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# Palladium(II)–allyl complexes containing chiral N-donor ferrocenyl ligands

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**Abstract**

A study of the reactivity of enantiopure ferrocenylimine ($S_C$)-[FcCH=N–CH(Me)(Ph)] {Fc = ($\eta^5$-$C_5H_5$)Fe{($\eta^5$-$C_5H_4$)–} (**1a**) with palladium(II)–allyl complexes [Pd($\eta^3$-1$R^1$,3$R^2$-$C_3H_3$)(μ-Cl)]$_2$ {$R^1$ = H and $R^2$ = H (**2**), Ph (**3**) or $R^1$ = $R^2$ = Ph (**4**)} is reported. Treatment of **1a** with **2** or **3** {in a molar ratio Pd(II):**1a** = 1} in $CH_2Cl_2$ at 298 K produced [Pd($\eta^3$-3$R^2$-$C_3H_4$){FcCH=N–CH(Me)(Ph)}Cl] {$R^2$ = H (**5a**) or Ph (**6a**)}. When the reaction was carried out under identical experimental conditions using complex **4** as starting material no evidence for the formation of [Pd($\eta^3$-1,3-$Ph_2$-$C_3H_3$){FcCH=N–CH(Me)(Ph)}Cl] (**7a**) was found. Additional studies on the reactivity of ($S_C$)-[FcCH=N–CH($R^3$)($CH_2$OH)] {$R^3$ = Me (**1b**) or $CHMe_2$ (**1c**)} with complex **4** showed the importance of the bulk of the substituents on the palladium(II) allyl–complex (**2**–**4**) or on the ferrocenylimines (**1**) in this type of reaction. The crystal structure of **5a** showed that: (a) the ferrocenylimine adopts an *anti*-(*E*) conformation and behaves as an N-donor ligand, (b) the chloride is in a *cis*-arrangement to the nitrogen and (c) the allyl group binds to the palladium(II) in a $\eta^3$-fashion. Solution NMR studies of **5a** and **6a** and [Pd($\eta^3$-1,3-$Ph_2$-$C_3H_3$){FcCH=N–CH(Me)($CH_2$OH)}Cl] (**7b**) revealed the coexistence of several isomers in solution. The stoichiometric reaction between **6a** and sodium diethyl 2-methylmalonate reveals that the formation of the achiral linear *trans*-(*E*) isomer of Ph–CH=CH–$CH_2$Nu (**8**) was preferred over the branched derivative (**9**). A comparative study of the potential utility of ligand **1a**, complex **5a** and the amine ($S_C$)-$H_2$N–CH(Me)(Ph) (**11**) as catalysts in the allylic alkylation of (*E*)-3-phenyl-2-propenyl (*cinnamyl*) acetate with the nucleophile diethyl 2-methylmalonate ($Nu^-$) is reported.


*Keywords:* Palladium(II)–allyl-complexes; Allylic alkylation; Ferrocene derivatives; Chiral palladium(II) compounds

## 1. Introduction

The development of new ferrocene derivatives having one or more heteroatoms with good donor abilities and their transition metal complexes has drawn considerable interest in the last years due to their physical and chemical properties or their potential applications in a wide variety of areas [1–7]. Examples of molecular devices and chemical sensors or receptors containing ferrocenyl units have been reported [3,4]. Furthermore, the study of the applications of this type of compounds in homogeneous catalysis has increased exponentially during the last decade [1,6–9]. One of the most widely studied processes is the catalytic allylic alkylation [7–9], which constitutes an effective tool for the formation of C–C and C–heteroatom bonds.

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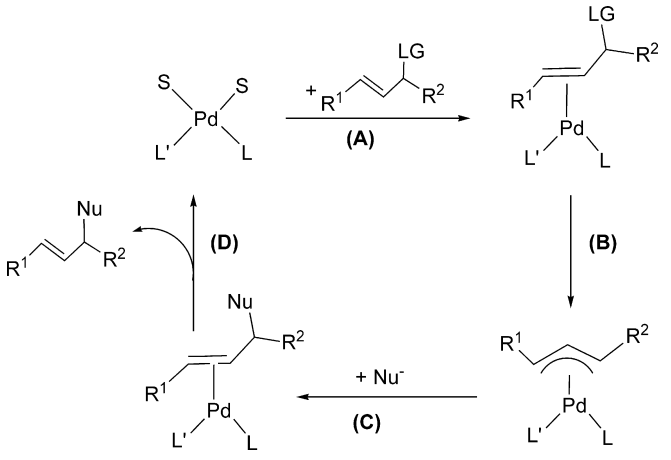
Consequently, it is of great importance in synthetic chemistry [10,11]. Usually, in these reactions the catalytic precursor is a palladium(II) complex containing the ($\eta^3$-$C_3H_5$) ligand and either one bidentate (L, L′) or two monodentate (L and L′ or L and X) ligands. Often these precursors are generated *in situ* by treatment of the [Pd($\eta^3$-$C_3H_5$)($\mu$-Cl)]$_2$ complex and the corresponding ligand. The mechanism accepted for the catalytic allylic alkylation process with stabilized nucleophiles proceeds in four consecutive steps (Scheme 1A–D) and the regio- as well as the stereoselectivity of the process are dependent on several factors that include the number and structures of the different isomeric forms of the intermediate species formed in step (B), their interconversion rates and the ease with which they undergo the nucleophilic attack [10,11].

Despite the large amount of ferrocene derivatives published so far, most of the reports concerning their application in the palladium(II) catalyzed allylic alkylation involve the presence of potentially bidentate ligands [7,8]. Studies dealing with enantiopure N-donor ferrocene derivatives or their palladium(II) complexes are not so common [9] and most of them focus on the use of ferrocenyl oxazolines [9c,9d] while related studies on ferrocenylimines are not known.

In this contribution we present some palladium(II)–allyl complexes of general formula: [Pd($\eta^3$-1R$^1$,3R$^2$-$C_3H_3$)-(L)-Cl] where L represents the enantiopure Schiff bases ($S_C$)-[FcCH=N–CH(Me)(Ph)] (**1a**) or ($S_C$)-[FcCH=N–CH- (R$^3$)($CH_2OH$)] {R$^3$=Me (**1b**) or $CHMe_2$ (**1c**)} together with a comparative study of the catalytic activity of **1a**, complex ($S_C$)-[Pd($\eta^3$-$C_3H_5$){FcCH=N–CH(Me)(Ph)}Cl] (**5a**) and the amine ($S_C$)-$H_2$N–CH(Me)(Ph) (**11**) in the allylic alkylation of (*E*)-3-phenyl-2-propenyl (*cinnamyl*) acetate with sodium diethyl 2-methylmalonate. Detailed NMR studies on the allyl complexes indicate that several isomers coexist in solution. For compound ($S_C$)-[Pd($\eta^3$-3-Ph–$C_3H_4$){FcCH=N–CH(Me)(Ph)}Cl] (**6a**), which is the key intermediate in the catalytic process, these studies as well as the results obtained from its reactivity with the nucleophile have allowed us to rationalize the regioselectivity of the process.




Scheme 1. Mechanism of the palladium-catalyzed allylic substitution reactions using stabilized nucleophiles {where *S* = solvent, L and L′ monodentate ligands or (L, L′) bidentate ligand, LG = leaving group and Nu$^-$ nucleophile.

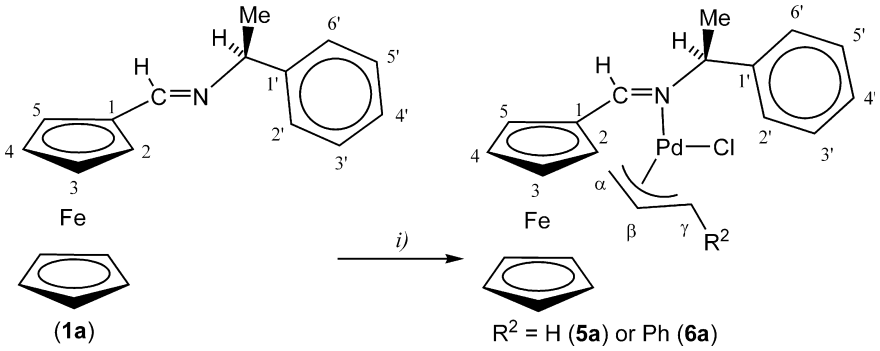
## 2. Results and discussion

### 2.1. Synthesis

The ligand ($S_C$)-[FcCH=N–CH(Me)(Ph)] (**1a**) was prepared according to the general procedure described for most ferrocenylaldimines [12]. Proton and $^{13}C\{^1H\}$ NMR spectra indicated that only one isomer was present in solution and the $\{^1H$–$^1H\}$ NOESY revealed that the ligand adopted the *anti*-(*E*) conformation. This result agrees with those obtained for ferrocenylaldimines and ketimines of general formula [FcC(R$^4$) = N-R$^5$], (R$^4$ = H, Me or Ph and R$^5$ = phenyl, benzyl or naphthyl groups) reported so far [13]. Besides that, it is well known that the reaction between aldehydes and optically pure amines such as: $H_2$N–CH(R$^3$)R$^6$ with R$^3$ = Me, $CHMe_2$ and R$^6$ = $CH_2OH$ or naphthyl or R$^3$ = $CO_2$Me and R$^6$ = $CH_2$–$CH_2$-SMe does not affect the chirality of the stereogenic centre [14–16]. Thus, the absolute configuration of **1a** is expected to be $S_C$.

Treatment of the ferrocenylimine **1a** with the corresponding allyl compound [Pd($\eta^3$-1R$^1$,3R$^2$-$C_3H_3$)($\mu$-Cl)]$_2$ {R$^1$ = H and R$^2$ = H (**2**) or Ph (**3**)} in a molar ratio Pd(II): **1a** = 1 in $CH_2Cl_2$ at 298 K gave, after concentration to dryness, [Pd($\eta^3$-3R$^2$-$C_3H_4$){FcCH=N–CH(Me)(Ph)}Cl] {with R$^2$ = H (**5a**) or Ph (**6a**), respectively} (Scheme 2).

In contrast with these results the reaction of **1a** with [Pd($\eta^3$-1,3-$Ph_2$-$C_3H_3$)($\mu$-Cl)]$_2$ (**4**) under identical experimental conditions showed no evidence for the formation of [Pd($\eta^3$-1,3-$Ph_2$-$C_3H_3$){FcCH=N–CH(Me)(Ph)}Cl] (**7a**) and the starting reagents were recovered unreacted. The addition of NaOH [in molar ratios NaOH:Pd(II) = 1] to the reaction medium lead to the decomposition of the reagents, giving metallic palladium and ferrocenecarboxaldehyde as the major products. These findings suggested that the presence of the two bulky phenyl groups in the allyl ligand inhibits the formation of complex **7a**. Molecular models of **7a** reveal that the presence of two phenyl groups in the (1,3-$Ph_2$-$C_3H_3$) unit does not permit a co-planar arrangement of the imine moiety and the centroids of the two C–C bonds of "$C_3$-backbone" of the allyl. Additionally, for a nearly orthogonal arrangement of these units, one of the phenyl groups will be extremely close to the hydrogen atoms of the "($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)" unit and the other will be too close to the aromatic ring on the stereogenic carbon. Consequently, the formation of **7a** is unlikely to occur. In order to elucidate the effect of the substituents on the viability of the formation of the palladium(II) allyl complexes, we also studied the reaction between [Pd($\eta^3$-1,3-$Ph_2$-$C_3H_3$)($\mu$-Cl)]$_2$ (**4**) and the imine ($S_C$)-[FcCH=N–CH(R$^3$)($CH_2OH$)] {R$^3$=Me (**1b**) in




Scheme 2. *i*) $[Pd(\eta^3\text{-}3\text{-}R^2\text{-}C_3H_4)(\mu\text{-}Cl)]_2$ in a molar ratio **1a**:Pd(II) = 1 in $CH_2Cl_2$ at 298K.

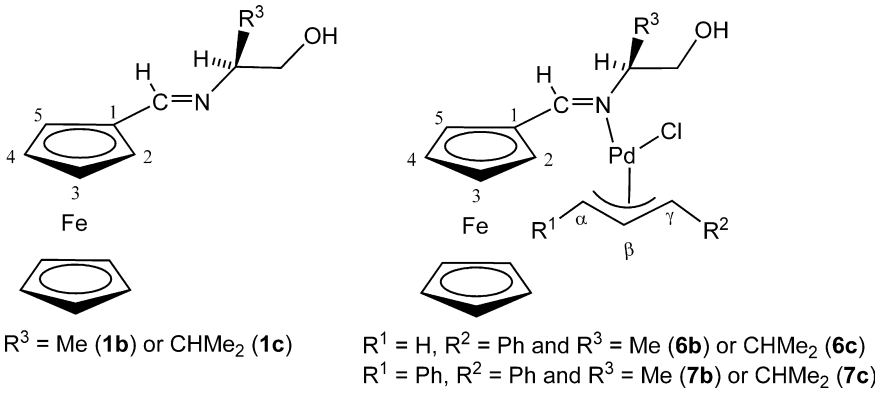



Fig. 1. Other ligands used in this study and their palladium(II)–allyl complexes.

Fig. 1} [14b,16], containing a smaller[2] [17] and more flexible substituent on the stereogenic carbon than **1a**. This gave an orange solid, whose characterization data (see Section 3) agreed with those expected for $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)\{FcCH{=}N\text{–}CH(Me)(CH_2OH)\}Cl]$ (**7b**) (Fig. 1). However, when the reaction was performed with $(S_C)$-$[FcCH{=}N\text{–}CH(CHMe_2)(CH_2OH)]$ (**1c** in Fig. 1) [14b,16], which arises from **1b** by replacement of the methyl group by a bulkier $–CHMe_2$ unit[3], the starting materials were recovered and no evidence for the formation of $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)\{FcCH{=}N\text{–}CH(CHMe_2)(CH_2OH)\}Cl]$ (**7c**) (Fig. 1) was detected. These findings provide additional proofs for the importance of the bulkiness of the substituents on the stereogenic carbon on the reactivity of ligands **1a**–**1c** with $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ (**4**), which determine the viability of the formation of the palladium(II)–allyl complexes (**7a**–**7c**).

### 2.2. Characterization

The new palladium(II)–allyl complexes can adopt a wide variety of isomeric forms. In particular for **5a**, the isomers may differ in the conformation of the Schiff base {*syn*-(*Z*) or *anti*-(*E*)}, the relative arrangements between the methyl group and the central $C^{\beta}$–$H^{\beta}$ bond of the allyl ligand (*endo*- or *exo*-) (Fig. 2). In addition for complexes **6a** and **7b** other sources of isomerism should also be considered. In these products, the phenyl rings could be in a *syn*- or *anti*- position in relation to the central hydrogen ($H^{\beta}$) of the allyl unit. For **6a**, which contains a non-symmetric allyl group, the substituted carbon of the allyl group ($C^{\gamma}$) may be located in a *cis*- or *trans*- arrangement in relation to the imine nitrogen. Furthermore, the inhibition of the free rotation around the $C_{ipso}$–$C_{imine}$ bond or the Pd–$N_{imine}$ bond may also produce rotameric species. This could be particularly relevant at low temperatures.

Compounds **5a**, **6a** and **7b** were characterized by elemental analyses, mass spectroscopy, IR and one and two-dimensional NMR spectroscopy. Elemental analyses (see Section 3) are consistent with the proposed formulae and their mass spectra showed peaks at $m/z = 501$ (for **5a**), 575 (for **6a**) 570 (for **7b**). The former two peaks are consistent with those expected for the cations $[Pd(\eta^3\text{-}3\text{-}R^2\text{-}C_3H_4)\{FcCH{=}N\text{–}CH(Me)(Ph)\}Cl]^+$ with $R^2 = H$ (**5a**) or Ph (**6a**), while the latter agrees with that of the ion $\{[M]–Cl\}^+$ of **7b**.

In the IR spectra of **5a**, **6a** and **7b**, the band due to the stretching of the ≻C=N– group appeared at lower energy than for the corresponding free ligand {1641 $cm^{-1}$ (**1a**)

[2] The Charton's steric parameters ($E_s$-CH) of the substituents Ph and $CH_2OH$ are 3.00 and 2.00, respectively [17].

[3] The $E_s$-CH parameters of Me and $CHMe_2$ are 1.00 and 3.00, respectively [17].

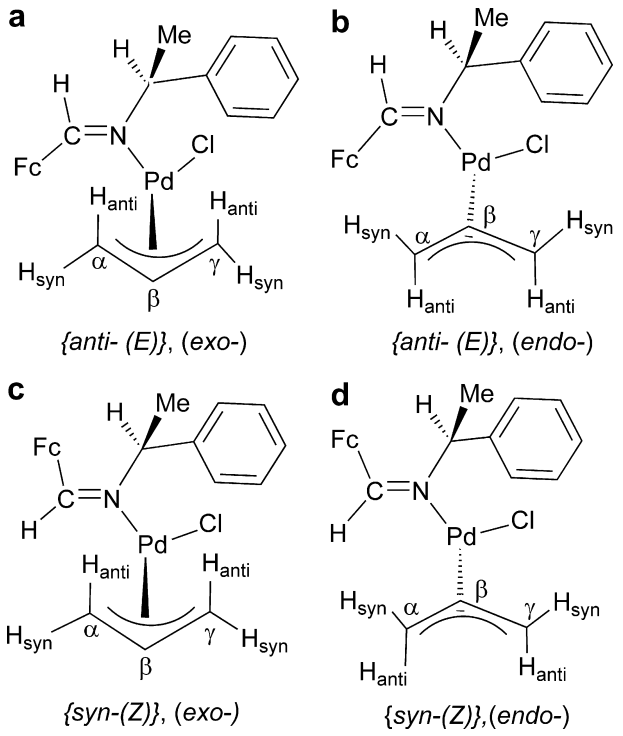



Fig. 2. Simplified view of the isomeric forms expected for **5a**. In two of them (**a,b**) the imine has the *anti*-(*E*) conformation, while in the pair (**c**, **d**) it adopts the *syn*-(*Z*) form. The main difference between **a** and **b** (or **c** and **d**) is the conformation of the allyl group {*exo*- (in **a** and **c**) and *endo*- (in **b** and **d**)}.

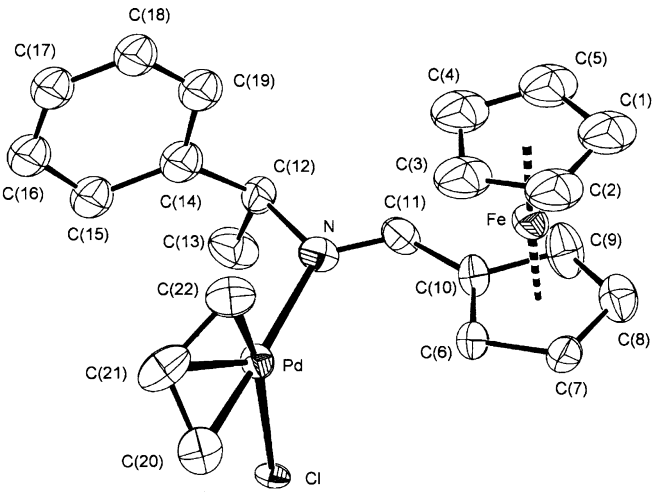



Fig. 3. ORTEP plot of [Pd($\eta^3$-$C_3H_5$){FcCH=N–CH(Me)(Ph)}Cl] (**5a**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and angles (in °): Pd–N, 2.123(4); Pd–Cl, 2.224(8); Pd–C(20), 2.058(5); Pd–C(21), 2.224(8); Pd–C(22), 2.086(6); C(10)–C(11), 1.457(6); C(11)–N, 1.255(6); N–C(12), 1.495(5); C(12)–C(13), 1.570(8); C(12)–C(14), 1.574(8); C(14)–C(15), 1.434(10); C(15)–C(16), 1.420(10); C(16)–C(17), 1.215(10); C(17)–C(18), 1.347(10); C(18)–C(19), 1.346(11); C(20)–C(21), 1.407(5); C(21)–C(22), 1.446(13); Cl–Pd–N, 96.14(10); N–Pd–C(22), 99.7(2); C(20)–Pd–Cl, 93.8(2); C(20)–Pd–C(22), 70.3(3); C(10)–C(11)–N, 127.0(4); N–C(12)–C(13), 197.5(4); N–C(12)–C(14), 106.7(4) and C(20)–C(21)–C(22), 113.5(7).

or 1638 $cm^{-1}$ (**1b**) [14b,16]}. This suggests, according to the literature [18], that the imine nitrogen coordinated to the palladium(II).

The crystal structure of **5a**[4] consists of molecules of [Pd($\eta^3$-$C_3H_5$){FcCH=N–CH(Me)(Ph)}Cl] separated by van der Waals distances. In each one of these heterodimetallic units (Fig. 3) the palladium(II) is bound to the imine nitrogen, a chloride and the $C_3H_5$ ligand in a $\eta^3$-fashion. The value of the N–Pd–Cl bond angle [95.14(10)°] indicates a *cis*-arrangement of the chloride and the imine nitrogen.

The Pd–N bond length [2.123(4) Å] is in good agreement with those reported for other palladium(II) complexes containing ferrocenyl Schiff bases [12–14c,19]. The Pd–C(20) bond length [2.058(5) Å] is shorter than the Pd–C(22) bond distance [2.086(6) Å]. This could be due to the different influence of the donor atoms in a *trans*-position [20]. In addition the C(20)–C(21) bond [1.407(5) Å] is shorter than the C(21)–C(22) bond [1.446(13) Å]. The C(21) carbon atom and the iron(II) centre are located on opposite sides of the coordination plane of the palladium(II) and the plane defined by the atoms C(20)–C(22) forms an angle of 62° with that of the imine group. The variations detected in the Cl–Pd–C(20) and N–Pd–C(22) bond angles [93.8(2)° and 99.7(2)°] suggest that the presence of the bulky substituents on the imine nitrogen may introduce steric hindrance between this ligand and the substituents on the C(22) carbon atom. Additionally, for the arrangement of the groups depicted in Fig. 3, the distance between the palladium and the hydrogen on the ortho site of the $C_5H_4$ ring, H(6), is rather small (2.061 Å) and suggests a weak Pd···H interaction. Similar features have also been described for other palladium(II) complexes containing one or two N-donor ligands [21].

Furthermore, the hydrogen bound to the C(22) atom and located on the *anti*-position is only 2.60 Å away from the H(3) hydrogen of the ferrocenyl unit. This suggests that the surroundings of the C(22) atom are rather crowded. In addition, the hydrogen atoms H(19) (on the ortho site of the phenyl ring) and H(4) are only 2.71 Å apart.

The >C=N– bond length [1.255(6) Å] is consistent with those reported for related palladium(II) complexes containing ferrocenylimines [12–14c,19] and the value of the torsion angle C(10)–C(11)–N–C(12) (174.1°) indicates that the imine adopts the *anti*-(*E*) conformation.

The two pentagonal rings of the ferrocenyl unit are planar and nearly parallel (*tilt angle* = 2.54°) and they deviate by *ca.* 2.1(1)° from the ideal eclipsed conformation. Bond lengths and angles of this moiety are similar to those reported for other monosubstituted ferrocene derivatives [19].

[4] *Crystal data*: $C_{22}H_{24}ClFeNPd$, FW = 500.12, $T$ = 293(3)K, *orthorhombic*, $a$ = 9.496(1) Å, $b$ = 10.520(1) Å, $c$ = 20.709(1) Å, $\alpha$ = 90.0°, $\beta$ = 90.01°, $\gamma$ = 89.85°, $V$ = 2068.3(3) $Å^3$, $Z$ = 4, $D_{calc}$ = 1.606 g $cm^{-3}$, $\mu$ = 1.704 $mm^{-1}$, $F(000)$ = 1008, final $R$ indices: $R_1$ = 0.0465, $wR_2$ = 0.1233 {for $I > 2\sigma(I)$} and $R_1$ = 0.0465 and $wR_2$ = 0.1508 (for all data).

### 2.3. Solution studies

As mentioned above the new palladium(II)–allyl complexes may exhibit different isomeric forms. NMR studies of **5a**, **6a** and **7b** have been very useful to determine the number of isomers and the differences between the major isomeric forms present in solution.

The $^1$H NMR spectrum of **5a** in $CD_2Cl_2$ at 298 K showed three sets of superimposed signals of relative intensities (10.0:7.6:0.3). This could be indicative of the presence of three isomeric forms of **5a** (**5a**$_I$, **5a**$_{II}$, **5a**$_{III}$, respectively). At 273 K **5a**$_I$–**5a**$_{III}$ coexisted in molar ratios of 10.0:5.4:0.3.

For **5a**$_I$ and **5a**$_{II}$, the {$^1$H–$^1$H} NOESY spectrum showed the existence of NOE interactions between the signals due to imine protons and that on the stereogenic carbon of (**5a**$_I$ and **5a**$_{II}$). This is only possible if the ligand adopts the *anti*-(*E*) conformation in the two isomers.

The resonances due to the allylic protons on the terminal carbon nuclei of **5a**$_I$ appeared as two doublets {at $\delta = 3.03$ ($J = 12.0$ Hz) [for $H^{\alpha}_{anti}$ and $H^{\gamma}_{anti}$] and 4.17 ppm ($J = 7.0$ Hz) [for $H^{\alpha}_{syn}$ and $H^{\gamma}_{syn}$]}; while for **5a**$_{II}$ four doublets {at $\delta = 2.60$ ($J = 12.0$ Hz), 2.73 ($J = 12.0$ Hz), 3.20 ($J = 7.0$ Hz) and 2.71 ($J = 7.0$ Hz)} were detected. Since the values of the $J(H_{anti}–H^{\beta})$ are greater than $J(H_{syn}–H^{\beta})$ [22] we assigned the signals at 3.03 (in **5a**$_I$) and the pair of resonances at 2.60 and 2.73 ppm of **5a**$_{II}$ to the protons in the *anti*-positions. The analyses of the cross-peaks detected in the {$^1$H–$^{13}$C} HSQC spectrum as well as the NOE peaks observed in the {$^1$H–$^1$H} spectrum allowed to identify unambiguously the signals due to the different types of protons and $^{13}$C-nuclei of the allyl group of **5a**$_I$ and **5a**$_{II}$. An interesting result obtained from the {$^1$H–$^1$H} NOESY spectrum is the presence of a NOE cross-peak between the resonance of the allylic proton $H^{\gamma}_{anti}$ and one proton of the phenyl group of **5b**$_{II}$, thus suggesting that these two moieties are proximal. This is only possible if the aromatic ring and the $H^{\gamma}_{anti}$ proton are on the same side of the coordination plane in **5b**$_{II}$ (Fig. 2, type **a**). For **5a**$_I$ the existence of a NOE contact between the pair of protons $H^2$ and $H^{\alpha}_{syn}$ suggests that in this case the orientation of the allyl group is that presented in Fig. 2 (type **b**).

Due to the low abundance of **5a**$_{III}$, we were neither able to establish the conformation of the imine (*syn*- or *anti*-) nor the conformation of the allyl group (*endo*- or *exo*-).

The proton-NMR spectrum of **6a** at 298 K showed four sets of superimposed broad signals. At 273 K the signals became narrower and the analyses of the resonances suggested the presence of four isomeric forms of **6a** (**6a**$_I$–**6a**$_{IV}$) in a relative abundance 10.0:5.1:0.4:0.1, respectively.

The {$^1$H–$^1$H} NOESY spectrum at 273 K indicated that for **6a**$_I$ and **6a**$_{II}$ the imine adopts the *anti*-(*E*) conformation. Besides that, the existence of NOE peaks between the signals due to the $H^{\beta}$ and the aromatic protons of the allyl unit suggested that in both cases the phenyl is in the *syn*-position. The most relevant differences detected in the NMR spectra of **6a**$_I$ and **6a**$_{II}$ affect the position of the signals due to: (a) the substituents (H and Me) on the stereogenic centre and (b) those of the allylic protons. In particular, for **6a**$_{II}$ the resonance of the methyl protons (at 1.61 ppm) appeared at higher fields than that of **6a**$_I$ (at 1.98 ppm) and the signals due to the proton of the >CH(Me) moiety exhibited the opposite trend ($\delta = 4.57$ and 4.82 ppm for **6a**$_I$ and **6a**$_{II}$, respectively). These variations, which were not observed for the major isomers of **5a** {**5a**$_I$ and **5a**$_{II}$}, suggested that the H and Me sub- stituents of **6a**$_I$ and **6a**$_{II}$ were affected by the ring current of the phenyl group of the allyl ligand. The existence of NOE peaks between the signal at 1.61 ppm and the resonance of an aromatic proton at 7.92 ppm confirmed the proximity between the phenyl and the methyl groups in **6a**$_{II}$.

For all the three isomers, the signals due to the allylic protons appeared as a multiplet {in the range of 5.0–6.0 ppm assigned to the central proton ($H^{\beta}$)} and three additional doublets in the area 2.6–4.0 ppm. The two-dimensional [{$^1$H–$^{13}$C} HSQC and {$^1$H–$^1$H} NOESY] NMR experiments gave evidence for the signals due to $H^{\alpha}_{anti}$, $H^{\alpha}_{syn}$ and $H^{\gamma}_{anti}$ protons of the ($\eta^3$-3-Ph–$C_3H_4$) ligand. Additionally, the existence of a NOE peak between the signal of the $H^{\alpha}_{anti}$ proton of **6a**$_{II}$ and that of the protons of the $C_5H_5$ ring indicates that in **6a**$_{II}$ these groups are close. All these results suggest that in **6a**$_I$ and **6a**$_{II}$: (a) the substituted carbon of the allyl ligand is close to the stereogenic centre and (b) the two isomers differ in the relative arrangement of the central $C^{\beta}–H^{\beta}$ bond in relation to the methyl group (*endo*- or *exo*-).

NMR studies of **7b** suggested the coexistence of four isomeric forms (**7b**$_I$–**7b**$_{IV}$, in a 10.0:6.6:0.9:0.8 ratio, respectively) in $CDCl_3$ at 298 K. The {$^1$H–$^1$H} NOESY spectrum (Fig. 4) showed cross-peaks between the signals due to the imine proton and those of the $H^5$ and >CH– protons of **7b**$_I$ and **7b**$_{II}$. This means that in both cases the ligand adopts the *anti*-(*E*) conformation. The values of the coupling constants between the allylic protons (see Section 3) were larger than 10 Hz and strong NOE cross-peaks between the signals due to $H^{\alpha}$ and $H^{\gamma}$ were also observed for **7b**$_I$ and **7b**$_{II}$. According to the bibliography [8] these two findings are consistent with a *syn*-, *syn*- arrangement of the two phenyl groups of the ($\eta^3$-1,3-$Ph_2$-$C_3H_3$) ligand. In view of this observation, we assumed that the main difference between **7b**$_I$ and **7b**$_{II}$ arises from the arrangement between the central $C^{\beta}–H^{\beta}$ bond of the allyl ligand and the methyl group on the stereogenic carbon (*endo*- or *exo*-).

The $^1$H NMR spectrum of **7b** showed that the signal due to the methyl protons of **7b**$_{II}$ ($\delta = 0.41$ ppm) was shifted to upfield compared to **7b**$_I$ ($\delta = 1.18$ ppm). This suggested that in **7b**$_{II}$ the Me unit could be affected by the ring current produced by the phenyl group of the allylic ligand. The {$^1$H–$^1$H} NOESY spectrum confirmed this by the presence of three NOE contacts (cross-peaks c–e, in Fig. 4) between the protons of one of the two Ph groups of the allyl unit

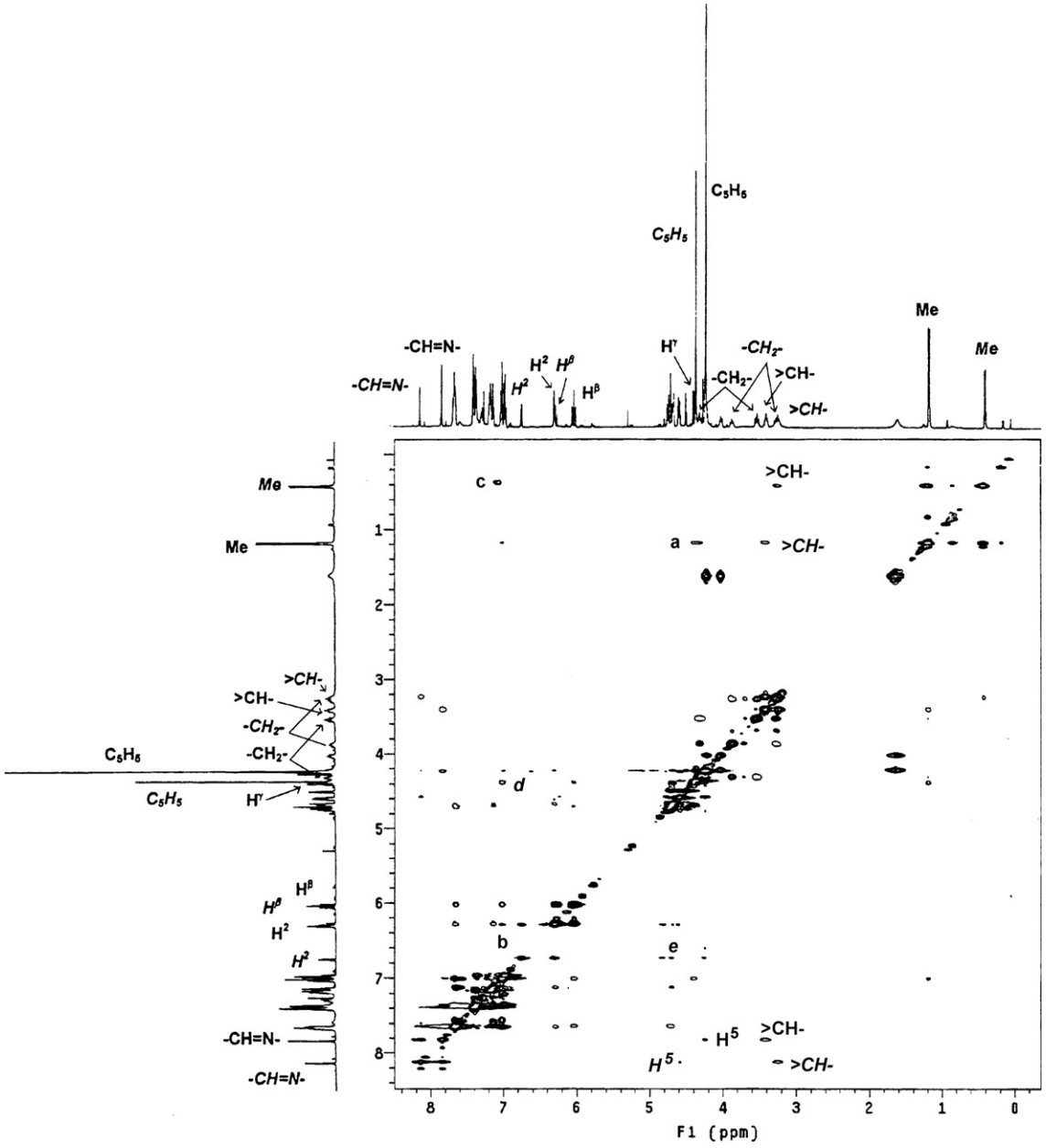



Fig. 4. $\{^1H–^1H\}$ NOESY spectrum of **7b** in $CDCl_3$ at 298 K showing the most relevant NOE peaks (**a**–**e**) detected for the major isomers $\mathbf{7b_I}$ and $\mathbf{7b_{II}}$ (labels in italics correspond to isomer $\mathbf{7b_{II}}$). For $\mathbf{7b_I}$, the cross-peaks **a**–**b** indicate NOE interactions between: the methyl protons and $H^{\gamma}$(**a**), and the $H^2$ nuclei of the $C_5H_4$ ring and an aromatic proton of the allyl ligand (**b**); while the peaks (**c**–**e**) detected for $\mathbf{7b_{II}}$, are due to NOE contacts between: the methyl and an aromatic proton of one of the $C_6H_5$ rings of the $\eta^3$-1,3-$Ph_2$-$C_3H_3$ group (**c**), the phenyl protons of the other ring of the allyl ligand and those of the non-substituted ring of the ferrocenyl unit (**d**) and the $H^{\alpha}_{anti}$ of the allyl group and the $H^2$ proton of the $C_5H_4$ moiety (**e**).

and those of the Me substituents, the $H^2$ proton of the ferrocenyl moiety and the $H^{\alpha}_{anti}$ proton and the resonances of the $C_5H_5$ ring and that of an aromatic ring of the "1,3-$Ph_2$-$C_3H_3$" unit. These findings are consistent with an *endo*-conformation of the 1,3-$Ph_2$-$C_3H_3$ group and consequently $\mathbf{7b_{II}}$ corresponds to the (*endo*-, *syn*-, *syn*-) (W-type) isomer (Fig. 5).

The assignment of the major component $\mathbf{7b_I}$ as the *exo*-, *syn*-, *syn*- (M-type) isomer (Fig. 5) was based on the presence of two NOE peaks (Fig. 4a and b) between the pairs of resonances due to $H^{\gamma}$ and Me, and $H^2$ (of the ferrocenyl unit) and one aromatic proton.

Unfortunately, the low abundance of $\mathbf{7b_{III}}$ and $\mathbf{7b_{IV}}$ prohibits the determination of the conformation of the imine {*anti*-(*E*) or *syn*-(*Z*)}, the arrangement between the methyl and the $C^{\beta}$–$H^{\beta}$ bond of the allyl ligand (*endo*- or *exo*-) or the positions of the phenyl rings (*anti*- or *syn*-) on the allyl ligand. The $\{^1H–^1H\}$ NOESY spectrum of **7b**, (Fig. 4) also showed that the isomeric forms $\mathbf{7b_I}$ and $\mathbf{7b_{II}}$ interchanged in solution.

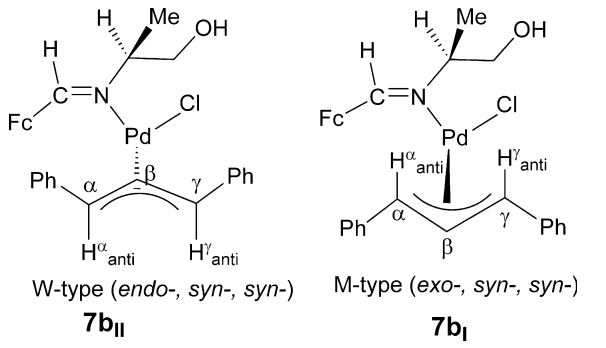



Fig. 5. Schematic view of two of the isomeric forms of $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)\{FcCH{=}N\text{–}CH(Me)(CH_2OH)\}Cl]$ (**7b**) (**7b**$_I$ and **7b**$_{II}$, respectively). In both cases the ferrocenyl ligand has the *anti*-(*E*) conformation, the phenyl rings of the allyl group occupy a *syn*- position in relation to the central $H^\beta$ atom. The main difference between **7b**$_I$ and **7b**$_{II}$ arises from the conformation of the allyl group. In **7b**$_{II}$ the central $C^\beta$–$H^\beta$ bond of the allyl unit and the methyl are on the same side of the coordination plane of the palladium(II) (*endo*-) {W-type orientation of the ($\eta^3$-1,3-$Ph_2$-$C_3H_3$) ligand}; while in **7b**$_I$ these two groups are on opposite sides (M-type conformation allyl unit).

### 2.4. Allylic alkylation reactions

In order to check the reactivity of the coordinated allyl group of **6a** in front of nucleophiles, **6a** was treated with an excess of sodium diethyl 2-methylmalonate in THF at 298 K (*stoichiometric reaction*, Scheme 3). Upon the addition of the nucleophile the colour of the mixture changed (from deep-red to orange) indicating that the reaction was instantaneous and the final product obtained after work-up consisted of a mixture of the linear *trans*-(*E*) derivative (**8**) and the branched product (**9**) in a molar ratio of **8**:**9** = 97.8:2.2.

The NMR studies of **6a** indicated that in the major isomeric forms present in solution (**6a**$_I$ and **6a**$_{II}$) the phenyl group of the allyl group is close to the substituents on the stereogenic centre {the hydrogen (in **6a**$_I$) and the methyl group (in **6a**$_{II}$)}. Consequently, the preferential formation of the linear *trans*-(*E*) product (**8**) can be explained assuming that the attack of the nucleophile takes place at the carbon at the other end of the allyl unit ($C^\alpha$).

In view of these results and in order to evaluate the potential utility of ligand **1a** or complex **5a** we also studied the alkylation of cinnamyl acetate with sodium diethyl 2-methylmalonate using catalytic amounts of (a) mixtures of the free ligand **1a** and $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ (in a 2:1 molar ratio) or (b) complex **5a**.

Data presented in Table 1 (entries I and II) show that **1a** is active in the catalytic alkylation of cinnamyl acetate under mild experimental conditions (room temperature and short reaction periods) giving a mixture of **8**, **9** (in molar ratios of 92.8:7.2 and 91.1:8.9, respectively) and a side-product **10**. Compound **10** was identified as 1-cinnamyl-3-ethyl-2-methylmalonate and it also forms when cinnamyl acetate is treated with the nucleophile in THF at room temperature in the absence of any catalyst. The formation of **10** reduces the effectiveness of the catalytic systems formed by **1a** and $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ in this process.

More interesting were the results obtained when **5a** was used as precursor (Table 1, entry III). The reaction was faster than in the previous experiments (Table 1, entries I and II) and there was no evidence for the presence of **10**.

For comparison purposes a parallel study with the amine ($S_C$)-$H_2N$–CH(Me)(Ph) (**11**) was also performed (Table 1, entry IV). In this case the formation of **8** and **9** was observed, but the conversion was lower than that obtained for **5a**. Furthermore, gas chromatography analyses and $^1H$ NMR spectra of the samples obtained after 20 h indicated the presence of unreacted cinnamyl acetate and product **10**.

To sum up, entries I–IV indicate that the best catalytic results were achieved with **5a** for which the reaction is faster and no evidences of the formation of undesired products, such as **10**, were detected. The comparison of the data obtained for **5a** with those previously reported for $[Pd(\eta^3\text{-}C_3H_5)\{FcCH{=}N\text{–}(C_6H_4\text{-}2SMe)\}]$ $[PF_6]$ (**12**) {with a (N,S) bidentate ligand} [23] and the allyl complex **13** depicted in Fig. 6 [24] (containing a neutral bidentate (N,O) ferrocenyl ligand) indicates that for **5a** the reaction is slower than when **12** was used and the regioselectivity towards the linear product also decreases. However, compound **5a** is more effective than **13**. The regioselectivities of the processes catalyzed by **5a** and **13** are similar {92.1:7.9 (after 20 h) and 93:7 (after 24 h), respectively} (Table 1, entries III and V), but the experimental conditions required for **5a** are milder than those reported for **13**.[5]

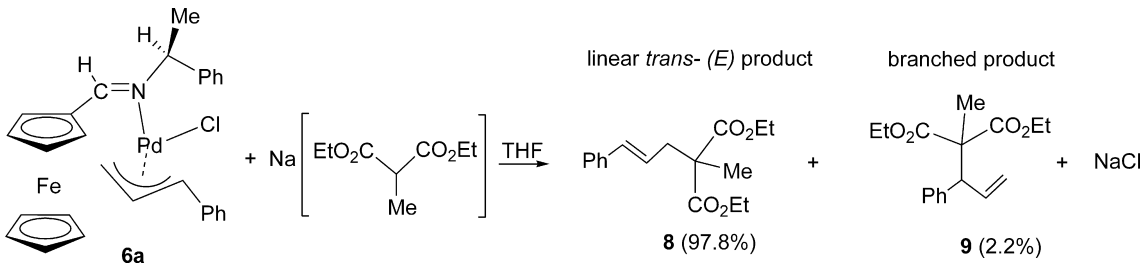
### 2.5. Conclusions

The work presented here has allowed the isolation and characterization of three novel chiral palladium(II)–allyl complexes (**5a**, **6a** and **7b**). The comparative study of the reactivity of the three imines (**1**) with compounds $[Pd(\eta^3\text{-}1R^1,3R^2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ {$R^1 = H$ and $R^2 = H$ (**2**), Ph (**3**) or $R^1 = R^2 = Ph$ (**4**)} has shown that the presence of bulky substituents on the stereogenic centre of the imines or on the allyl complexes is so important as to determine the viability of the formation of compound **7** that contain a ($\eta^3$-1,3-$Ph_2$-$C_3H_3$) ligand.

Furthermore, the catalytic studies summarized here have shown that **1a**, **5a** and the amine **11** (which is used for the preparation of **1a**) are active in the allylic alkylation of (*E*)-3-phenyl-2-propenyl (*cinnamyl*) acetate with sodium diethyl 2-methylmalonate (Nu). Among the catalytic systems tested, for **5a** the reaction was faster and did not produce the undesired product **10**.

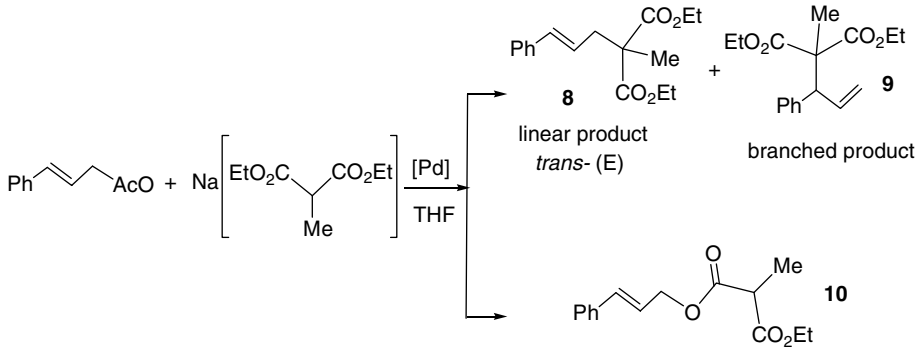
NMR studies of the palladium–allyl complexes have shown that several isomeric species coexist in solution.

[5] For **13**, the catalytic study was performed at 343 K and the yield was 93%.




Scheme 3. Reaction of [Pd($\eta^3$-3-$R^2$-$C_3H_4$){FcCH=N–CH(Me)(Ph)}Cl] (**6a**) with sodium diethyl 2-methylmalonate.

Table 1
Results of the catalytic allylic alkylation of cinnamyl acetate with sodium diethyl 2-methylmalonate[a]




| Entry | [Pd] | $t$ (h) | Conversion (%) | Molar ratio[b] **8:9:10** |
|---|---|---|---|---|
| I | **1a** and [Pd($\eta^3$-$C_3H_5$)($\mu$-Cl)]$_2$ | 20 | 72.1 | 25.6:2.0:72.4 |
| II | **1a** and [Pd($\eta^3$-$C_3H_5$)($\mu$-Cl)]$_2$ | 44 | 86.9 | 21.4:2.1:76.5 |
| III | **5a** | 20 | 100.0 | 92.1:7.9:0 |
| IV | **11** and [Pd($\eta^3$-$C_3H_5$)($\mu$-Cl)]$_2$ | 20 | 83.7 | 33.5:2.9:63.6 |
| V[c] | **13** | 24 | [d] | 93:7:0[e] |

[a] *Experimental conditions*: mixtures containing $2.5 \times 10^{-3}$ mmol of [Pd($\eta^3$-$C_3H_5$)($\mu$-Cl)]$_2$ and $5.0 \times 10^{-3}$ mmol of **1a** (entries I and II) (or **11** in entry *IV*) or $5.0 \times 10^{-3}$ mmol of **5a** (entry *III*), 0.5 mmol of the allylic substrate, 1 mmol of sodium diethyl 2-methylmalonate, THF (5 mL) and decane (0.258 mmol) at 298 K.
[b] Determined by GC.
[c] Data from Ref. [24].
[d] Data not given.
[e] The reaction was performed at 343 K.

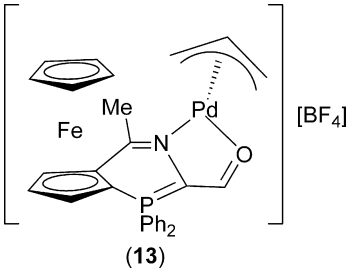



Fig. 6. Chemical formula of the palladium(II)–allyl complex (**13**).

The results obtained for **6a**, which is the key intermediate of the catalytic process under study, are particularly relevant in order to explain the regioselectivity of the reaction. In the two major isomers (**6a**$_I$ and **6a**$_{II}$) present in solution the ligand adopts the *anti*-(*E*) conformation and the substituted carbon of the allyl group ($C^\gamma$) is in a *cis*-arrangement to the $Cl^-$ ligand and they only differ in the conformation of the allyl group (*endo*- or *exo*-). The preferential formation of the *trans*-(*E*) isomer (**8**) of the linear product in the catalytic process and in the stoichiometric reaction should arise from the attack of the nucleophile to the non-substituted carbon atom ($C^\alpha$).

Finally, it should be noted that the presence of a stereogenic centre in the backbones of ligands **1** and in complex **5a** is especially interesting in view of their potential utility as catalysts in asymmetric allylic alkylation processes.

## 3. Experimental

### 3.1. Materials and methods

Ferrocenecarboxaldehyde and ($S_C$)-$H_2N$–CH(Me)(Ph) (**11**) were obtained from Aldrich and used as received. Ligands ($S_C$)-[FcCH=N–CH($R^3$)($CH_2OH$)] {$R^3$ = Me (**1b**) or $CHMe_2$ (**1c**)} and complexes [Pd($\eta^3$-1$R^1$,3$R^2$-$C_3H_3$)(μ-Cl)]$_2$ {$R^1$ = H and $R^2$ = H (**2**), Ph (**3**) or $R^1$ = $R^2$ = Ph (**4**)} were prepared as described previously [14b,16,25–27]. Sodium diethyl 2-methylmalonate (0.5 M in THF) was prepared from diethyl 2-methylmalonate and NaH in THF at 273 K. The solvents used in this work were dried and distilled before use, except benzene [28]. Some of the preparations described below require the use of benzene, which should be handled with *CAUTION!*

Elemental analyses were carried out at the *Serveis Cientifico-Tècnics* (Univ. Barcelona) and *Servei de Recursos Cientifics i Tècnics* (Univ. Rovira i Virgili, Tarragona). Infrared spectra were obtained with a Nicolet Impact 400-instrument using KBr discs. Proton and the two-dimensional NMR experiments [{$^1$H–$^1$H}-(COSY) and (NOESY) and the {$^1$H–$^{13}$C} (HSQC) and (HMBC)] were run at 500 MHz with either a Varian VRX-500 or a Bruker Avance 500DMX instruments. This latter equipment was also used for the variable temperature NMR studies.The solvents used for the $^1$H NMR experiments were $CDCl_3$ (99.9%) or $CD_2Cl_2$ (99.9%) with $SiMe_4$ as the internal reference.

In all cases the chemical shifts ($\delta$) are given in ppm and the coupling constants ($J$) in Hz. The optical rotation of a solution of **1a** in $CH_2Cl_2$ was determined at 293 K using a Perkin–Elmer 241 MC polarimeter. Mass spectra ($FAB^+$or $ESI^+$) were obtained with a VG-Quattro Fisions instrument using 3-nitrobenzylalcohol (NBA) as matrix (for $FAB^+$) and a Waters Micromass instrument (for $ESI^+$).

### 3.2. Preparation of the compounds

#### 3.2.1. ($S_C$)-[FcCH=N–CH(Me)(Ph)] (*1a*)

Ferrocenecarboxaldehyde (2.729 g, $12.7\times10^{-3}$ mol) was dissolved in 50 mL of benzene, stirred at 293 K for 30 min and filtered out. Then, a stoichiometric amount of ($S_C$)-$H_2N$–CH(Me)(Ph) (**11**) (1.64 mL, $12.7\times10^{-3}$ mol) was added to the filtrate. The reaction flask was connected to a Dean–Stark apparatus and refluxed until *ca.* 15 mL of the azeotrope (benzene/water) was condensed on the Dean–Stark. The hot reaction mixture was filtered out with caution and the filtrate was concentrated to dryness using a rotary evaporator. Next, the residue was treated with *n*-hexane (*ca.* 30 mL) and stirred at 298 K for *ca.* 30 min. The orange solid formed was collected by filtration and air-dried (yield: 3.542 g, 88%). Anal. Calc. for $C_{19}H_{19}NFe$: C, 71.94; H, 6.06; N, 4.42. Found: C, 72.0; H, 5.9; N, 4.42%. MS($FAB^+$): $m/z$ = 317 $[M]^+$. IR: $\nu$(>C=N–) = 1641 $cm^{-1}$. $[\alpha]_D$ (293 K) ($c$ = 0.1 g/100 mL, $CH_2Cl_2$) = +112. $^1$H NMR data [29]: $\delta$ = 8.21(s, 1H, –CH=N–), 4.11(s, 5H, $C_5H_5$), 4.70(s, 1H, $H^2$), 4.34(s, 2H, $H^3$ and $H^4$), 4.63(s, 1H, $H^5$), 1.56(d, 3H, $J$ = 6.0, Me), 4.41(m, 1H, >CH–), 7.38(d, 2H, $H^{2'}$ and $H^{6'}$), 7.32(m, 2H, $H^{3'}$ and $H^{5'}$) and 7.22(d, 1H, $H^{4'}$). $^{13}$C{$^1$H} NMR data [29]: $\delta$ = 159.9(–CH=N–), 69.1($C_5H_5$), 80.8($C^1$), 68.3($C^2$), 70.5($C^3$), 69.8($C^4$), 68.8($C^5$), 24.3(Me), 69.5(>CH–), 126.7($C^{2'}$ and $C^{6'}$), 126.7($C^{4'}$), 128.5($C^{3'}$ and $C^{5'}$), 145.9($C^{1'}$).

#### 3.2.2. [Pd($\eta^3$-$C_3H_5$){FcCH=N–CH(Me)(Ph)}Cl] (*5a*)

A mixture containing ligand **1a** (0.197 g, $6.2\times10^{-4}$ mol), [Pd($\eta^3$-$C_3H_5$)(μ-Cl)]$_2$ (0.114 g, $3.11\times10^{-4}$ mol) and 15 mL of $CH_2Cl_2$ was protected from the light with aluminium foil and stirred at *ca.* 298 K for 1 h. After this period the orange solution was filtered out, the undissolved materials were removed by filtration. The filtrate was concentrated to dryness on a rotary evaporator. The gummy residue was dissolved in the minimum amount of $CH_2Cl_2$ and the solution was treated with anhydrous $Na_2SO_4$ and then filtered. Addition of hexane to the filtrate followed by slow evaporation produced the formation of orange prisms of **5a**, which were collected and dried (yield: 0.153 g, 49%). Anal. Calc. for $C_{22}H_{24}NClFePd$: C, 52.83; H, 4.89; N, 2.80. Found: C, 52.8; H, 4.7; N, 2.7%. MS($FAB^+$): $m/z$ = 501 $[M]^+$. IR: $\nu$(>C=N–) = 1622 $cm^{-1}$. $^1$H NMR data (in $CD_2Cl_2$) at 273 K three sets of superimposed signals of relative intensities (10.0:5.4:0.3) were detected and suggested the presence of three isomeric forms of **5** (hereafter referred to as $\mathbf{5a}_I$, $\mathbf{5a}_{II}$ and $\mathbf{5a}_{III}$, respectively) in solution. For $\mathbf{5a}_I$ [29,30]: $\delta$ = 8.34(s, 1H, –CH=N–), 4.27(s, 5H, $C_5H_5$), 4.72(s, 1H, $H^2$), 4.49(br s, 2H, $H^3$ and $H^4$), 4.91(s, 1H, $H^5$), 1.81(d, 3H, $J$ = 6.5, Me), 4.80(m, 1H, >CH–), 3.03(d, 2H, $J$ = 12.0, $H^{\alpha}_{anti}$ and $H^{\gamma}_{anti}$), 5.42(m, 1H, $J$ = 12.0 and 6.5, $H^{\beta}$), 4.17(d, $J$ = 6.5, $H^{\alpha}_{syn}$ and $H^{\gamma}_{syn}$). For $\mathbf{5a}_{II}$ [29,30]: $\delta$ = 8.26(s, 1H, –CH=N–), 4.26(s, 5H, $C_5H_5$), 5.40(br s, 2H, $H^2$ and $H^5$), 4.55(s, 2H, $H^3$ and $H^4$), 1.98(d, 3H, $J$ = 6.5, Me), 4.65(m, 1H, >CH–), 2.60(d, 1H, $J$ = 12, $H^{\alpha}_{anti}$), 3.20(d, 1H, $J$ = 7.0, $H^{\alpha}_{syn}$), 4.71(m, 1H, $J$ = 12.0 and $J$ = 7.0, $H^{\beta}$), 2.73(d, 1H, $J$ = 12.0, $H^{\gamma}_{anti}$) and 2.71(d, 1H, $J$ = 7.0, $H^{\gamma}_{syn}$). $^{13}$C{$^1$H} NMR data for $\mathbf{5a}_I$ [29,30]: $\delta$ = 69.7($C_5H_5$), 71.9($C^1$), 71.5($C^2$), 72.3($C^3$ and $C^4$), 71.8($C^5$), 21.0(Me), 53.8(>CH-), 64.6($C^{\alpha}$ and $C^{\gamma}$), 111.0($C^{\beta}$) and 165.4(–CH=N–). For $\mathbf{5a}_{II}$ [29,30]: $\delta$ = 69.9($C_5H_5$), 21.8(Me), 54.2(>CH–), 62.1($C^{\alpha}$), 111.7($C^{\beta}$), 58.3($C^{\gamma}$) and 165.2(–CH=N–).

#### 3.2.3. [Pd($\eta^3$-3-Ph–$C_3H_4$){FcCH=N–CH(Me)(Ph)}Cl] (*6a*)

This compound was prepared using the same procedure as described above for **5a** but using 0.162 g ($3.14\times10^{-4}$ mol) of [Pd($\eta^3$-3-Ph–$C_3H_4$)(μ-Cl)]$_2$. In this case concentration of the reaction mixture gave an orange solid which was collected and recrystallized in a 1:1 mixture of $CH_2Cl_2$ and *n*-hexane (yield: 0.326 g, 86%). Anal. Calc. for $C_{28}H_{28}NClFePd$: C, 58.36; H, 4.90; N, 2.43. Found: C, 58.3; H, 4.78; N, 2.5%. MS(ESI): $m/z$ = 575 $[M]^+$ and 540.0 $[M-Cl]^+$. IR: $\nu$(>C=N–) = 1619 $cm^{-1}$. $^1$H NMR

data (in $CD_2Cl_2$): at 273 K four sets of superimposed signals of relative intensities (10.0:5.1:0.4:0.1) were detected and suggested the presence of four isomeric forms of **6a** (hereafter referred to as $\mathbf{6a_I}$–$\mathbf{6a_{IV}}$, respectively) in solution. For $\mathbf{6a_I}$ [29,30]: 7.71(s, 1H, –CH=N–), 4.20(s, 5H, $C_5H_5$), 4.37(s, 1H, $H^2$), 4.12(s, 1H, $H^3$), 4.03(s, 1H, $H^4$), 4.54(s, 1H, $H^5$), 1.98(d, 3H, $J = 6.6$, Me), 4.57(q, 1H, $J = 12$ and 7, >CH–), 2.66(d, 1H, $J = 12$, $H^{\alpha}_{anti}$), 3.27(d, 1H, $J = 7$, $H^{\alpha}_{syn}$), 5.50(m, 1H, $H^{\beta}$) and 2.92(s, 1H, $J = 12$, $H^{\alpha}_{anti}$); for $\mathbf{6a_{II}}$ [29,30]: 7.65(s, 1H, –CH=N–), 4.16(s, 5H, $C_5H_5$), 4.48(s, 1H, $H^2$), 4.28(s, 1H, $H^3$), 4.33(s, 1H, $H^4$), 4.62(s, 1H, $H^5$), 1.61(d, 3H, $J = 6.6$, Me), 4.82(q, 1H, $J = 6.6$, >CH–), 3.05(s, 1H, $J = 12$, $H^{\alpha}_{anti}$), 3.92(d, 1H, $J = 7$, $H^{\alpha}_{syn}$), 5.67(m, 1H, $H^{\beta}$) and 2.96(d, 1H, $J = 12$, $H^{\gamma}_{anti}$); for $\mathbf{6a_{III}}$ [29,30]: 7.62(s, 1H, –CH=N–), 4.08(s, 5H, $C_5H_5$), 4.33(s, 1H, $H^2$ partially overlapped by the resonance due to the $H^4$ of isomer $\mathbf{6a_{II}}$), 4.26(s, 1H, $H^3$), 4.27(s, 1H, $H^4$), 4.35(s, 1H, $H^5$), 1.68(d, 3H, $J = 6.6$, Me), 4.90(q, 1H, $J = 6.6$, >CH–), 2.80(d, 1H, $J = 12$, $H^{\alpha}_{anti}$), 3.87(d, 1H, $J = 7$, $H^{\alpha}_{syn}$), 5.61(m, 1H, $H^{\beta}$) and 2.93(s, 1H, $J = 12$, $H^{\gamma}_{anti}$, partially overlapped by the resonance due to the $H^{\gamma}_{anti}$ of $\mathbf{6a_{II}}$). $^{13}C\{^1H\}$ NMR data for $\mathbf{6a_I}$ [29,30]: 69.1($C_5H_5$), 25.2(Me), 57.4($C^{\alpha}$), 107.4($C^{\beta}$), 78.1($C^{\gamma}$) and 164.4(–CH=N–); for $\mathbf{6a_{II}}$ [29,30]: 69.6($C_5H_5$), 23.2(Me), 56.2($C^{\alpha}$), 104.8($C^{\beta}$), 78.1($C^{\gamma}$) and 165.0(–CH=N–).

#### 3.2.4. [Pd($\eta^3$-1,3-$Ph_2$-$C_3H_3$){FcCH=N–CH(Me)-($CH_2OH$)}Cl] (7b)

Ligand **1b** (0.082 g, $3.01 \times 10^{-4}$ mol) was dissolved in 15 mL of $CH_2Cl_2$, then [Pd($\eta^3$-1,3-$Ph_2$-$C_3H_3$)(μ-Cl)]$_2$ (0.101 g, $1.51 \times 10^{-4}$ mol) was added. The resulting reaction mixture was stirred at room temperature for 1 h and then filtered over *Celite*. The filtrate was concentrated to dryness on a rotary evaporator giving an orange solid that was collected and air-dried (yield: 0.168 g, 91.8%). Anal. Calc. for $C_{29}H_{30}NClFeOPd$: C, 57.45; H, 4.99; N, 2.31. Found: C, 57.8; H, 5.0; N, 2.4%. MS(ESI): $m/z = 570$ $[M-Cl]^+$. IR: $\nu$(>C=N–) = 1627 $cm^{-1}$ and $\nu$(>O–H) = 3377 $cm^{-1}$. $^1H$ NMR data (in $CDCl_3$ at 298 K): Four superimposed sets of signals of relative intensities 10.0:6.6:0.9:0.8 were detected, this suggested the coexistence of four isomeric forms of **7b** ($\mathbf{7b_I}$–$\mathbf{7b_{IV}}$) in solution. Due to the low abundance of $\mathbf{7b_{III}}$ and $\mathbf{7b_{IV}}$, only the resonances due to $\mathbf{7b_I}$ and $\mathbf{7b_{II}}$ could be assigned. For $\mathbf{7b_I}$ (major component) [30,31]: $\delta = 7.82$(s, 1H, –CH = N–), 4.22(s, 5H, $C_5H_5$), 6.29(s, 1H, $H^2$), 4.70(s, 1H, $H^3$), 4.49(s, 1H, $H^4$), 4.23(s, 1H, $H^5$), 3.38(m, 1H, >CH–), 1.18(d, $J = 6$, 3H, Me), 3.52 and 4.30(br m, 2H, –$CH_2$–), 4.21(br s, 1H, –OH), 4.71(d, $J = 11.5$, $H^{\alpha}$), 6.02(d, $J = 11.5$, $H^{\beta}$), 4.38(d, 1H, $J = 11.5$, $H^{\gamma}$) and 6.90–7.70 (m, 10H, aromatic protons). For $\mathbf{7b_{II}}$ [30,31]: $\delta = 8.12$(s, 1H, –CH=N–), 4.35(s, 5H, $C_5H_5$), 6.73(s, 1H, $H^2$), 4.74(s, 1H, $H^3$), 4.59(s, 1H, $H^4$), 4.57(s, 1H, $H^5$), 3.23(m, 1H, >CH–), 0.41(d, $J = 6$, 3H, Me), 3.27 and 3.86(br m, 2H, –$CH_2$–), 4.00(br s, 1H, –OH), 4.66(br, 2H, $H^{\alpha}$ and $H^{\gamma}$), 6.27(d, 1H, $J = 11.5$, $H^{\beta}$) and 6.90–7.70(m, 10H, aromatic protons). $^{13}C\{^1H\}$ NMR data (in $CDCl_3$ at 298K) for $\mathbf{7b_I}$ [30,31]: 166.2(–CH=N–), 70.1($C_5H_5$), 78.0($C^1$), 68.0($C^2$), 72.2($C^3$), 72.0($C^4$), 73.8($C^5$), 72.4(>CH–), 18.3(Me), 65.6(–$CH_2$–), 76.8($C^{\alpha}$), 104.9($C^{\beta}$), 75.7($C^{\gamma}$), 138.3 and 137.7 ($C^{ipso}$ of the two phenyl rings) and for $\mathbf{7b_{II}}$: 166.4(–CH=N–), 70.4($C_5H_5$), 78.4($C^1$), 68.2($C^2$), 72.8($C^3$), 72.3($C^4$), 73.6($C^5$), 72.6(>CH–), 17.5(Me), 65.1(–$CH_2$–), 78.0($C^{\alpha}$), 100.2($C^{\beta}$), 74.1 ($C^{\gamma}$), 138.4 and 137.3 ($C^{ipso}$ of the two phenyl rings).

### 3.3. Alkylation reactions

All these studies were performed under nitrogen. The stoichiometric reaction of **6a** with sodium diethyl 2-methylmalonate was carried out at 298 K by adding an excess of the nucleophile (0.7 mL of a 0.5 M solution in THF) to a solution containing 70 mg ($1.21 \times 10^{-4}$ mol) of **6a**. The reaction was instantaneous and after 10 min $H_2O$ was added. The reaction mixture was filtered over *Celite* and the filtrate was treated with $Et_2O$ (*ca.* 15 mL). The organic layer was washed three times with water, the ether layer was dried over $MgSO_4$ and the resulting filtrate was concentrated to dryness on a rotary evaporator. The residue was then dissolved in a minimum amount of $Et_2O$ and passed over a short $SiO_2$ column (4.0 cm × 0.6 cm). The band released was collected, concentrated to dryness giving an oily residue that, according to $^1H$ NMR(500 Hz) and GC contained a mixture of compounds **8** and **9** in a molar ratio **8**:**9** = 97.8:2.2.

The catalytic reactions were performed at 298 K in THF (5 mL) using $5.0 \times 10^{-3}$ mmol of **5a** or mixtures containing $2.5 \times 10^{-3}$ mmol of [Pd($\eta^3$-$C_3H_5$)(μ-Cl)]$_2$ and $5.0 \times 10^{-3}$ mmol of **1a** or **11**, 0.5 mmol of cinnamyl acetate and 1.0 mmol of sodium diethyl 2-methylmalonate. The reaction was monitored by taking samples from the reaction. Each aliquote was diluted in $Et_2O$, washed with $H_2O$, dried over $MgSO_4$ and then analysed by GC using decane (0.258 mmol) as internal standard.

### 3.4. Crystallography

A prismatic crystal (0.1 mm × 0.1 mm × 0.2 mm) of **5a** was selected and mounted on a MAR345 diffractometer with a image plate detector. Unit-cell parameters were determined from 18515 reflections ($3° < \theta < 31°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation. Reflections (16,625) were measured (in the range $2.36° \leqslant \theta \leqslant 31.66°$), of which 5717 were non-equivalent by symmetry {$R_{int}$(on $I$) = 0.037} and 5152 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz-polarization but no absorption corrections were made.

The structure was solved by Patterson synthesis, using SHELXS computer program [32] and refined by full-matrix least-squares method with SHELX97 computer program [33] using 5717 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w \|F_o|^2 - |F_c|^2|^2$,

where $w = [\sigma^2(\mathrm{I}) + (0.1066P)^2]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$, $f$, $f'$ and $f''$ were taken from the literature [34]. All H atoms were computed and refined using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which are linked. The final $R$(on $F$) factor was 0.041, $wR$ (on$|F|^2$) = 0.012 and goodness of fit = 1.114 for all observed reflections and the Flack coefficient [35] was 0.14(3). The number of refined parameters was 235. Max. shift/esd = 0.00, Mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis was 0.827 and −0.517 eÅ$^{-3}$, respectively.

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## Appendix A. Supplementary material

CCDC 635695 contains the supplementary crystallographic data for **5a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.016.

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