Organometallics **1999,** *18,* 1267−1274 1267

Heterodi- and Heterotrimetallic Compounds Containing Five-Membered Rings and σ(Pd−$C_{sp^2,\ ferrocene}$) Bonds. X-ray Crystal Structure of the *meso*-Form of $[Pd_2\{Fe[(\eta^5\text{-}C_5H_3)-C(CH_3){=}N-C_6H_5]\}_2Cl_2(PPh_3)_2]$

Ramon Bosque,[†] Concepción López,*[,†] Xavier Solans,[‡] and Mercè Font-Bardia[‡]

Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona,
Martí Franquès 1-11, 08028-Barcelona, Spain, and Departament de Cristal.lografia,
Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona,
Marti Franquès s/n, 08028-Barcelona, Spain

Received October 6, 1998

The syntheses and characterization of heterodi- and heterotrimetallic complexes of general formulas $[Pd\{[(\eta^5\text{-}C_5H_3)-C(R){=}N-R']Fe[(\eta^5\text{-}C_5H_4)-C(R){=}N-R']\}Cl(PPh_3)]$, $[Pd\{[(\eta^5\text{-}C_5H_3)-C(C_6H_5){=}N-C_6H_5]Fe[(\eta^5\text{-}C_5H_4)-C(O){=}N-C_6H_5]\}Cl(PPh_3)]$, and $[Pd_2\{Fe[(\eta^5\text{-}C_5H_3)-C(R){=}N-R']_2\}Cl_2(PPh_3)_2]$ {with R = H, CH_3, or C_6H_5 and R′= phenyl or benzyl groups} are reported. The X-ray crystal structure of the *meso*-form of $[Pd_2\{Fe[(\eta^5\text{-}C_5H_3)-C(CH_3){=}N-C_6H_5]_2\}Cl_2(PPh_3)_2]$ **(2b)** is also described.

The study of heteropolynuclear organometallic compounds has attracted great interest during the past decade, mainly due to their applications in several areas. One of the methods used to prepare heteropolynuclear compounds is based on the use of ferrocenyl substrates containing heteroatoms {mainly nitrogen, sulfur, phosphorus, or oxygen} and/or unsaturated groups with good donor abilities, which may allow the coordination of one or more metal ions.[1,2] Among the procedures described so far for the preparation of this sort of compound, those involving the coordination of the heteroatom and the activation of a $\sigma(C_{sp^2,ferrocene}-H)$ bond are especially important since they produce *cyclometalated* derivatives,[3−6] which have been found to be useful substrates in different areas.[7] Cyclopalladated and cycloplatinated complexes containing N-donor ferrocenyl ligands and a $\sigma(M-C_{sp^2,ferrocene})$ bond have been studied extensively in the past decade. However, doubly cyclometalated derivatives are scarce.[8−10] To our knowledge four articles have been published in this field. Robinson *et al.*[8] reported the bis(cycloplatination) of the 1,1′-ferrocenyldiamine $[Fe\{(\eta^5\text{-}C_5H_4)-CH_2-N(CH_3)_2\}_2]$. The three remaining articles deal with bis(cyclopalladated) compounds, two of which (Figure 1, **A** and **B**) arise from the orthopalladation of two different ferrocenyl moieties.[9] However, only one example of 1,1′-bis(cyclopalladation) of the ferrocenyl fragment has been reported (Figure 1, **C**).[10]

Recent studies on cyclopalladation of monoferrocenylimines of general formula $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(R){=}N-R'\}]$ have shown that the palladacycles form under mild experimental conditions.[6] On this basis, we attemped to prepare 1,1′-ferrocenyldiimines and to study their proclivity to undergo mono- or biscyclopalladation. In this paper we present the synthesis of the 1,1′-diimines $[Fe\{(\eta^5\text{-}C_5H_4)-C(R){=}N-R'\}_2]$ with R = H, R′ = $CH_2-C_6H_5$ **(1a)**; R = CH_3, R′ = C_6H_5 **(1b)**, C_6H_4-4-CH_3 **(1c)**, and R = R′ = C_6H_5 **(1d)** (Figure 1, **D**) and their cyclopalladated complexes containing one or two $\sigma(Pd-C_{sp^2,ferrocene})$ bonds.

The diimine $[Fe\{(\eta^5\text{-}C_5H_4)-C(H){=}N-CH_2-C_6H_5\}_2]$ **(1a)** was prepared by condensation of 1,1′-diformylferrocene[11] and benzylamine in a 1:2 molar ratio, using the procedure described before for $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}$

[†] Departament de Química Inorgànica.

[‡] Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals.

(1) Togni, A.; Hayashi, T. In *Ferrocenes. Homogeneous Catalysis. Organic Synthesis and Materials Science*; VCH: Weinheim, Germany, 1995.

(2) For recent publications involving heteropolynuclear compounds containing ferrocenyl units see also: Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: San Diego, CA, 1998; Vol. 42, p 291. Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Sarroca, C. *Chem. Commun.* **1998**, 1481. Severin, K.; Bergs, R.; Beck, W. *Angew. Chem., Int. Ed., Engl.* **1998**, *37*, 1635. Zhuravel, M. A.; Glueck, D. S.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1998**, *17*, 574.

(3) Ryabov, A. D.; Panyashkina, I. M.; Polyakov, V. A.; Howard, J. A. K.; Kuz'mina, L. G.; Daft, M. S.; Sacht, B. *Organometallics* **1998**, *17*, 3615. Ryabov, A. D.; Kazankov, G. M.; Panyashkina, I. M.; Grozovsky, O. V.; Dyachenko, O. G.; Polyakov, V. A.; Kuz'mina, L. G. *J. Chem. Soc., Dalton Trans.* **1997**, 4385.

(4) Crawford, S. S.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 3193.

(5) Wu, Y. J.; Huo, S. Q.; Yang, L.; Du, C. X. *J. Organomet. Chem.* **1995**, *490*, 249. Huo, S. Q.; Zhu, Y.; Wu, Y. J. *J. Organomet. Chem.* **1995**, *490*, 243. Wu, Y. J.; Huo, S. Q.; Zhu, Y.; Yang, L. *J. Organomet. Chem.* **1994**, *481*, 235. Zhao, G.; Wang, Q. G.; Mak, T. C. W. *Organometallics* **1998**, *17*, 3437.

(6) (a) López, C.; Sales, J.; Solans, X.; Zquiak, R. *J. Chem. Soc., Dalton Trans.* **1992**, 2321. (b) Bosque, R.; López, C.; Sales, J.; Solans, X.; Font-Bardia, M., *J. Chem. Soc., Dalton Trans.* **1994**, 735. (c) Bosque, R.; López, C.; Sales, J.; Solans, X. *J. Organomet. Chem.* **1994**, *483*, 61. (d) Wu, Y. J.; Liu, Y. H.; Ding, K. L.; Yuan, H. Z.; Mao, X. A. *J. Organomet. Chem.* **1995**, *505*, 37.

(7) Zhao, G.; Xue, F.; Zhang, Z. Y.; Mak, T. C. W. *Organometallics* **1997**, *16*, 4023. López, C.; Bosque, R.; Sainz, D.; Solans, X.; Font-Bardía, M. *Organometallics* **1997**, *16*, 3261.

(8) Ranatunge-Bandarage, P. R. R.; Duffy, N. W.; Johnson, S. M.; Robinson, B. H.; Simpson, J. *Organometallics* **1994**, *13*, 511.

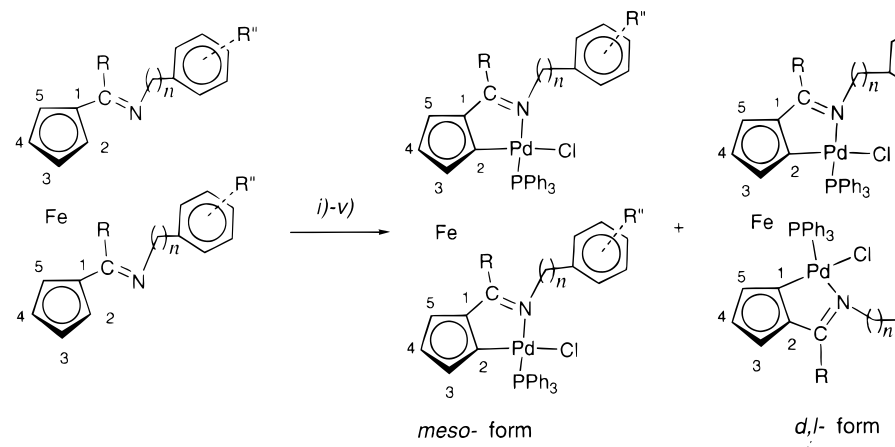
(9) López, C.; Bosque, R. *J. Organomet. Chem.* **1996**, *524*, 247. Bosque, R.; López, C.; Sales, J.; Solans, X.; Silver, J. *J. Chem. Soc., Dalton Trans.* **1996**, 3195.

(10) Sugimoto, M.; Nonoyama, M. *Inorg., Nucl. Chem. Lett.* **1979**, 405.

(11) Balavoine, G. G. A.; Doisneau, G.; Fillebeen-Khan, T. *J. Organomet. Chem.* **1991**, *412*, 381.

10.1021/om980834e CCC: $18.00 © 1999 American Chemical Society
Publication on Web 03/11/1999

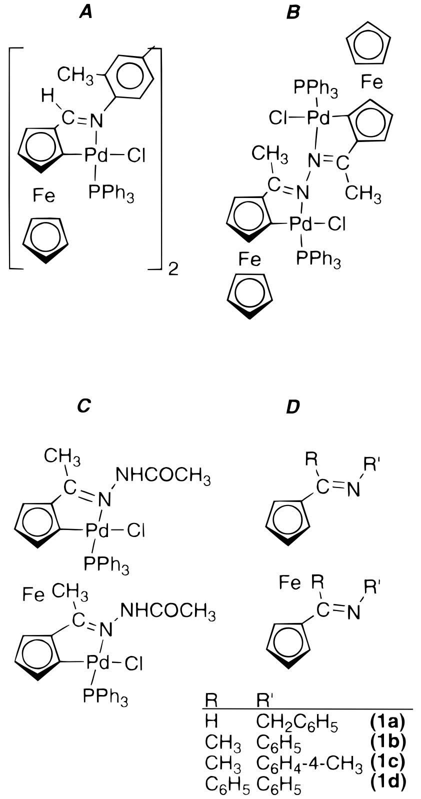
Scheme 1[a]



n	R	R"	ligand
1	H	H	**1a**
0	CH_3	H	**1b**
0	CH_3	4-CH_3	**1c**

n	R	R"	complex
1	H	H	**2a**
0	CH_3	H	**2b**
0	CH_3	4-CH_3	**2c**

[a] (i) $Na_2[PdCl_4]$, $Na(CH_3COO)\cdot 3H_2O$, in MeOH at room temperature. (ii) PPh_3, in benzene at room temperature. (iii) SiO_2 column chromatography, CH_2Cl_2 as eluant. (iv) Small amounts of $[PdCl_2(PPh_3)_2]$ were also formed in these reactions (see text). (v) Traces of the monocyclopalladated complexes **3a** and **3c** were also obtained when the reactions were carried out using the ferrocenylimines **1a** or **1c** as starting materials (see text).



R	R'	
H	$CH_2C_6H_5$	**(1a)**
CH_3	C_6H_5	**(1b)**
CH_3	C_6H_4-4-CH_3	**(1c)**
C_6H_5	C_6H_5	**(1d)**

Figure 1. Schematic view of the bis(cyclopalladated) complexes containing $\sigma(Pd-C_{sp^2,ferrocene})$ bonds described so far and of the 1,1′-ferrocenyldiimines of general formula $[Fe\{(\eta^5\text{-}C_5H_4)-C(R)=N-R'\}_2)]$ (**1a**−**1d**) under study.

$C_5H_4)-C(H)=N-R'\}]$, with R′ = phenyl or benzyl groups,[6a,b] which consists of the reaction of the starting materials in benzene using a Dean−Stark apparatus to remove the azeotrope (benzene/water) formed in the course of the reaction.[6a,b] This method failed for the syntheses of the 1,1′-diimines $[Fe\{(\eta^5\text{-}C_5H_4)-C(CH_3)=N-C_6H_4\text{-}4\text{-}R\}_2]$ {with R = H **(1b)** or CH_3 **(1c)**}. This finding is consistent with the results reported for $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(R)=N-R'\}]$ {with R′ = H or CH_3}.[6a,b] However, **1b** and **1c** were prepared successfully by reaction of 1,1′-diacetylferrocene and the amines in refluxing toluene and in the presence of freshly activated alumina.[12] In these reactions large excesses of the amines were needed to force the displacement of the equilibria. Ligand **1d**[13] was prepared in a similar way, but using 1,1′-dibenzoylferrocene as starting material. For **1d**, the reaction requires longer times, ca. 2 weeks, and larger excesses of aniline. The difficulties of preparing ligands **1** increase according to the sequence **1a** $\ll$ **1b** $\approx$ **1c** < **1d**; this variation might be attributed to the larger bulk of the substituent on the >C(O) group {CH_3 or C_6H_5} versus hydrogen.[14]

Compounds **1** are orange **(1b**, **1c)** or red solids **(1a**, **1d)** at room temperature and have been characterized by elemental analyses and infrared and NMR spectroscopies. The NMR studies of these compounds suggested that only one isomer (*anti*) was present in solution.

The reaction of ligand **1a** with $Na_2[PdCl_4]$ and $Na(CH_3COO)\cdot 3H_2O$ (in a 1:2:2 molar ratio) in methanol at room temperature for 2 days produced a red solid. Subsequent treatment of this material with PPh_3 in benzene for 3 h and concentration of the solution to dryness gave a deep red solid (Scheme 1), and three complexes could

---

(12) The success of the syntheses of compounds **1b** and **1c** is strongly dependent on the proper activation of the alumina. In our case the activation was carried out by heating Al_2O_3 in a hood at 250 °C for 24 h. After this period the alumina was transferred to an oven at 130 °C to avoid rehydration.

(13) This complex can also be synthesized using the procedure described by Cais, M.; Ashkenazi, P.; Dani, S.; Gottlieb, J. In *J. Organomet. Chem.* **1977**, *124*, 49, which requires the use of $TiCl_4$ and the aniline 1,1′-dibenzoylferrocene, molar ratio equal to 44:1, and benzene as solvent. In addition, this procedure produces a mixture of several compounds, and ligand **1d** was separated (also in a low yield: 35%) by column chromatography.

(14) Hansch, C.; Leo, A.; Koekman, D. *Exploring QSAR, Hydrophobic, Electronic and Steric Constants*; ACS, Prof. Reference Book: Washington, DC, 1995.

be isolated by column chromatography: $[PdCl_2(PPh_3)_2]$, $[Pd_2\{Fe[(\eta^5\text{-}C_5H_3)-C(H)=N-CH_2-C_6H_5]_2\}Cl_2(PPh_3)_2]$ **(2a)**, and small amounts (ca. 7−8%) of $[Pd\{[(\eta^5\text{-}C_5H_3)-C(H)=N-CH_2-C_6H_5]Fe[(\eta^5\text{-}C_5H_4)-C(H)=N-CH_2-C_6H_5]\}Cl(PPh_3)]$ **(3a)**. Compounds **3a** and **2a** arise from the mono- and 1,1′-bis(metalation) of the ligand, respectively.

The activation of two *ortho* $\sigma(C_{sp^2,\ ferrocene}-H)$ bonds in N-donor ferrocenyl ligands introduces planar chirality,[2,15] and consequently, two stereoisomers {*meso*- and *d,l*-forms} could be expected in the double cyclopalladation of **1** (Scheme 1). Attempts to separate the two isomers of **2a** by either column chromatography or fractional crystallization failed. However, the assignment of the signals observed in the ^{1}H NMR for each of the isomers was carried out by comparison with the results obtained for compounds $[Pd_2\{Fe[(\eta^5\text{-}C_5H_3)-C(CH_3)=N-R']_2)\}Cl_2(PPh_3)_2]$ **(2b**, **2c)** (vide infra), and the integration of the signals due to protons of the $>CH=N-$ group and the C_5H_3 ring revealed that the two isomers coexisted in the molar ratio *meso*/*d,l* = 1.2.

When the reaction was carried out using **1b** or **1c** and identical experimental conditions, the coordination complex $[PdCl_2(PPh_3)_2]$ and the two stereoisomers {*meso*- and *d,l*-forms} of compounds $[Pd_2\{Fe[(\eta^5\text{-}C_5H_3)-C(CH_3)=N-R']_2\}Cl_2(PPh_3)_2]$ {with $R' = C_6H_5$ **(2b)**, $C_6H_4\text{-}4\text{-}CH_3$ **(2c)**} were isolated. The ratio between the two stereoisomers {*meso*-form/*d,l*-form = 3.2 for **2b** and 2.9 for **2c**} was clearly greater than for **2a** (1.2). When the reaction was performed using ligand **1c**, a small amount (ca. 8%) of $[Pd\{[(\eta^5\text{-}C_5H_3)-C(CH_3)=N-CH_2-C_6H_5]\}Fe[(\eta^5\text{-}C_5H_4)-C(CH_3)=N-CH_2-C_6H_5]\}Cl(PPh_3)]$ **(3c)** was also obtained. In contrast, no evidence of the presence of $[Pd\{[(\eta^5\text{-}C_5H_3)-C(CH_3)=N-(C_6H_4\text{-}4\text{-}CH_3)]Fe[(\eta^5\text{-}C_5H_4)-C(CH_3)=N-C_6H_5]\}Cl(PPh_3)]$ **(3b)** was detected when the reaction was carried out with **1b**.

Although these reactions were performed in identical experimental conditions, compounds **2b** and **2c** were obtained with a higher yield (52 and 46%) than **2a** (32%). This fact is consistent with previous studies on the cyclopalladation of the ferrocenylimines $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(R)=N-R'\}]$ (with R = H or CH_3), since for ligands with R = CH_3 the formation of the palladacycle is achieved faster than for those with R = H.[6b] The two isomers of compounds **2b** and **2c** were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies (see Experimental Section).

A perspective drawing of the molecular structure of the *meso*-form of **2b** is depicted in Figure 2. A selection of bond lengths and angles is presented in Table 1. The structure consists of discrete molecules of $[Pd_2\{Fe[(\eta^5\text{-}C_5H_3)-C(CH_3)=N-C_6H_5]_2\}Cl_2(PPh_3)_2]$ separated by van der Waals contacts. Each molecule has two "$[Pd\{(\eta^5\text{-}C_5H_3)-C(CH_3)=N-C_6H_5\}Cl(PPh_3)]$" fragments, which contain a five-membered metallacycle formed by the palladium, the nitrogen, and carbon atoms involved in the imine bond and two carbon atoms of the C_5H_3 ring {C(1) and C(5)}, thus confirming that cyclometalation had taken place on the ferrocenyl unit. The bicyclic system formed by the metallacycle and the C_5H_3 moiety is practically planar, and their planes form an angle of 5.5°.

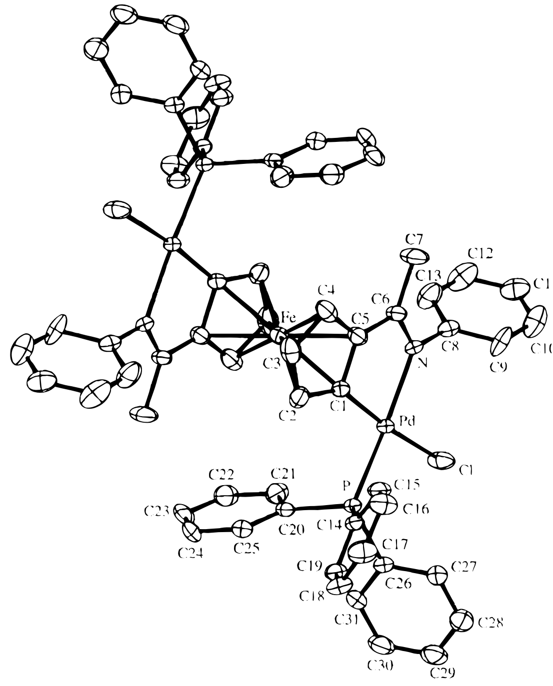


Figure 2. View of the molecular structure together with the atom-numbering scheme for the *meso*-form of $[Pd_2\{Fe[(\eta^5\text{-}C_5H_3)-C(CH_3)=N-C_6H_5]_2\}Cl_2(PPh_3)_2]$ (**2b**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the *meso*-Form of Compound $[Pd_2\{Fe[(\eta^5\text{-}C_5H_3)-C(CH_3)=N-C_6H_5]_2\}Cl_2(PPh_3)_2]$ (2b) with Estimated Standard Deviations in Parentheses

(A) Bond Lengths			
Pd−P	2.333(10)	Pd−Cl	2.3519(12)
Pd−N	2.128(3)	Pd−C(1)	2.006(4)
C(1)−C(5)	1.421(6)	C(5)−C(6)	1.346(7)
N−C(6)	1.305(5)	N−C(8)	1.422(5)
C(6)−C(7)	1.506(6)	Fe−C[a]	2.04(2)
C−C[a]	1.42(12)		
(B) Bond Angles			
P−Pd−Cl	93.37(4)	Cl−Pd−N	93.65(10)
N−Pd−C(1)	80.3(2)	C(1)−Pd−P	92.78(12)
Pd−C(1)−C(5)	111.0(3)	C(1)−C(5)−C(6)	119.1(4)
C(5)−C(6)−N	114.3(4)	C(6)−N−Pd	114.2(3)
C(5)−C(6)−C(7)	121.3(4)	C(7)−C(6)−N	124.3(4)
Pd−N−C(8)	126.8(3)		

[a] Average value for the C_5H_3 units.

The palladium atom is tetracoordinated, since it is bound to a chloride, the phosphorus atom of the PPh_3, the imine nitrogen, and the C(1) carbon atom of the ferrocenyl fragment, giving a slightly distorted square-planar environment around the palladium.[16] The Pd−ligand bond lengths (Table 1) as well as bond angles between adjacent atoms in the coordination sphere of the palladium are similar to those obtained in five-membered palladacycles containing a $\sigma(Pd-C_{sp^2,ferrocene})$ bond.[6]

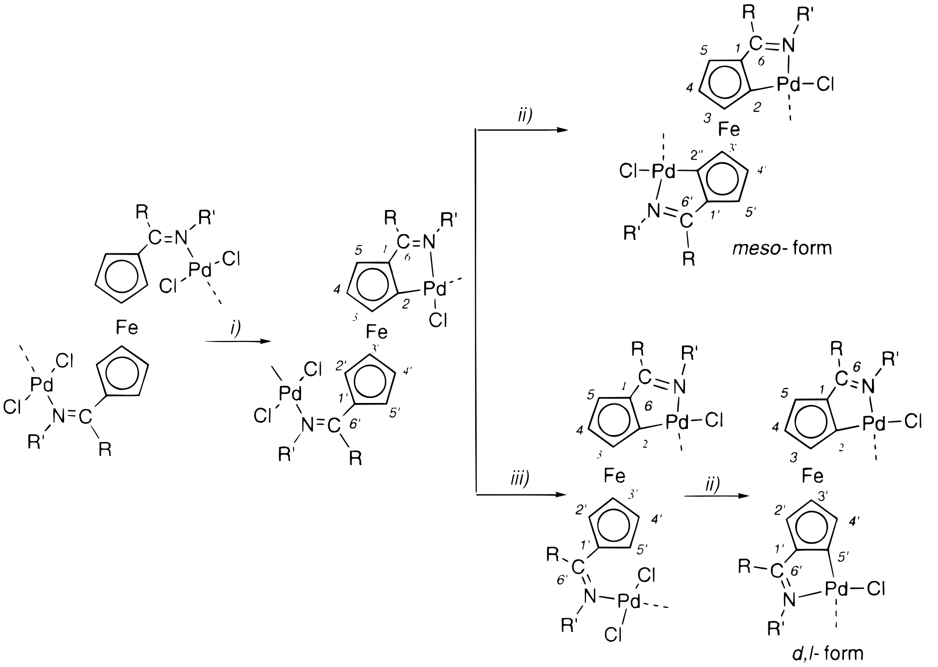
In complex **2b** the two imine groups have an *anti*-conformation, as reflected in the torsion angle C(5)−C(6)−N−C(8) = 173.9(4)°}. The $>C=N-$ bond length [1.305(5) Å] is similar to those reported for the related ferrocenyl Schiff bases[17] and their monocyclopalladated

---

[15] Sokolov, V. I. *Chirality and Optical Activity in Organometallic Chemistry*; Gordon and Breach: London, 1991.

[16] The least-squares equation of the plane defined by the atoms Pd, P, N, Cl, and C(1) is (0.7958)XO + (−0.1388)YO + (0.5895)ZO = 5.4698. The deviations from the plane are Pd, −0.011; P, +0.036; Cl, −0.034; N, 0.043 and C(1), −0.005 Å.

Scheme 2[a]



[a] (i) Monometalation. (ii) Metalation. (iii) Rotation around the $C_{1'}-C_{1'}$ bond.

complexes $[Pd\{[(\eta^5\text{-}C_5H_3)-C(R)=N-R']Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ {with R = H, CH_3, or Ph, and R′ = phenyl or benzyl groups}.[6]

The phosphorus and the imine nitrogen are in *trans*-arrangement {P−Pd−N bond angle = 172.49(10)°}, thus consistent with the results obtained from ^{31}P NMR. The phenyl rings are planar and geometry of the ferrocenyl moiety has average $Fe-C_{ring}$ and $C-C_{ring}$ bond lengths, in good agreement with data reported for other ferrocene derivatives.[18]

According to the general mechanism proposed for cyclopalladation, the reaction proceeds in two steps: the binding of the palladium to the nitrogen and the subsequent electrophilic attack.[19] When N-donor ferrocenyl ligands such as $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(R)=N-R'\}]$ are used as starting materials, the reaction produces di-μ-chloro-bridged cyclopalladated derivatives, i.e., $[Pd\{[(\eta^5\text{-}C_5H_3)-C(R)=N-R']Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$, which are highly insoluble and difficult to characterize. These polynuclear complexes react with Lewis bases, L, giving $[Pd\{[(\eta^5\text{-}C_5H_3)-C(R)=N-R']Fe(\eta^5\text{-}C_5H_5)\}Cl(L)]$. On these bases, the formation of the two stereoisomers (*meso*- and *d,l*-forms) of compounds **2a**−**2c** can be easily explained since once the first metallacycle is formed (Scheme 2), the orientation of the other cyclopentadienyl ring during the subsequent metalation determines the stereochemistry of the reaction. That is to say, if the electrophilic attack of the palladium takes place on the $C_{2'}$, site the *meso*-isomer would be formed. The formation of the other stereoisomer (*d,l*-form) requires (a) the rotation around the $C_{1'}-C_{6'}$ bond and (b) the subsequent electrophilic attack of the palladium to the $C_{5'}$. It is worth noting that the interconversion of the two stereoisomers (*d,l*-form ↔ *meso*-form) would require the cleavage of the σ(Pd−C) bond.

In addition, it is well-known that the reaction of the di-μ-chloro-bridged complexes with Lewis bases, such PPh_3, does not involve cleavage of the Pd−N bond. Thus, the differences in the relative proportion of the two stereoisomers (*meso*-/*d,l*-form) in **2a** (1.2), **2b** (3.2), and **2c** (2.9) might be related to the ease with which the rotation around the $C_{1'}-C_{6'}$ bond occurs. A similar argument has been used to explain the stereoselectivity of the bis(cycloplatination) of $[Fe\{(\eta^5\text{-}C_5H_4)-CH_2-N-(CH_3)_2\}_2]$.[8]

The presence of bulky substituents on the imine group would hinder the free rotation around the $C_{1'}-C_{6'}$ bond. Thus, an increase in the ratio *meso*-/*d,l*-form would be expected. Since the substituents R and R′ in imines **1b** and **1c** are bulkier[14] than in **1a**, the free rotation around the $C_{1'}-C_{6'}$ bond would be more difficult and the formation of the *d,l*-form of **2b** and **2c** would be less favored.

More interesting are the results obtained when the reaction was carried out using ligand **1d** and identical experimental conditions. The ^{1}H and ^{13}C NMR spectra of the final product were more complex than expected. Seven signals (of identical intensity) in the range 3.20−5.20 ppm were observed in the ^{1}H NMR spectrum. The 2D heteronuclear {^{1}H−^{13}C} correlation showed seven cross-peaks in the range 3.0−5.2 ppm (Figure 3).

The ^{13}C NMR spectra showed 10 signals in the range 105.0−70.0 ppm and two low-intensity signals at ca. 182.85 and 197.98 ppm, respectively. Comparison of the position of these signals with ^{13}C NMR data of **2a**−**2c** and of the monometalated derivative $[Pd\{[(\eta^5\text{-}C_5H_3)-C(C_6H_5)=N-C_6H_5]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ **(3e)** {δ^{13}C (>C=N−) = 183.44 ppm[6c]} allowed us to assign the

---

(17) López, C.; Bosque, R.; Solans, X.; Font-Bardía, M. *New J. Chem.* **1996**, *20*, 1295.

(18) Allen, T. H.; Kennard, O. *Chem. Des. Automat. News* **1993**, *8*, 146.

(19) Ryabov, A. D.; Sakodinskaya, I. K.; Yatsimirski, A. K. *J. Chem. Soc., Dalton Trans.* **1985**, 2629. Ryabov, A. D.; Yatsimirski, A. K. *Inorg. Chem.* **1984**, *23*, 789. Ryabov, A. D. *Inorg. Chem.* **1987**, *26*, 1252. Gómez, M.; Granell, J.; Martinez, M. *Organometallics* **1997**, *16*, 2539. Gómez, M.; Granell, J.; Martinez, M. *J. Chem. Soc., Dalton Trans.* **1998**, 37.

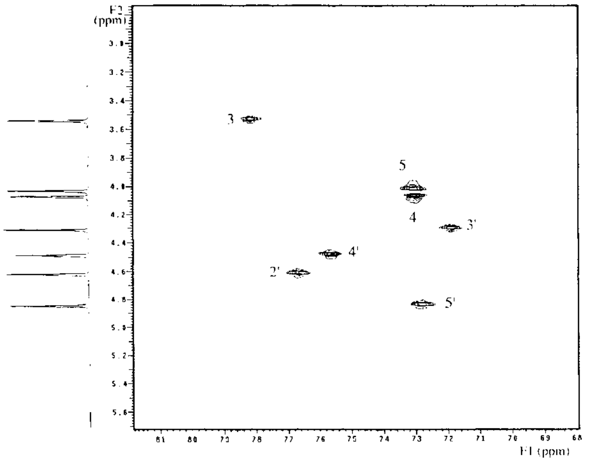


Figure 3. Partial view of the 2D heteronuclear {$^1H-^{13}C$} correlation (500 MHz) of the solid isolated in the reaction of **1d**. The numbers 3, 4, and 5 correspond to the protons or carbons of the metalated C_5H_3 ring, and the numbers 2′, 3′, 4′, and 5′ refer to the nonmetalated C_5H_4 ring.

signal at ca. 182.85 ppm to the >C=N− group. The position of the singlet at 197.97 ppm was similar to that observed in the ^{13}C NMR spectrum of 1,1′-dibenzoylferrocene [198.46 ppm][20] and could be ascribed to the >C(O) group. In addition, two bands [at 1628 and 1637 cm^{-1}] were detected in the infrared spectrum. These absorptions are ascribed to the stretching of the >C=N− and >C(O) groups, {ν{>C(O)}[20] = 1637 cm^{-1} for 1,1′-dibenzoylferrocene[20]}. The elemental analyses agreed with those expected for $[Pd\{[(\eta^5\text{-}C_5H_3)-C(C_6H_5)=N-C_6H_5]Fe[(\eta^5\text{-}C_5H_4)-C(O)=N-C_6H_5]\}Cl(PPh_3)]$ **(4d)**, which arises from the monocyclopalladation of the ligand and the hydrolysis of one of the two >C=N− groups of ligand **1d**. The IR spectrum of the crude solid isolated after the reaction also showed a band at 1637 cm^{-1}. This suggested that the hydrolysis took place before the chromatography. No evidence of the formation of any other cyclopalladated complex was detected in this case.

As mentioned above, the reaction of **1a**, **1b,** or **1c**, with $Na_2[PdCl_4]$ and $Na(CH_3COO)\cdot 3H_2O$, produced the bis(cyclopalladated) compounds **2a**−**2c**. For **1a** and **1c**, small amounts of the monometalated derivatives **(3a**, **3c)** were also isolated. However, in none of these reactions was there any evidence of the hydrolysis of either of the two >C=N− bonds. In contrast, when **1d** was used, complex $[Pd\{[(\eta^5\text{-}C_5H_3)-C(C_6H_5)=N-C_6H_5]\text{-}Fe[(\eta^5\text{-}C_5H_4)-C(O)=N-C_6H_5]\}Cl(PPh_3)]$ **(4d)** (which requires the hydrolysis of the imine group) was formed instead of the bis(cyclopalladated) derivative $[Pd_2\{Fe\text{-}[(\eta^5\text{-}C_5H_3)-C(C_6H_5)=N-C_6H_5]_2\}Cl_2(PPh_3)_2]$ **(2d)** (which is formally analogous to **2a**−**2c**), and the monometalated derivative $[Pd\{[(\eta^5\text{-}C_5H_3)-C(C_6H_5)=N-C_6H_5]Fe\text{-}[(\eta^5\text{-}C_5H_4)-C(C_6H_5)=N-C_6H_5]\}Cl(PPh_3)]$ **(3d)** was not detected.

To elucidate whether the differences observed in the nature of the final products isolated in the cyclopalladation of **1d**, when compared with those of **1a**−**1c**, could be related to the steric hindrance introduced by the bulky phenyl rings bound to the >C=N− groups in **1c**, molecular models for the ligand and for the two stereoisomers complex **2d** were built. Their manipulation showed that the phenyl rings bound to the imine carbon cannot be coplanar with the C_5H_3 unit. This is consistent with the arrangement of rings found in the crystal structures of the imines $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(R)=N-R'\}]$.[17]

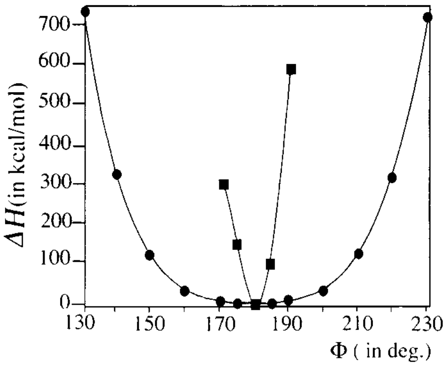


Figure 4. Plots of the variation of the formation enthalpy, ΔH (in kcal/mol), for the *meso*-forms of **2b** (filled circles) and **2d** (filled squares) versus the torsion angle Φ (in degrees). The variation of the formation enthalpy, ΔH, was calculated according to the expression $\Delta H = \Delta H_{form}$ (for a Φ value) - ΔH_{form} (for a $\Phi = 180°$).

In compounds **2**, the relative orientation of the two palladacycles can be described by the torsion angle defined by C_6, χ, χ', and $C_{6'}$ (hereafter referred to as Φ), where C_6 and $C_{6'}$ are the imine carbon atoms of the two C_5H_3 rings and χ, χ' represent the centroids of these rings. The use of molecular models for **2** suggests that a parallel orientation of the two metallacycles ($\Phi = 0°$) is not possible due to strong steric hindrance produced by short contacts between the phenyl rings of the two PPh_3 {for the *meso*-form} or between the phenyl rings of the PPh_3 ligand in one moiety and the substituents on the imine carbon {in the *d*,*l*-form}. For the *meso*-form of **2**, the less hindered orientation corresponds to $\Phi \approx 180°$ (which agrees with the X-ray data of **2b**). The use of the Spartan 4.1 program[21] has allowed us to compare the formation enthalpy for the different arrangements of the two metallacycles in the *meso*-form of **2b**. Figure 4 shows the variation of the formation enthalpy {ΔH} for a wide variety of orientations {Φ from 130° to 230°}. For Φ values larger than 230° (or smaller than 130°) the system collapses due to short contacts between the CH_3 group in one of the moieties and the aryl rings of the PPh_3 group in the other fragment. Data shown in Figure 4 indicate that the rotation is resticted to a narrow interval of Φ.

In complex **3d**, which can be visualized as derived from **2b** by replacement of the two methyl groups by phenyl rings, the distribution of the substituents in each one of the moieties is more crowded, leading to an increase of the steric hindrance, which would destabilize the molecule. In fact, even for the less hindered arrangement of the metallacycles in the *meso*-form of **3d** ($\Phi = 180°$) short contacts between the hydrogen atoms on the *meta*-sites of the phenyl rings of the PPh_3 ligand (in one of the moieties) and two carbon atoms of the imine C_6H_5 ring of the other half appeared ($H_{meta}\cdots C_{meta}$ 0.85 Å and $H_{meta}\cdots C_{para}$ 0.85 Å). Besides that, it is

---

[20] *Gmelins Handbuch der Anorganische Chemie: Ferrocen*; Springer-Verlag: Heidelberg, Germany, 1977; Vol. A3, p 181.

[21] *SPARTAN 4.0*; Wavefunction Inc.: 18401 Von Karman Ave 3370, Irvine, CA 92715, 1995.

noteworthy to remark that in **3d** tiny modifications of the Φ angle (i.e. $\Phi = 180 \pm 5°$) produce a significant increase of the formation enthalpy (Figure 4). These facts could be related with the ease with which the hydrolysis of one of the two >C═N− groups takes place. This process would significatly reduce the steric hindrance around the coordinative nitrogen and the palladium.

Experimental Section

Elemental analyses (C, H, and N) were carried out at the Serveis Cientifico-Tècnics de la Universitat de Barcelona. Infrared spectra were obtained with a NICOLET-Impact 400 spectrophotometer using KBr pellets. ^{31}P NMR spectra of **2**, **3**, and **4d** were obtained with a Bruker-250-DRX instrument using $CDCl_3$ as solvent and $P(OCH_3)_3$ as reference [δ^{31}P-{$P(OCH_3)_3$} = 140.17 ppm]. ^{13}C{^{1}H} NMR spectra were obtained with a Varian-300 MHz instrument using $CDCl_3$ as solvent and TMS as internal standard. High-resolution ^{1}H NMR spectra and the heteronuclear {^{1}H−^{13}C} NMR experiments were undertaken with a Bruker 500 MHz instrument and using $CDCl_3$ as solvent and TMS as internal standard.

Materials and Syntheses. 1,1′-Diacetylferrocene, 1,1′-dibenzoylferrocene, and the amines were obtained from commercial sources and used as received. 1,1′-Diformylferrocene was prepared as reported previously.[12] The solvents except benzene were distilled and dried before use (CH_2Cl_2 over CaO and CH_3OH over $CaCl_2$).

Some of the preparations described below require the use of benzene, which should be handled with **CAUTION**.

[Fe{(η^5-C_5H_4)−CH═N−CH_2−C_6H_4}$_2$] (1a). A 1.0 g amount (4.14 mmol) of 1,1-[Fe{(η^5-C_5H_4)−CH(O)]^{12} was suspended in 50 cm^3 of benzene, stirred at room temperature for 30 min, and filtered out. Then, the stoichiometric amount of benzylamine (8.28 mmol) was added to the filtrate. The reaction flask was then connected to a condenser equipped with a Dean−Stark apparatus, and the reaction mixture was refluxed until ca. 15 cm^3 had condensed. The resulting solution was filtered, and the filtrate was concentrated to dryness on a rotary evaporator, giving a deep red solid, which was collected and dried in vaccum (yield: 725 mg, 42%). **Characterization Data for 1a.** Anal. (%) Calcd for $C_{26}H_{24}N_2Fe$ (found): C, 74.29 (74.5); H, 5.75 (5.9); N, 6.66 (6.5). IR: 1625 cm^{-1}. ^{1}H NMR (in ppm):[22] ferrocenyl moiety, 4.66 [4 H, H^2 and H^5] and 4.36 [4 H, H^3 and H^4]; 8.10 [2 H, −*CH*═*N*−]; 4.59 [2 H, −CH_2−]; 7.2−7.8 [10 H, *aromatic*]. ^{13}C NMR (in ppm):[22] ferrocenyl moiety, 81.96 [C^1], 71.93 [C^2, C^5]; 70.19 [C^3, C^4]; 65.75 [−CH_2−], 161.78 [−*C*H═N−] and 139.89, 129.01, 128.4, and 127.46 [*aromatic*].

[Fe{(η^5-C_5H_4)−C(CH_3)═N−C_6H_4-4-R}$_2$] {with R = H (1b) or CH_3 (1c)}. 1,1′-Diacetylferrocene (1.0 g, 3.7 mmol), freshly activated alumina (2.5 g), and 3.7 mmol of aniline (for **1b**) or 4-methylaniline (for **1c**) were suspended in dried toluene (50 cm^3) and refluxed. To control the progress of the condensation reaction, the infrared spectra of the solution were recorded. Daily additions of small quantities of the amines (ca. 0.5 cm^3) and activated alumina (1.0 g) were needed to force the displacement of the equilibria. This procedure was repeated for 8−10 days until the infrared spectra did not exhibit the band due to the asymmetric stretching of the >C═O group [ν(C═O) = 1665 cm^{-1}].[20] The undissolved materials were then removed by filtration and washed with dried toluene until the washings became colorless. The orange-red solution was concentrated to dryness on a rotary evaporator, and the oil formed was treated with *n*-hexane (ca. 30 cm^3) and stirred at room temperature for 30 min. The solids formed were collected by filtration and air-dried {yields: 903 mg, (58%) for **1b** and 764 mg (46%) for **1c**}.

Characterization Data for 1b. Anal. (%) Calcd for $C_{26}H_{24}N_2Fe$ (found): C, 74.29 (74.0); H, 5.75 (5.7); N, 6.66 (6.6). IR: ν(>C═N−) = 1618 cm^{-1}.^{1}H NMR (in ppm):[21] ferrocenyl moiety, 4.85 [4 H, H^2 and H^5], 4.50 [4 H, H^3 and H^4]; 2.15 [6 H, −C(CH_3)═N−] and aromatic protons, 7.39 [4 H, H^α], 7.09 [4H, H^β] and 6.81 [2 H, H^γ]. ^{13}C NMR (in ppm):[22] ferrocenyl moiety, 85.56 [C^1], 72.39 [C^2 and C^5], 70.56 [C^3 and C^4]; 18.46 [CH_3], 167.34 [>*C*═N−], and 152.01, 129.36, 123.56, and 120.15 [*aromatic*].

1c. Anal. (%) Calcd for $C_{28}H_{28}N_2Fe$ (found): C, 75.03 (74.9); H, 6.25 (6.1); N, 6.30 (6.2). IR: ν(>C═N−) = 1623 cm^{-1}.^{1}H NMR (in ppm):[22] ferrocenyl moiety, 4.80 [4 H, H^2 and H^5], 4.48 [4 H, H^3 and H^4]; 2.15 [6 H, −C(CH_3)═N−]; 2.32 [6 H, CH_3] and aromatic protons, 7.10 [4 H, H^α] and 6.64 [4 H, H^β]. ^{13}C NMR (in ppm):[22] ferrocenyl moiety: 85.70 [C^1], 72.31 [C^2 and C^5], 69.98 [C^3 and C^4]; 18.59 [CH_3], 167.34 [>*C*═N−], 17.6 [CH_3], 149.45, 132.91, and 122.54 [*aromatic*].

[Fe{(η^5-C_5H_4)−C(C_6H_5)═N−C_6H_5}$_2$] (1d). This compound was prepared using the same procedure as for **1b** and **1c**; in this case the progress of the reaction was monitored by IR spectroscopy (yield: 38%).

Characterization Data for 1d. Anal. (%) Calcd for $C_{36}H_{28}N_2Fe$ (found): C, 79.41 (79.3); H, 5.18 (5.25); N, 5.14 (5.0). IR: 1602 cm^{-1}. ^{1}H NMR data (in ppm):[22] ferrocenyl moiety, 4.87 [4 H, H^2 and H^5] and 4.53 [4 H, H^3 and H^4]; 6.9−7.6 [20 H, *aromatic*].

[Pd_2{Fe[(η^5-C_5H_3)−C(R)═N−R′]$_2$}Cl_2(PPh_3)$_2$] {with R = H, R′ = CH_2−C_6H_5 (2a), R = CH_3, R′ = C_6H_5 (2b), or C_6H_4-4-CH_3 (2c)}. The corresponding 1,1′-ferrocenyldiimine (**1a**−**1c**) (0.720 mmol), $Na_2[PdCl_4]$ (0.426 g, 1.45 mmol), and $Na(CH_3COO)\cdot 3H_2O$ (0.197 g, 1.46 mmol) were suspended in methanol (50 cm^3). The reaction flask was protected from light with aluminum foil and stirred at room temperature (ca. 20 °C) for 2 days. The dark red precipitate formed was collected by vacuum filtration, washed with three portions (10 cm^3) of methanol, and air-dried. This material was then treated with PPh_3 (1.46 mmol) in 20 cm^3 of benzene. The resulting mixture was stirred at room temperature for 3 h. The undissolved materials were removed by filtration, and the red filtrate was concentrated to dryness on a rotary evaporator. The residue was dissolved in CH_2Cl_2 (ca. 30 cm^3) and filtered. The filtrate was then passed through a SiO_2 column (250 × 10 mm), using CH_2Cl_2 as eluant. When the reaction was carried out using ligand **1a**, three different bands were collected. After concentration to dryness of the first band eluted it gave complex [$PdCl_2(PPh_3)_2$]. A mixture of the two stereoisomers of **2a** (*meso*- and *d,l*-forms in a 1.2 molar ratio) was isolated after the concentration to dryness of the second band and the subsequent treatment of the residue with 20 cm^3 of *n*-hexane. The reddish solid formed was collected by filtration and air-dried (yield: 32%).

Three bands were collected when the reaction was performed with ligand **1b** or **1c**; the first band contained the coordination compound [$PdCl_2(PPh_3)_2$]. The two stereoisomers of compounds **2b** and **2c** were isolated from the two remaining bands using the identical procedure as for **2a**, yielding an orange (*meso*-isomers) and a red solid (*d,l*-isomer). The molar ratios (*meso*-form/*d,l*-form) were 3.2 and 2.9 for **2a** and **2b**, respectively. The *meso*-forms exhibited in both cases higher R_f values than the *d,l*-forms {yields: 460 mg (52%) for **2a** and 402 mg (46%) for **2b**}.

Characterization Data for 2a. Anal. (%) Calcd for $C_{62}H_{52}N_2Cl_2FeP_2Pd_2$ (found): C, 59.14 (59.1); H, 4.18 (4.1); N, 2.23 (2.2). IR: ν(>C═N−) = 1578 cm^{-1}. (*meso*-form) ^{1}H NMR (in ppm):[22] ferrocenyl moiety, 3.25 [2 H, H^3], 3.60 [2 H, H^4], 3.72 [2 H, H^5]; 5.16 and 4.60 [4 H, −CH_2−]; 8.10 [2 H, −CH═

---

[22] Selected data. Numbering of the atoms corresponds to that shown in Scheme 1.

N−[23]]. ^{31}P NMR (in ppm): 35.63. (*d,l*-form) ^{1}H NMR (in ppm):[22] ferrocenyl moiety, 2.87 [2 H, H^3]; 4.11 [2 H, H^4], 4.22 [2 H, H^5]; 4.88 and 4.48 [4 H, −CH_2−]; 8.19 [2 H, −C*H*=N−[23]]. ^{31}P NMR (in ppm): 36.92. ^{13}C NMR (in ppm):[22] ferrocenyl moiety, 93.18 [C^1], 101.52 [C^2], 78.28 [C^3], 78.19 [C^4] and 71.56 [C^5]; 182.60 [>*C*=N−], 17.95 [*C*H_3].

For 2b. Anal. (%) Calcd for $C_{62}H_{52}N_2Cl_2FeP_2Pd_2$ (found): C, 60.71 (60.75); H, 4.27 (4.3); N, 2.28 (2.2). IR: ν(>C=N−) = 1590 cm^{-1}. (*meso*-form) ^{1}H NMR (in ppm):[22] ferrocenyl moiety, 3.09 [2 H, H^3]; 4.16 [2 H, H^4], 4.19 [2 H, H^5]; 1.54 [6 H, −C(CH_3)=N−]. ^{31}P NMR (in ppm): 37.53. ^{13}C NMR (in ppm):[22] ferrocenyl moiety, 89.36 [C^1], 103.37 [C^2], 73.74 [C^3], 77.17 [C^4] and 69.78 [C^5]; 181.20 [>*C*=N−], 21.69 [*C*H_3]. (*d,l* − form): ^{1}H NMR (in ppm):[22] ferrocenyl moiety, 2.85 [2 H, H^3]; 3.98 [2 H, H^4], 4.22 [2 H, H^5]; 2.09 [6 H, −C(CH_3)=N−].^{31}P NMR (in ppm): 38.85. ^{13}C NMR (in ppm):[22] ferrocenyl moiety, 93.18 [C^1], 101.52 [C^2], 78.28 [C^3], 78.19 [C^4] and 71.56 [C^5]; 182.60 [>*C*=N−], 17.95 [CH_3].

For 2c. Anal. (%) Calcd for $C_{64}H_{56}N_2Cl_2FeP_2Pd_2$ (found): C, 61.27 (61.0); H, 4.50 (4.55); N, 2.23 (2.25). IR: ν(>C=N−) = 1585 cm^{-1}. (*meso*-form) ^{1}H NMR (in ppm):[22] ferrocenyl moiety, 3.09 [2 H, H^3]; 4.11 [2 H, H^4], 4.15 [2 H, H^5]; 1.63 [6 H, −C(CH_3)=N−]; 2.37 [6 H, CH_3]. ^{31}P NMR (in ppm): 36.01. ^{13}C NMR (in ppm):[22] ferrocenyl moiety, 74.76 [C^3], 75.90 [C^4], 70.41 [C^5]; 183.26 [>*C*=N−]. (*d,l*-form) ^{1}H NMR (in ppm):[22] ferrocenyl moiety, 2.86 [2 H, H^3]; 3.85 [2 H, H^4]; 4.10 [2 H, H^5]; 2.05 [6 H, −C(CH_3)=N−]. ^{31}P NMR (in ppm): 37.03. ^{13}C NMR (in ppm):[22] ferrocenyl moiety, 73.53 [C^3], 71.11 [C^4]; 70.92 [C^5] and 184.51 [−*C*H=N−].

[Pd{[(η^5-C_5H_3)−C(R)=N−R′]Fe[(η^5-C_5H_4)−C(R)=N−R′]}-Cl(PPh_3)] {with R = H, R′ = CH_2−C_6H_5 (3a), R = CH_3, R′ = C_6H_5-4-CH_3 (3c)}. These compounds were isolated in a low yield as byproducts in the syntheses of **2a** and **2b**. The isolation of small amounts (yields < 10%) of these complexes was carried out according to the following procedure: once the bands containing compounds **2** were collected, a mixture of CH_2Cl_2/MeOH {100:1} was used as eluant. The red band was then collected and concentrated to dryness on a rotary evaporator, giving a deep red residue, which was collected and air-dried.

Characterization Data for 3a. Anal. (%) Calcd for $C_{44}H_{38}N_2ClFePPd$ (found): C, 64.58 (64.7); H, 4.65 (4.6); N, 3.40 (3.3). ^{1}H NMR (in ppm):[22] metalated ring, 3.40 [1 H, H^3]; 3.81 [1 H, H^4], 3.98 [1 H, H^4]; 7.90 [1 H, −C*H*=N−];[23] nonmetalated ring, 4.33 [1 H, H^2], 4.37 [1 H, H^3]; 4.65 [1 H, H^4], 4.76 [1 H, H^4] and 8.11 [1 H, −C*H*=N−]. ^{31}P NMR (in ppm): 38.40.

For 3c. Anal. (%) Calcd for $C_{44}H_{42}N_2ClFePPd$ (found): C, 64.88 (64.8); H, 4.97 (5.05); N, 3.29 (3.3). ^{1}H NMR (in ppm):[22] metalated ring, 3.37 [1 H, H^3]; 4.06 [1 H, H^4], 4.09 [1 H, H^5]; 2.07 [3 H, −C(CH_3)=N−]; nonmetalated ring, 4.38 [1 H, H^2], 4.22 [1 H, H^3]; 4.48 [1 H, H^4], 4.67 [1 H, H^5]; 2.25 [3 H, −C(CH_3)=N−]. ^{31}P NMR (in ppm): 38.40.

[Pd{[(η^5-C_5H_3)−C(C_6H_5)=N−C_6H_5]}Fe[(η^5-C_5H_4)−C(O)-(C_6H_5)]}Cl (PPh_3)] (4d). The diimine **1d** (0.500 g, 0.92 mmol), $Na_2[PdCl_4]$ (0.541 g, 1.84 mmol), and $NaCH_3COO\cdot 3H_2O$ (0.251 g,1.84 mmol), were suspended in 50 cm^3 of methanol. The reaction flask was protected from light with aluminum foil and stirred at ca. 20 °C for 2 days. The dark red solid formed was filtered out, washed with methanol until colorless mother liquors were obtained, and air-dried. This material was then suspended in 50 cm^3 of benzene and treated with 0.482 g (1.84 mmol) of PPh_3. The reaction mixture was stirred at room temperature (ca. 20 °C) for 3 h. After this period the undissolved materials were removed by filtration and discarded, and the red filtrate was concentrated to dryness on a rotary evaporator. The residue formed was dissolved in CH_2Cl_2 (15 cm^3) and passed through an SiO_2 column (15 × 1.5 mm). Elution with CH_2Cl_2 produced the release of a red band, which was collected and concentrated to dryness on a rotary evaporator. Addition of *n*-hexane followed by stirring at room temperature gave a bright red solid, which was collected and dried in a vacuum (yield: 385 mg, 46%).

Table 2. Crystallographic Data and Details of the Refinement of the Crystal Structure of the *meso*-Form of [Pd_2{Fe[(η^5-C_5H_3)−C(CH_3)=N−C_6H_5]$_2$}Cl_2(PPh_3)$_2$] (2b)

empirical formula	$C_{62}H_{52}Cl_2FeN_2P_2Pd_2$
M	1226.55
cryst size/mm	0.1 × 0.1 × 0.2
crystallographic system	monoclinic
a/Å	9.8267(13)
b/Å	14.3970(10)
c/Å	20.126(3) Å
$\alpha = \gamma$/deg	90.0
β/deg	90.130(10)
space group	$P2_1/c$
Z	2
D_c/g cm^{-3}	1.431
abs coeff/mm^{-1}	1.066
λ (Mo Kα)/Å	0.710 69
F(000)	1240
Θ range for data collection/deg	from 2.02 to 30.01
h, *k*, *l* ranges	$-13 \le h \le 13$, $0 \le k \le 20$, $0 \le l \le 28$
no. of reflns collected	6735
no. of ind reflns	6498 [*R*(int) = 0.0375]
no. of data	6448
no. of params	416
goodness of fit on F^2	1.050
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0548, wR2 = 0.1374
R indices (all data)	R1 = 0.0656, wR2 = 0.1520
extinction coeff	0.0003(2)
largest diff peak and hole/e Å^{-3}	0.635 and −0.407

Characterization Data for 4d. Anal. (%) Calcd for $C_{48}H_{38}$-ClFeNOPPd: C, 66.08 (65.95); H, 4.27 (4.3); N, 1.61 (1.6). IR: ν(>CO) = 1637 and ν(>C=N−) = 1628 cm^{-1}. ^{1}H NMR (in ppm):[22] ferrocenyl moiety, 3.54 [1 H, H^3]; 4.18 [1 H, H^4], 4.02 [1 H, H^5]; 4.31 [1 H, $H^{3'}$]; 4.48 [1 H, $H^{4'}$], 4.62 [1 H, $H^{2'}$] and 4.82 [1 H, $H^{5'}$].^{13}C NMR (in ppm):[22] ferrocenyl moiety, metalated ring, 102.76 [C^1], 92.47 [C^2], 78.26 [C^3], 73.20 [C^4] and 73.18 [C^5]; nonmetalated ring, 78.71 [$C^{1'}$], 73.18 [$C^{2'}$], 71.90 [$C^{3'}$], 75.62 [$C^{4'}$] and 72.8 [$C^{5'}$]; 182.84 [>*C*=N−] and 197.97 [>*C*(O)]. ^{31}P NMR (in ppm): 36.70 ppm.

Crystallography. A summary of the crystal data for the *meso*-form of **2b** is given in Table 2. A prismatic red crystal (0.1 mm × 0.1 mm × 0.2 mm) was selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit cell parameters were calculated from accurate settings of 25 automatically centered reflections in the range $12° \le \theta \le 21°$ and refined by the least-squares method. Intensities were collected with graphite-monochromated Mo Kα radiation, using $\omega-2\theta$ scans. The numbers of collected reflections in the range $2.02° \le \theta \le 30.01°$ and those assumed as observed [$I > 2\sigma(I)$] are given in Table 2. Three reflections were measured every 2 h as orientation and intensity control, and no significant intensity decay was observed. Lorentz−polarization corrections were made but not for absorption.

The structure was solved by direct methods using the SHELXS computer program[24] and refined by the full-matrix least-squares method with the SHELX93 computer program,[25] using 6448 reflections (very negative intensities were not assumed). The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0990P)^2 + 0.1314P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. Values of *f*, *f*′, and *f*″ were taken from the literature.[26]

---

[23] Doublet due to phosphorus coupling $^{3}J_{(P-H)}$ (in Hz) = 7.3 (**2a**) and 7.1 (**3a**).

[24] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[25] Sheldrick, G. M. *SHELX93. A computer program for determination of X-ray crystal structures*; University of Göttingen: Germany, 1990.

Twenty-three hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor, and three hydrogen atoms were computed and refined with an overal isotropic temperature factor using a riding model. The number of refined parameters was 416. The final *R* indices and further details concerning the refinement of the crystal structure are summarized in Table 2.

Computational Details. The SPARTAN 4.0 program[21] was used to calculate the formation enthalpy $\{\Delta H_{form}\}$ of the *meso*-forms of **2b** and **2d** for a wide variety of the torsion angle: Φ defined by C_6, χ, χ', and $C_{6'}$, where C_6 and $C_{6'}$ are the imine carbon atoms of the two C_5H_3 rings and χ, χ' represent the centroids of these rings. For **2b**, the atomic coordinates of all atoms obtained from the X-ray studies ($\Phi = 180°$) were used as imput in the CERIUS2.0 program[27] to generate the different arrangements of the two halves of the molecule, and the atomic coordinates obtained for each one of the Φ values were transferred to the SPARTAN 4.0 program[21] in order to obtain the formation enthalpy for each one of the conformations {defined by the Φ value}. For **2d**, the calculations were performed similarly, but replacing the two methyl groups of **2b** by phenyl rings.

Acknowledgment. We are grateful to the Ministerio de Educación and to the Generalitat de Catalunya for financial support (Grants PB96-0164 and 1997-SGR-0044).

Supporting Information Available: Tables containing final atomic coordinates for non-hydrogen atoms and equivalent isotropic displacement parameters (S1), a complete list of bond lengths and angles (S2), anisotropic displacement parameters (S3), hydrogen coordinates (S4), and hydrogen bond lengths and angles (S5) for the *meso*-form of **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980834E

---

[26] *International Tables of X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974, Vol. 4, pp 99, 100, and 149.

[27] *CERIUS2.0, Modeling Environment*; Molecular Simulation Incorporated, San Diego, CA 92121-3742, 1994.