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# Synthesis and stereochemistry of bis(cyclopalladium) complexes of 1,1'-bis[1-(arylimino)ethyl]ferrocenes

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**Abstract**—Double cyclopalladation of 1,1'-bis[(arylimino)ethyl]ferrocenes with Li<sub>2</sub>PdCl<sub>4</sub> followed by treatment with PPh<sub>3</sub> afforded *meso* and *dl* stereoisomers of bis(palladium) complexes and the individual stereoisomers were isolated successfully by column chromatography. The composition and the structure of the metallocycles were characterized by elemental analysis, IR and <sup>1</sup>H NMR spectroscopy. A mechanism for the formation of stereoisomers in the cyclopalladation reaction was suggested. Copyright © 1996 Elsevier Science Ltd

The chemistry of cyclometalated compounds, especially those containing N-donor ligands and palladium is one of the most advanced areas of modern organometallic chemistry. These cyclopalladated compounds have been successfully used organic syntheses, catalysis, asymmetric in synthesis, photochemistry, and as potential biologically active materials.<sup>1</sup> More recently, the cyclopalladation of some ferrocenylimines has been reported by López's and our laboratories. It was found that the reaction occurred predominantly at the ortho position of the substituted Cp ring to afford the corresponding cyclopalladated derivatives.<sup>2,3</sup> But double cyclopalladation of 1,1'-disubstituted ferrocene is scarce, only the double cyclopalladations of 1,1'-diacetylferrocene bis (acetylhydrazone)<sup>4</sup> and N,N,N',N'-tetramethylferrocene-1,1'-dicarbothioamide<sup>5</sup> have been reported in the literature. In the present paper, we report our studies on the synthesis and characterization of the stereoisomers of bis[palladium(II)] complexes of 1,1'-bis[(arylimino)ethyl]ferrocenes.

## **RESULTS AND DISCUSSION**

The novel bisferrocenylimines  $[(\eta^5 - C_5 H_4)$ CMe=NAr)<sub>2</sub>Fe] designated as bis (FKM)] were synthesized by the reaction of bis-acetylferrocene with the corresponding amine in the presence of freshly activated Al<sub>2</sub>O<sub>3</sub>.<sup>6</sup> The cyclopalladation reaction was carried out with bis(FKM) 1 and two mole equivalents of Li<sub>2</sub>PdCl<sub>4</sub> and anhydrous sodium acetate in CH<sub>2</sub>Cl<sub>2</sub>—MeOH mixed solvent at room temperature for about 20 h, then the solvent was evaporated in vacuo to give a brown-red solid which was tentatively assigned to be a polymeric or dimeric dipalladio derivative 2. Given the high solubility of 2 in chloroform, dichloromethane etc., the formation of the dimeric form is highly possible. Owing to the inevitable contamination by the bis adducts of PdCl<sub>2</sub> with ligand 1 formed in the cyclopalladation reaction and the decomposition of the products during purification by column chromato-

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 $Ar = p - CH_3OC_6H_4 (a), \quad p - CH_3C_6H_4 (b), \quad C_6H_5 (c), \quad p - ClC_6H_4 (d), \quad p - BrC_6H_4 (e), \\ p - NO_2C_6H_4 (f), \quad m - CH_3C_6H_4 (g), \quad m - ClC_6H_4 (b), \quad m - BrC_6H_4 (i).$ 

graphy on silica gel, a pure sample of 2 was not isolated. The brown-red solid was directly subjected to bridge-splitting reaction with ligand triphenylphosphine to produce the meso and dl monomeric stereoisomers (the total yields of meso and dl isomers are 15–46%), which is a typical reaction of a chlorine-bridged binuclear complex of palladium.<sup>7</sup> What is most interesting is that the meso and dl isomers can be separated successfully by silica gel column chromatography except for 3a and 3b, which provided the key to an interpretation of the spectra. The homoannular ring formed by chelation of a ferrocenylimine ligand to Pd<sup>II</sup> also displays stereoisomerism arising from planar chirality. All the new compounds 3 are air stable powders, and very soluble in chloroform, dichloromethane, and slightly soluble in methanol. The yields, analytical data and IR data of the compounds are shown in Table 1, and the <sup>1</sup>H NMR data in Table 2. The compounds 3 melt at high temperature ( $>200^{\circ}$ C) and with decomposition.

The IR spectral features of *meso* and *dl* isomers are very similar to each other. No absorption bands can be found at 1000 cm<sup>-1</sup> and 1100 cm<sup>-1</sup>, which indicated the substitution of two cyclopentadienyl rings.<sup>8</sup> The C==N absorptions (~1570 cm<sup>-1</sup>) in **3**  are shifted to lower energy by ~50 cm<sup>-1</sup> in comparison with those of the corresponding bis(FKM), indicating the coordination of nitrogen to palladium through its lone pair of electrons.<sup>9</sup> The strong absorption at about 745 cm<sup>-1</sup> and 690 cm<sup>-1</sup> observed in 3, being the feature of monosubstituted phenyl ring, are assigned to the  $\delta$ (CH) of PPh<sub>3</sub>.

The assignments of the signals of the Cp ring protons in <sup>1</sup>H NMR spectra of two isomers are similar to the mono (palladium) complex  $[PdCl{(\eta^5 - C_5H_5)Fe(\eta^5 - C_5H_3CMe = NAr)}(PPh_3)].$ The chemical shifts are different between the isomers because the Cp ring protons are in different magnetic environments. The pair of the proton signals for Cp rings and C-methyl group for the individual stereoisomers, meso-3c and dl-3c, occur at 3.09, 4.15, 4.16, 1.62 and 2.84, 3.98, 4.23, 2.10 ppm, respectively, compared with 3.37, 4.11, 4.45, 2.06 ppm for the mono (palladium) analogue. It seems impossible that the cyclopentadiene rings of the ferrocene moiety in the two isomers could adopt the eclipsed configuration, because of the significant steric interactions between the cyclopentadienyl substituents, although it is recognized<sup>10</sup> that the balance between intramolecular ring interactions and intermolecular packing forces usually

			Yield	Elemental analyses"					
Compound		Empirical formula	(%)	С	н	N	IR data (cm <sup>-1</sup> )		
3a		$C_{64}H_{56}Cl_2FeN_2O_2P_2Pd_2$	32	59.6	4.7	2.5	1570	1500	1435
				(59.7)	(4.4)	(2.2)	1248	820	750
3b		$C_{64}H_{56}Cl_2FeN_2P_2Pd_2$	46	61.2	4.7	2.3	1571	1437	818
				(61.3)	(4.5)	(2.2)	748	695	
3c	meso	$C_{62}H_{52}Cl_2FeN_2P_2Pd_2$	17	60.3	4.2	2.4	1570	1433	740
	dl		26	60.4	4.1	2.4	690		
				(60.7)	(4.3)	(2.3)			
3d	meso	$C_{62}H_{50}Cl_4FeN_2P_2Pd_2$	10	57.1	4.2	2.2	1575	1438	820
	dl		17	57.3	4.2	2.3	749	698	
				(57.5)	(3.9)	(2.2)			
3e	meso	C <sub>42</sub> H <sub>50</sub> Br <sub>2</sub> Cl <sub>2</sub> FeN <sub>2</sub> P <sub>2</sub> Pd <sub>2</sub>	7	54.1	4.1	2.2	1568	1432	817
	dl		13	54.3	4.2	2.2	740	690	
				(53.8)	(3.6)	(2.0)			
3f	meso	C <sub>42</sub> H <sub>40</sub> Cl <sub>2</sub> FeN <sub>4</sub> O <sub>4</sub> P <sub>2</sub> Pd <sub>2</sub>	13	55.9	3.4	4.2	1570	1433	1340
	dl		16	55.9	35	4.0	825	746	690
			10	(56.6)	(3.8)	(4.3)	020	110	070
30	meso	C. H. CLEEN P.P.d.	11	61.0	4.8	2.2	1570	1433	748
55	dl		14	60.9	4.8	2.2	692	1455	740
	ш		14	(61.3)	(4.5)	(2,2)	072		
21			1.2	(01.5)	(4.5)	(2.2)	1570	1471	715
3h	meso	$C_{62}H_{50}Cl_4Feln_2P_2Pd_2$	13	57.5	4.1	2.2	15/0	1431	/45
	đl		14	57.5	4.2	2.2	690		
				(57.5)	(3.9)	(2.2)			
3i	meso	$C_{62}H_{50}Br_2Cl_2FeN_2P_2Pd_2$	13	53.7	3.9	2.1	1565	1431	742
	dl		23	53.7	4.1	2.4	690		
				(53.8)	(3.6)	(2.0)			

Table 1. Yields, analytical data and IR data of 3

"Calculated values in parentheses.

Table 2. <sup>1</sup>H NMR data of compds.  $3^a$  (1.00–6.00 ppm)

Compound		3	4	5	Others	
3a	meso	3.07bs	4.14bs	4.16bs	1.63s	3.77s
	dl	2.83bs	3.80bs	4.23bs	2.12s	3.74s
3b	meso	3.06bs	4.15bs	4.17bs	1.62s	2.32s
3c	meso	3.09bs	4.15bs	4.16bs	1.62s	
	dl	2.84bs	3.98bs	4.23bs	2.10s	
3d	meso	3.10bs	4.14bs	4.18bs	1.63s	
	dl	2.86bs	3.93bs	4.16bs	2.11s	
3e	meso	3.10bs	4.14bs	4.17bs	1.62s	
	dl	2.86bs	3.93bs	4.16bs	2.03s	
3f	meso	3.20bs	4.18bs	4.25bs	1.65s	
	dl	2.92bs	4.08bs	4.27bs	2.11s	
3g	meso	3.21bs	4.15bs	4.20bs	1.60s	2.37s
0	dl	2.86bs	3.98bs	4.23bs	2.11s	2.31s
3h	meso	3.09bs	4.16bs	4.16bs	1.63s	
	dl	2.87bs	4.03bs	4.22bs	2.10s	
3i	meso	3.09bs	4.15bs	4.23bs	1.63s	
	dl	2.88bs	4.03bs	4.22bs	2.12s	

" Chemical shifts in ppm, TMS as the internal standard.

results in a preference for an eclipsed conformation of the cyclopentadiene rings. In the dl configuration, protons 3-H can be shielded by two PPh<sub>3</sub> groups, whereas in the meso configuration protons 3-H are shielded only by one PPh<sub>3</sub> group. According to <sup>1</sup>H NMR study of the mono(palladium) complex one can conclude that the shielding effect of the PPh<sub>3</sub> group is very large. For example, in comparison with the di-µ-chloro-bridged cyclopalladated complex  $[{Pd[(\eta^5 - C_5H_5)Fe(\eta^5 - C_5H_3)Fe(\eta^5 - C_5H_3)Fe(\eta^5$ CMe = NAr)] (µ—Cl)}<sub>2</sub>] (Ar = p—C<sub>6</sub>H<sub>13</sub>OC<sub>6</sub>H<sub>4</sub>,  $p - C_{12}H_{25}OC_6H_4$  and  $p - C_{16}H_{33}OC_6H_4$ ), the resonance of the substituted Cp protons 3-H, 4-H, 5-H and unsubstituted Cp ring protons in their corresponding monomeric cyclopalladated triphenylphosphine derivatives shifts to upfield significantly by ca 0.48, 0.16, 0.20, 0.47 ppm, respectively.<sup>11</sup> So in the present cases, the signals of protons 3-H in *dl* form should appear at upfield by comparison with those in meso form. Thus we suggest that in each separation, the band possessing the highest R<sub>f</sub> value contains the meso form and the second band contains *dl* form. In general, the chemical shifts of protons in Cp ring show no dependence on substituents in the N—phenyl ring, this may be due to the nonplanarity between the ferrocenyl ring and the N—phenyl ring, which can influence the transmission of the electronic effects of the substituents in the phenyl ring through the C==N bond to the ferrocenyl moiety.

A proposed explanation for the formation of stereoisomers in cyclopalladation reactions of a bis(palladium) complex is shown in Scheme 1. The bis(FKM) may exist in the forms of conformer-I and conformer-II; double cyclopalladation of I and II affords the corresponding dl and meso isomers, respectively, which in meso product, the sites of electrophilic attack are at 2- and 2'-positions whereas attack on the 2- and diametrically opposite side 5'-position leads to the dl form. After the two chelate rings are formed, interconversion of the stereoisomers is not possible without breaking the  $\sigma$ Pd—C bond of one chelate ring.

### **EXPERIMENTAL**

#### Materials and instruments

<sup>1</sup>H NMR spectra were recorded on a Bruker AM 400 spectrometer, using CDCl<sub>3</sub> as the solvent and

tetramethylsilane as an internal standard. IR spectra were recorded on a Perkin-Elmer FTIR 1750 spectrophotometer. Elemental analyses were determined with a Carlo Erba 1106 elemental analyser. Chromatographic work was carried out using silica gel under reduced pressure.

A lithium tetrachloropalladate(II) solution in methanol (0.1 M) was prepared by stirring two equivalents of anhydrous lithium chloride and one equivalent of anhydrous palladium chloride in methanol until a homogeneous solution was formed. The novel bisferrocenylimines were synthesized by the reaction of bis-acetyl-ferrocene with the corresponding amine in the presence of freshly activated  $Al_2O_3$ .<sup>6</sup>

## General procedure for the double cyclopalladation of 1

A solution of lithium tetrachloropalladate(II) in 5 cm<sup>3</sup> of methanol (0.13 g of Li<sub>2</sub>PdCl<sub>4</sub>, 0.5 mmol) was added to a solution of bisferrocenylimines (0.25 mmol) and anhydrous sodium acetate (41 mg, 0.5 mmol) in 16 cm<sup>3</sup> of dichloromethane/methanol (8:1, v/v). The mixture was stirred at room temperature for about 20 h, then the solvent evaporated *in vacuo* until a brown-red solid formed. The crude brown-red product was washed several times with



a small amount of methanol, then without further purification, it was treated with PPh<sub>3</sub> (0.13 g, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 0.5 h. The product was separated by passing through a short silica gel column with CH<sub>2</sub>Cl<sub>2</sub> as eluent, which the first band (the highest  $R_f$  value) contained the *meso* form and the second band contained the *dl* form. After the evaporation of the solvent, the residue was recrystallized from dichloromethane-petroleum ether (60–90°C) to give *meso*-3 and *dl*-3 with the yields shown in Table 1.

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