

Four-coordinate complexes of bis(1-diphenylphosphinoindenyl)iron(II)

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

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)] tetrphenylborate 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.

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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-PPPh₂-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

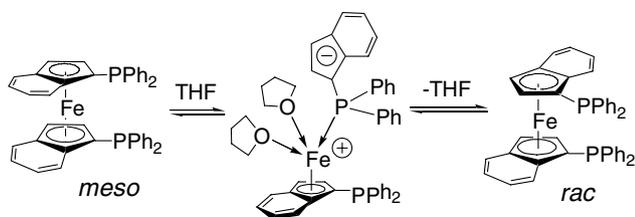
ring-slippage, and indenide dechelation with phosphine coordination to give a zwitterionic intermediate (Scheme 1). To further understand the factors influencing this unprecedented ferrocene isomerization process, a number of derivatives were reported [4].

Ferrocenylphosphines are widely employed in the formation of polymeric 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

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Scheme 1. Isomerisation of [(1-PPh₂-η⁵-C₉H₆)₂Fe] (**1**) in THF.

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 C₂ 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 Grignard 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**.

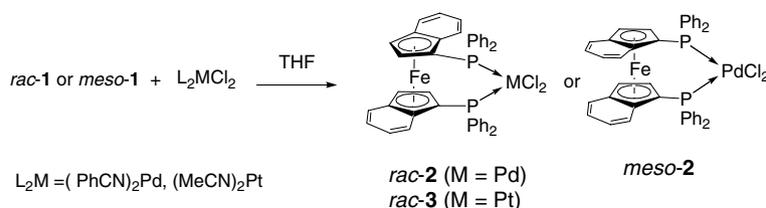
The platinum analogue of *rac*-**2**, *rac*-**3**, was prepared similarly from *rac*-**1** and (PhCN)₂PtCl₂. The proton resonances for H2 and H3 appear in positions similar to those observed for *rac*-**2**, an indication that the conformation of the two complexes in solution is similar. The ¹³C{¹H} 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} =

Table 1
¹H NMR chemical shifts (for H2 and H3) and ³¹P NMR chemical shifts of the ferrocenes in CDCl₃^a

Compound	H2	H3	³¹ P
dppf ^b	4.07	4.32	-17.2
<i>meso</i> - 1	3.48	3.81	-26.5
<i>rac</i> - 1	3.07	4.92	-22.3
(dppf)PdCl ₂ ^b	4.18	4.36	34.9
<i>meso</i> - 2	3.95	4.65	33.9
<i>rac</i> - 2	2.53	4.70	35.3
<i>rac</i> - 3	2.42	4.62	12.7
<i>rac</i> - 4	2.81	4.96	29.1

^a Chemical shifts are in ppm (δ) downfield from Me₄Si (¹H) and 85% H₃PO₄ (³¹P); spectra obtained in CDCl₃.

^b H2 and H3 refer to the α and β protons of the cyclopentadienyl ring, respectively. Data from Refs. [17,18].

Scheme 2. Synthesis of Pd and Pt complexes of **1**.

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