less positive than (dppf)PdCl₂ and in keeping with the electron-rich character of the indenyl ligand when compared with the cyclopentadienyl ligand [8,24]. The electrochemistry of *rac-3* exhibits a redox process at 248 mV versus Fc/Fc⁺. As would be expected, this is at a potential 325 mV less positive than (dppf)PtCl₂ [8,25].

2.4 Cross-coupling reactions

Since the reporting of the nickel-phosphine catalyzed cross-coupling of Grignard reagents with aryl halides in 1972 [26], a wide variety of similar coupling reactions have been developed and used successfully in organic chemistry [27]. Palladium catalysts have been found to be particularly effective at mediating the cross-coupling of Grignard reagents with aryl halides. However, the introduction of a secondary alkyl group to aryl halides remains problematic due to the isomerization of the alkyl group and/or the reduction of the halide. The catalyst (dppf)PdCl₂ was found to be highly effective at couplings involving secondary alkyl groups, with near perfect *sec-/n-* selectivity [17]. The cross-coupling of *n-* and *sec-*butylmagnesium chloride with bromobenzene was carried out in the presence of *rac-2*. The results and reaction conditions are summarized in Table 4.

Complex *rac-2* was found to catalyze the reaction of bromobenzene with *n-*butylmagnesium chloride to give *n-*butylbenzene in a modest yield (45%) after 17 h at a catalyst loading of 1 mol% of palladium. The reaction, however, was not selective with considerable amounts of *sec-*butylbenzene and benzene also being formed. The ratio of *n-* and *sec-*butylbenzene formed was 63:37. Decreasing the catalyst loading to 0.5 mol% of palladium results in a decrease in both yield and selectivity. The results are similar to those obtained for the equivalent reaction using (PPh₃)₂PdCl₂, with a *n-/sec-* ratio of 59:41 observed. Hayashi et al. reported that (dppf)PdCl₂ catalyses the coupling of bromobenzene with *n-*butylmagnesium chloride in excellent yield (92%) and with high selectivity (100%) [17].

The cross-coupling of bromobenzene with *sec-*butylmagnesium chloride was carried out with *rac-2* to yield *sec-*butylbenzene (47% after 18 h) with a *sec-/n-* ratio of 63:37, at a catalyst loading of 1 mol% of palladium. Increasing the catalyst loading to 5 mol% of palladium reduces the

reaction time (2 h for the same yield), without loss of selectivity. The equivalent reaction with (dppf)PdCl₂ produced *sec*-butylbenzene in excellent yield (95%) and with high selectivity (100%) [17].

Correlations have previously been made between catalyst activity and the Cl-Pd-Cl bond angle, with small angles proposed to accelerate the reductive elimination of the coupled product [17]. The Cl-Pd-Cl bond angle for *rac*-**2** was determined to be 86.8°, similar to that of (dppf)PdCl₂. With this small angle, it was anticipated that coupling reactions catalyzed by *rac*-**2** would proceed with high yields and selectivity. The results obtained here suggest that the β-hydride elimination is still competing strongly with the reductive elimination step of the catalytic cycle, despite the small bond angle. One should note, however, that due to solubility problems with *rac*-**2**, the cross-coupling reactions were performed in THF and not diethyl ether as was used in the previous studies. The choice of solvent has been shown to be important for high selectivity, with reduced *sec*-/*n*- ratios and increased amounts of the reduced aryl halide observed for cross-coupling reactions performed in THF [28].

3. Conclusions

In this paper we have described some Pd, Pt and Ph complexes of the bisplanar chiral ligand **1**. Comparison of the X-ray structures of the *rac* and *meso* isomers of the PdCl₂ complex **2** show little effect of the benzo rings: there is little distortion and the phenyl conformations are very similar. This is in contrast to the six-coordinate Mo(CO)₄ analogues. Catalytic cross-coupling reactions with *rac*-**2** in THF showed little difference with (PPh₃)₂PdCl₂, but a poorer performance than the dppf analogue in diethylether, although solvent may be a factor in the poor performance of *rac*-**2** when compared to the dppf analogue.

4. Experimental

All manipulations and reactions were carried out under an inert atmosphere (Ar or N₂) by use of standard Schlenk line techniques. Reagent grade solvents were dried and distilled prior to use: diethyl ether and tetrahydrofuran from Na/benzophenone; dichloromethane and petroleum ether (50–70 °C fraction) from CaH₂. Bis(1-(diphenylphosphino)-η⁵-indenyl)iron(II) [2,3], (PhCN)₂PtCl₂ [29] and (PhCN)₂PdCl₂ [29] were prepared by published procedures. All other reagents were

purchased from Aldrich or Sigma Chemical Companies. ^1H -, $^{13}\text{C}\{^1\text{H}\}$ - and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy data were collected on a Varian UNITY-300 spectrometer operating at 300, 75 and 121 MHz respectively. NOE, ^1H - ^1H COSY, ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC experiments were run on a Varian INOVA-500 spectrometer operating at 500 and 125 MHz for ^1H and ^{13}C , respectively. Spectra were measured at ambient temperature with residue solvent peaks as internal standard for ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -spectroscopy. Couplings in the ^{13}C -NMR spectra are to phosphorus. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy chemical shifts were reported relative to external 85% H_3PO_4 , positive shifts representing deshielding. EI mass spectra were collected on a Kratos MS80RFA mass spectrometer. Elemental analyses were carried out by Campbell Microanalytical Services, University of Otago, Dunedin. Cyclic voltammetry was performed using a PAR 173 Potentiostat coupled to a PAR 175 Universal Programmer and a Graphtec WX 1200 chart recorder. All electrochemical measurements were made with 1 mM solutions in CH_2Cl_2 with 0.1 M $[\text{Bu}_4\text{N}]\text{PF}_6$ electrolyte using a three-electrode cell comprising of a platinum-disk working electrode (1 mm diameter), a platinum-wire auxiliary electrode, and a Ag/Ag^+ (0.01 M AgNO_3 , 0.1 M $[\text{Bu}_4\text{N}]\text{PF}_6$ - CH_2Cl_2) reference electrode. All potentials are reported versus the ferrocene/ferrocenium (Fc/Fc^+) couple after referencing to *in situ* ferrocene. Before use, the electrodes were polished with 1 μm diamond paste and cleaned with acetone and distilled water. Electrochemical measurements were made at ambient temperature under an inert atmosphere.

4.1 Preparation of *rac*-bis(1-diphenylphosphinoindenyl)iron(II)-*cis*-dichloro palladium(II)(*rac*-2)

To a solution of *rac*-1 (0.19 g, 0.29 mmol) in THF (50 mL) was added $(\text{PhCN})_2\text{PdCl}_2$ (0.12 g, 0.29 mmol). After stirring at ambient temperature for 4 h, the solvent was removed *in vacuo*. The resulting brown residue was dissolved in dichloromethane (30 mL) and filtered through Celite. The Celite was washed with a further 20 mL of CH_2Cl_2 . The volume was reduced to 15 mL, and diethylether (25 mL) was added. The flask was placed in a freezer, and the crystals were collected by filtration to yield 0.18 g (73%) of *rac*-2 as brown crystals.

^1H -NMR (CDCl_3): δ 8.12–6.75 (m, 28H, H4–7 & Ph), 4.70 (s, 2H, H3), 2.53 (s, 2H, H2). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): δ 135.8 (t, $^1J_{\text{PC}} = 6$ Hz, *ipso*-Ph), 135.3 (t, $^1J_{\text{PC}} = 5$ Hz, *ipso*-Ph), 132.6 (s, *o*-Ph), 131.2 (s, *o*-Ph), 129.4–127.9 (m, C4, C7, *m*-Ph & *p*-Ph), 126.5 (s, C5), 124.9 (s, C6), 90.2 (s, C3a), 86.9 (t, $^2J_{\text{PC}} = 5$ Hz, C7a), 80.4 (s, C2), 70.7 (d, $^1J_{\text{PC}} = 8$ Hz, C1), 66.7 (s, C3). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): δ 35.79. CV (CH_2Cl_2): $E_{1/2} = 240$ mV, $\Delta E_{\text{p}} = 75$ mV. Mass spectrum (EI, m/z (%)): 831

(4, M⁺), 705 (81, [(PPh₂C₉H₇)₂Pd]⁺). Anal. Calc. For C₄₂H₃₂Cl₂P₂FePd: C, 60.64; H, 3.88. Found: C, 59.12; H, 4.35.

4.2 Preparation of meso-bis(1-diphenylphosphinoindenyl)iron(II)-cis-dichloropalladium(II)(meso-2)

To a solution of **1** (*meso/rac* ratio of 4:1) (0.65 g, 1.0 mmol) in THF (100 mL) was added (MeCN)₂PdCl₂ (0.26 g, 1.0 mmol). After stirring at ambient temperature for 2 h, the solvent was removed *in vacuo*. The resulting brown residue was dissolved in CH₂Cl₂ (30 mL) and filtered through Celite. The Celite was washed with a further 20 mL of CH₂Cl₂. Recrystallisation from CH₂Cl₂/diethylether gave red/brown crystals (0.60 g, 70%) of *meso-2*.

¹H-NMR (CDCl₃): δ 8.25–6.65 (m, 28H, H4–7 & Ph), 4.65 (s, 2H, H3), 3.95 (s, 2H, H2). ¹³C{¹H}-NMR (CDCl₃): δ 136.8 (t, ¹J_{PC} = 6 Hz, *ipso*-Ph), 134.5 (t, ¹J_{PC} = 5 Hz, *ipso*-Ph), 131.9 (s, *o*-Ph), 130.6 (*o*-Ph), 128.4–125.0 (m, C4, C7, *m*-Ph and *p*-Ph), 124.1 (s, C5), 124.1 (s, C6), 91.5 (t, ²J_{PC} = 5 Hz, C3a), 90.9 (t, ²J_{PC} = 5 Hz, C7a), 82.1 (s, C2), 65.8 (s, C1), 64.6 (s, C3). ³¹P{¹H}-NMR (CDCl₃): δ 33.94. Mass spectrum (EI, *m/z* (%)): 831 (2, M⁺), 795 (35, M⁺-Cl), 760 (25, M⁺-2Cl), 704 (20, [(PPh₂C₉H₇)₂Pd]⁺). As with *rac-2*, low carbon microanalytical results were obtained with *meso-2* despite good crystallinity and NMR spectra.

4.3 Preparation of rac-bis(1-diphenylphosphinoindenyl)iron(II)-cis-dichloroplatinum(II) (*rac-3*)

To a solution of *rac-1* (0.20 g, 0.30 mmol) in THF (50 mL) was added (PhCN)₂PtCl₂ (0.14 g, 0.30 mmol). After stirring overnight at ambient temperature, the solvent was removed *in vacuo*. The resulting brown residue was dissolved in CH₂Cl₂ (10 mL) and filtered through Celite. Washing with CH₂Cl₂ (30 mL) produced a light brown solution that was then reduced in volume to 10 mL. To this solution was added diethylether (20 mL). The flask was then placed in a freezer and left overnight to give a brown precipitate of *rac-3* (0.22 g, 80%). Crystals suitable for X-ray structural analysis were grown by vapour diffusion of diethylether into a CH₂Cl₂ solution.

¹H-NMR (CDCl₃): δ 8.04 (m, 4H, *o*-Ph), 7.65 (d, ³J_{HH} = 8 Hz, 2H, H7), 7.57 (d, ³J_{HH} = 8 Hz, 2H, H4), 7.53 (m, 4H, *o*-Ph), 7.37 (t, ³J_{HH} = 7 Hz, 2H, *p*-Ph), 7.32 (t, ³J_{HH} = 7 Hz, 2H, *p*-Ph), 7.26–7.21 (m, 8H, *m*-Ph), 6.94 (t, ³J_{HH} = 8 Hz, 2H, H6), 6.65 (t, ³J_{HH} = 8 Hz, 2H, H5), 4.62 (d, ³J_{HH} = 2 Hz, 2H, H3), 2.42 (d, ³J_{HH} = 2 Hz, 2H, H2). ¹³C{¹H}-NMR (CDCl₃): δ 135.66 (t, ¹J_{PC} = 6 Hz, *ipso*-Ph), 135.02 (t, ¹J_{PC} = 5 Hz, *ipso*-Ph), 131.34 (s, *o*-Ph), 130.85 (s, *o*-Ph), 129.83 (s, C7), 128.22 (s, C4),

127.91–127.50 (m, *m*-Ph & *p*-Ph), 126.24 (s, C5), 124.85 (s, C6), 89.89 (s, C3a), 86.19 (t, $^2J_{\text{PC}} = 5$ Hz, C7a), 81.37 (s, C2), 71.12 (d, $^1J_{\text{PC}} = 68$ Hz, C1), 66.33 (s, C3). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): δ 12.65 ($J_{\text{PtP}} = 3818$ Hz). CV (CH_2Cl_2): $E_{1/2} = 248$ mV, $\Delta E_{\text{p}} = 75$ mV. Mass spectrum (EI, m/z (%)): 884 (100, $[(\text{PPh}_2\text{C}_9\text{H}_6)_2\text{FePtCl}]^+$), 830 (54, $[(\text{PPh}_2\text{C}_9\text{H}_7)_2\text{PtCl}]^+$). Anal. Calc. For $\text{C}_{42}\text{H}_{32}\text{Cl}_2\text{P}_2\text{FePt}$: C, 54.80; H, 3.50. Found: C, 54.24; H, 3.52.

4.4 Synthesis of *[bis(diphenylphosphinoindenyl)iron(II)(cyclooctadiene)rhodium(I)] tetraphenylborate (rac-4)*

To a solution of *rac-1* (0.48 g, 0.73 mmol) in CH_2Cl_2 (25 mL) was added a solution of $[\text{Rh}(\text{COD})_2]\text{BF}_4$ (0.15 g, 0.36 mmol) in CH_2Cl_2 (15 mL) and the resulting solution stirred at ambient temperature for 3 h. the solvent was removed *in vacuo* to leave a brown powder. The crude product was dissolved in CH_2Cl_2 (5 mL), $\text{Na}[\text{BPh}_4]$ (0.123 g, 0.36 mmol) was added and the solution stirred for 10 min. Diethylether was then added to give a yellow precipitate which was collected by filtration to yield 0.53 g (80%) of *rac-4*.

^1H -NMR (CDCl_3): δ 7.73–6.80 (m, 48H, H4–7 & Ph), 4.96 (s, 2H, H3), 4.37 (m, 4H, COD-CH), 2.81 (s, 2H, H2), 2.56 (m, 8H, COD-CH₂). $^{13}\text{C}\{^1\text{H}\}$ -NMR (Acetone-*d*₆): δ 134.2 (m, *ipso*-Ph), 132.7 (m, *ipso*-Ph), 130.7 (s, *o*-Ph), 130.2 (s, *o*-Ph), 128.2 (s, *p*-Ph), 127.8–127.1 (m, C4&7, *m*-Ph and COD-CH), 124.9 (s, C5 or 6), 124.3 (s, C5 or 6), 102.4 (m, C7a or 3a), 97.5 (m, C7a or 3a), 90.7 (d, $^1J_{\text{PC}} = 3$ Hz, C1), 80.1 (s, C2), 67.4 (t, $^3J_{\text{PC}} = 3$ Hz, C3), 30.1 (s, COD-CH₂). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): δ 29.1 (d, $^1J_{\text{PRh}} = 150$ Hz). CV (CH_2Cl_2): $E_{1/2} = 248$ mV, $\Delta E_{\text{p}} = 88$ mV. Mass spectrum (EI, m/z (%)): 865 (100, M^+), 511 (20, $[(\text{PPh}_2\text{C}_9\text{H}_7)\text{Rh}(\text{COD})]^+$). Anal. Calc. For $\text{C}_{74}\text{H}_{64}\text{P}_2\text{BFeRh}$: C, 75.02; H, 5.44. Found: C, 74.40; H, 5.70.

4.5 Cross-Coupling of bromobenzene with Grignard reagents using *rac-2*

Grignard Preparation: To a suspension of activated magnesium turnings (1.28 g, 52.7 mmol) in THF (30 mL) was added, dropwise, a solution of chlorobutane (5.50 mL, 52.7 mmol) in THF (60 mL). After initiation, the mixture was refluxed until the magnesium was consumed. The solution was cooled to ambient temperature and the concentration of the Grignard verified by titration.

Cross-Coupling: To a solution of bromobenzene (4 mmol) and Pd catalyst (0.5–5 mol%) in THF (50 mL) at -80 °C, was added the butylmagnesium chloride (8 mmol). The reaction mixture was

allowed to warm to ambient temperature and stirred for a period of time (1–18 h) as given in Table 4. The reaction mixture was quenched with 10% aqueous HCl, and an appropriate internal standard was added to the organic layer, which was then analysed by GLC. The organic layer and aqueous phase washings were combined, washed with saturated NaHCO₃ solution, water, and then dried over MgSO₄. The solvent was evaporated and the resulting oil analysed by ¹H- and ¹³C-NMR spectroscopy. Results are summarized in Table 4.

4.6 X-ray Structure Determinations for *rac-2*, *meso-2* and *rac-3*

Crystal data and experimental details are given in Table 2. For each compound, a crystal was attached to a thin glass fiber and mounted on a Siemens P4 SMART diffractometer with a Siemens CCD area detector. The program SADABS [30] was utilized for the scaling of diffraction data, the application of a decay correction, and empirical absorption correction based on redundant reflections. Data processing was undertaken with SAINT [30] and the structures were solved by direct methods and refined by least-squares methods on F^2 using the SHELXTL program library [31]. Hydrogen atoms were added as riding contributors at calculated positions, with isotropic thermal parameters based on the attached carbon atom. Non-hydrogen atoms were refined anisotropically. During the refinement of *meso-2*, the high angle data was removed because the crystal diffracted weakly.

5. Supplementary materials

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre: CCDC No. 287920 for *rac-2*; CCDC No. 287919 for *meso-2*; and CCDC No. 287918 for *rac-3*. Copies of the information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. Fax. (int code) +44(1223)336-033 or by Email at deposit@ccdc.cam.ac.uk or from the www at <http://www.ccdc.cam.ac.uk>.

Acknowledgements

We wish to thank New Zealand Lotteries Science for the purchase of precious metals and Dr Alison J. Downard for the use of electrochemical equipment.

References

- [1] (a) G. Wagner, R. Herrmann, in: A. Togni, T. Hayashi (Eds.), *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*, VCH, Weinheim, 1995, pp 173-218. (b) A. Togni, in: A. Togni, R.L. Halterman (Eds.), *Metallocenes: Synthesis Reactivity Applications*, Vol. 2, Wiley-VCH, Weinheim, 1998; pp 685-722. (c) T. Hayashi, in: A. Togni, T. Hayashi (Eds.), *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*, VCH, Weinheim, 1995, pp 105-142. (d) A. Togni, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 1475. (e) L.-X. Dai, T. Tu, S.-L. You, W.-P. Deng, X.-L. Hou, *Acc. Chem. Res.* 36 (2003) 659. (f) T.J. Colacot, *Chem. Rev.* 103 (2003) 3101. (g) P.J. Walsh, A.E. Lurain, J. Balsells, *Chem. Rev.* 103 (2003) 3297. (h) W. Tang, X. Zhang, *Chem. Rev.* 103 (2003) 3029. (i) X. Zhang, US Patent number 6,534,657.
- [2] J.J. Adams, D.E. Berry, J. Browning, D. Burth, O.J. Curnow, *J. Organomet. Chem.* 580 (1999) 245.
- [3] (a) O.J. Curnow, G.M. Fern, *Organometallics* 21 (2002) 2827. (b) O.J. Curnow, G.M. Fern, M.L. Hamilton, A. Zahl, R. van Eldik, *Organometallics* 23 (2004) 906.
- [4] O.J. Curnow, G.M. Fern, M.L. Hamilton, E.M. Jenkins, *J. Organomet. Chem.* 689 (2004) 1897.
- [5] A.W. Rudie, D.W. Lichtenberg, M.L. Katcher, A. Davison, *Inorg. Chem.* 17 (1978) 2859.
- [6] (a) T.S.A. Hor, L.-T. Phang, *J. Organomet. Chem.* 373 (1989) 319. (b) T.S.A. Hor, L.-T. Phang, *Polyhedron* 9 (1990) 2305. (c) T.S.A. Hor, L.-T. Phang, *J. Organomet. Chem.* 381 (1990) 121.
- [7] A.L. Bandini, G. Banditelli, M.A. Cinellu, G. Sanna, G. Minghette, F. Demartin, M. Mannassero, *Inorg. Chem.* 28 (1989) 404.
- [8] B. Corain, G. Longato, G. Favero, D. Ajo, G. Pilloni, U. Russo, F.R. Kreissl, *Inorg. Chim. Acta* 157 (1989) 259.
- [9] G. Bandoli, A. Dolmella, *Coord. Chem. Rev.* 209 (2000) 161.
- [10] K.-S. Gan, T.S.A. Hor, In *Ferrocenes*; A. Togni, T. Hayashi, Eds.; VCH: New York, 1995; Chapter 1, pp 3-104.

- [11] (a) T. Hayashi, M. Konishi, M. Kumada, *Tetrahedron Lett.* (1979) 1871. (b) T. Katayama, M. Umeno, *Chem. Lett.* (1991) 2073. (c) L.N. Pridgen, L.B. Killmer, *J. Org. Chem.* 46 (1981) 5402.
- [12] (a) N.W. Alcock, J.M. Brown, M. Rose, A. Wienand, *Tetrahedron: Asymmetry* 2 (1991) 47. (b) W.R. Cullen, N.F. Han, *Appl. Organomet. Chem.* 1 (1987) 1.
- [13] W.R. Cullen, T.-J. Kim, F.W.B. Einstein, T. Jones, *Organometallics* 4 (1985) 346.
- [14] W.R. Cullen, S.V. Evans, H.F. Han, J. Trotter, *Inorg. Chem.* 26 (1987) 514.
- [15] (a) T. Hayashi, A. Yamamoto, M. Hojo, Y. Ito, *J. Chem. Soc., Chem. Commun.* (1989) 495. (b) T. Hayashi, N. Kawamura, Y. Ito, *J. Amer. Chem. Soc.* 109 (1987) 7876. (c) A. Togni, G. Rihs, R.E. Blumer, *Organometallics* 11 (1992) 613.
- [16] M.T. Reetz, E.W. Beuttenmuller, R. Goddard, M. Pasto, *Tetrahedron Lett.* 40 (1999) 4977.
- [17] T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, K. Hirotsu, *J. Amer. Chem. Soc.* 106 (1984) 158.
- [18] A.L. Bandini, G. Banditelli, M.A. Cinellu, G. Sanna, G. Minghetti, F. Demartin, M. Manassero, *Inorg. Chem.* 28 (1989) 404.
- [19] A.G. Avent, R.B. Bedford, P.A. Chaloner, S.Z. Dewa, P.B. Hitchcock, *J. Chem. Soc., Dalton Trans.* (1996) 4633.
- [20] W.R. Cullen, T.-J. Kim, F.W.B. Einstein, T. Jones, *Organometallics* 2 (1983) 714.
- [21] U. Casellato, B. Corain, R. Graziana, B. Longato, G. Pilloni, *Inorg. Chem.* 29 (1990) 1193.
- [22] B. Longato, G. Pilloni, R. Graziani, U. Casellato, *J. Organomet. Chem.* 407 (1991) 369.
- [23] W.L. Steffen, G.J. Palenik, *Inorg. Chem.* 15 (1976) 2432.
- [24] B. McCulloch, D.L. Ward, J.D. Woolins, C.H. Brubaker, *Organometallics* 4 (1985) 1425.
- [25] D.A. Clemente, G. Pilloni, B. Corain, B. Longato, M. Tiripicchio-Camellini, *Inorg. Chim. Acta* 115 (1986) L9.
- [26] (a) R.J.P. Corriu, J.P. Masse, *J. Chem. Soc., Chem. Commun.* (1972) 144. (b) K. Tamao, K. Sumitani, M. Kumada, *J. Amer. Chem. Soc.* 94 (1972) 4374.

- [27] E. Negeshi, *Acc. Chem. Res.* 15 (1982) 340.
- [28] T. Hayashi, M. Ogasawara, K. Yoshida, *Organometallics* 19 (2000) 1567.
- [29] G.K. Anderson, M. Lin, *Inorg. Synth.* 28 (1980) 60.
- [30] SAINT and SADABS, Siemens Analytical, Madison, WI, 1994.
- [31] G.M. Sheldrick, SHELXTL ver 5.1, Bruker AXS, Madison, WI, 1998.