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Schiff bases containing ferrocenyl and thienyl units and their utility in the palladium catalyzed allylic alkylation of cinnamyl acetate

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Abstract

The synthesis and characterization of two new ferrocenyl Schiff bases: [Fc-CH=N–$(CH_2)_n$–(C_4H_3S)] (**2**) {Fc represents (η^5-C_5H_5)Fe(η^5-C_5H_4)– and $n = 1$(**2a**) or 2(**2b**)} containing the thienyl (C_4H_3S) group are reported. NMR studies indicate that **2** have the *anti*-(*E*) conformation in solution and the X-ray crystal structure of **2a** confirms that it also adopts the *anti*-(*E*) form in the solid state. Ligands **2** have been tested in the palladium catalyzed allylic alkylation of (*E*)-3-phenyl-2-propen-1-yl (*cinnamyl*) acetate using sodium diethyl 2-methylmalonate as nucleophile. The reaction of **2** with [Pd(η^3-1-Ph–C_3H_4)(μ-Cl)]$_2$ in the presence of a slight excess K[PF_6] produced [Pd(η^3-1-Ph–C_3H_4){Fc-CH=N–$(CH_2)_n$-(C_4H_3S)}][PF_6] {$n = 1$(**5a**) or 2(**5b**)}, which are the intermediates of this catalytic process. NMR studies of **5** reveal the coexistence of several isomers in solution. The stoichiometric reactions of **5** with the nucleophile are also reported. The comparison of the results obtained for **2**, [Fc-CH=N–(C_6H_4–2SMe)] (**1a**) and [(2,4,6-Me_3-C_6H_2)–CH=N–(C_6H_4–2SMe)] (**1b**) has allowed to establish the importance of the nature of the substituents on the imine group on the regioselectivity of the process.

Keywords: Ferrocene derivatives; Ferrocenyl-Schiff bases; Allylic alkylation; Palladium(II)-allyl compounds

1. Introduction

Ferrocene derivatives and their palladium(II) complexes have attracted great attention in recent years due to their applications in a wide variety of fields including organic and organometallic synthesis and bio-organometallic chemistry [1–6]. The interest of such compounds as precursors or catalysts in homogeneous catalysis is growing, the palladium(II) catalyzed allylic alkylation being one of the most attractive processes [7,8]. This reaction involves the formation of C–C bonds and it is extremely useful in organic synthesis [8]. In this type of catalytic process, the catalyst precursor is a complex containing simultaneously an allyl moiety and either two mono- or a bidentate ligand. Due to the importance of this chemical process, many papers have been focused on studying the influence of the nature of the donor atoms of bidentate organic ligands on the enantioselectivity of the reaction. For the catalytic allylic alkylation process with soft nucleophiles (Scheme 1), when the substrates used have $R^1 = R^2$, the palladium(II) complex formed in step **b** has a symmetrically substituted allyl ligand and the attack of the nucleophile in either of the two possible carbons introduces chirality. However, when $R^2 = H$ four different products could be formed: the two isomers (*E* and *Z*) of the non-chiral linear product when the attack occurs at the non-substituted carbon (C^α) and the branched derivatives coming

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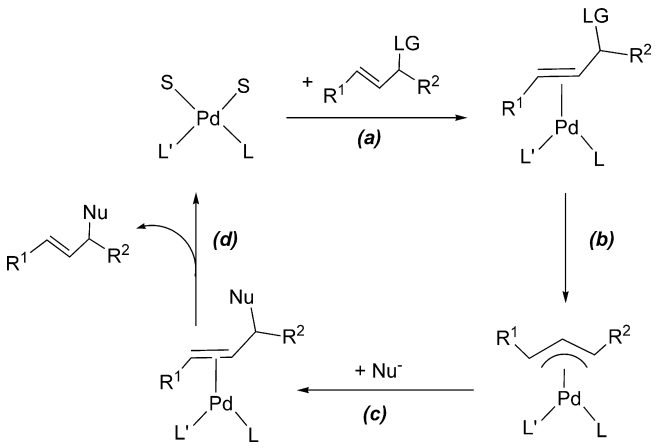
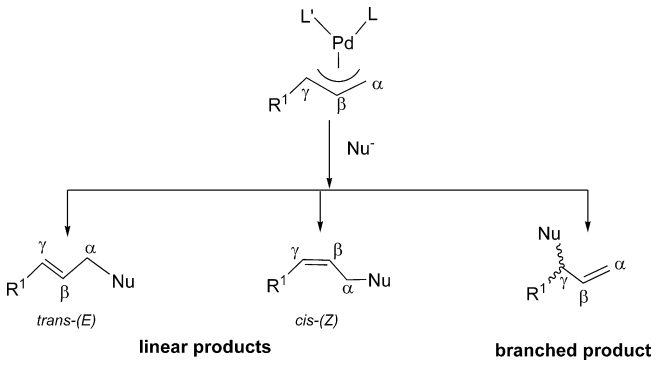


Scheme 1. Mechanism for the palladium-catalyzed allylic substitution reactions using soft nucleophiles, where S represents the solvent, L and L′ monodentate ligands or (L,L′) bidentate ligand, Nu^- the nucleophile and LG is a leaving group.

from the nucleophilic substitution at C^{γ} (Scheme 2). Thus, in these cases regiocontrol becomes necessary prior to enantiocontrol.

Despite the large amount of articles centered on the study of ferrocene derivatives and their palladium(II) complexes in enantioselective allylic alkylation [2,9], the effect of the nature of the donor atoms of the ferrocenyl ligands on the regioselectivity has not been so deeply studied yet. A few articles focused on the effects induced by bidentate (P, E) (E = P′, N or S) or (N, O) ligands on the regioselectivity of palladium(II) catalyzed allylic alkylations have been published [10,11], but related studies involving (N, S) ligands are scarce [12]. We have recently shown that the ferrocenylthioimine [Fc-CH=N–(C_6H_4–2SMe)] (**1a**) [13] (Fig. 1) namely its palladium(II) complex [Pd-(η^3-C_3H_5){Fc-CH=N–(C_6H_4–2SMe)}][PF_6] is an active catalysts for the allylic alkylation of (*E*)-3-phenyl-2-propen-1-yl (*cinnamyl*) acetate using sodium diethyl 2-methylmalonate as nucleophile [12]. In view of this and in order to elucidate the influence of the donor properties of the sulphur atom and/or the flexibility and size of the "Pd(N, S)" chelate, we were prompted to prepare and study the catalytic activity of the novel Schiff bases [Fc-CH=N–(CH_2)$_n$–(C_4H_3S)] with $n = 1$(**2a**) or 2(**2b**) (Fig. 1). In both ligands, the sulphur atom belongs to the thienyl ring but they differ in the length of the –(CH_2)$_n$– chain. This modifies the size of the chelate formed after the coordination to the Pd(II) {a five- (for **2a**) or a six- (for **2b**) membered ring}, which could affect the regioselectivity of the catalytic process.



Scheme 2. Allylic alkylation of an asymmetric π-allyl complex {L and L′ represent monodentate ligands or (L,L′) bidentate ligand and Nu^- the nucleophile}.

2. Results and discussion

2.1. Synthesis and characterization of the ligands

The ligands [Fc-CH=N–(CH_2)$_n$–(C_4H_3S)] {with $n = 1$(**2a**) or 2(**2b**)} were prepared in fairly good yields (80% and 72%, respectively) using the general method reported for the synthesis of related ferrocenylaldimines: Fc-CH=N-R^3 (with R^3 = phenyl, benzyl or naphthyl group) [14]; but using H_2N–(CH_2)$_n$–(C_4H_3S) ($n = 1$ or 2) as starting materials. Elemental analyses and mass spectra of **2** were consistent with the proposed formulae. Compounds **2** were also characterized by mono- [^{1}H and ^{13}C{^{1}H}] and two dimensional [{^{1}H–^{1}H}-NOESY and {^{1}H–^{13}C}-HSQC and HMBC] NMR experiments. The most relevant feature detected in the {^{1}H–^{1}H}-NOESY spectra is the existence of NOE peaks between the signals due to the imine proton and those of the =N–CH_2– unit (Fig. 2) indicating that the ligands **2** adopt the *anti*-(*E*) conformation in solution.

Compound **2a** was also characterized by X-ray diffraction.[1] Its crystal structure (Fig. 3) consists of molecules of [Fc-CH=N–(CH_2)–(C_4H_3S)] separated by van der Waals distances.

The C(11)–N bond length [1.263(4) Å] is similar to those reported for related ferrocenylimines [15,16] and the value of the C(10)–C(11)–N–C(12) torsion angle [179.2°] is consistent with an *anti*-(*E*) conformation of the ligand. The thienyl ring is planar and its main plane forms angles of 84.6° and 86.5° with the substituted pentagonal ring of the ferrocenyl unit and with the imine moiety, respectively.

Bond lengths and angles of the "(η^5-C_5H_5)Fe(η^5-C_5H_4)–" unit agree with those reported for most monosubstituted ferrocene derivatives [15]. The two pentagonal rings are planar, nearly parallel (*tilt angle* = 2.1°) and their conformation deviates by 3.5° from the ideal eclipsed conformation.

[1] Crystal data for **2a**: $C_{16}H_{15}FeNS$, MAR345 diffractometer, $\lambda = 0.71073$ Å, $T = 293(2)$ K, triclinic, $a = 5.872(4)$ Å, $b = 9.610(5)$ Å, $c = 12.712(6)$ Å, $\alpha = 101.28(3)°$, $\beta = 92.19(4)°$, $\gamma = 98.64(4)°$, $V = 693.8(7)$ Å^3, $Z = 2$, $D_{calc} = 1.480$ g/cm^3, $\mu = 1.212$ mm^{-1}, $F(000) = 320$, number of reflections collected = 4901, number of unique reflections 2622 [$R_{int} = 0.0220$], number of parameters = 173, goodness-of-fit = 1.170 and R indices: $R_1 = 0.0460$ and $wR_2 = 0.1253$ [for $I > 2\sigma(I)$] and $R_1 = 0.0465$ and $wR_2 = 0.1257$ (for all data).

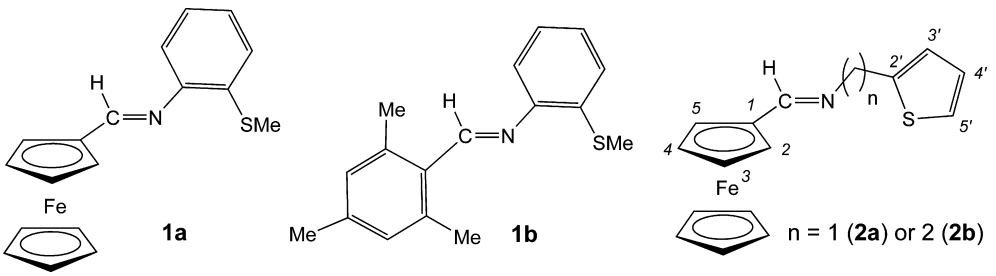


Fig. 1. Chemical formulae of the ferrocenylthioimines [Fc-CH=N-(C_6H_4-2SMe)] (**1a**) and [(2,4,6-Me_3-C_6H_2)-CH=N-(C_6H_4-2SMe)] (**1b**) used in the palladium(II) catalyzed allylic alkylation of cinnamyl acetate [12] and the ligands [Fc-CH=N-$(CH_2)_n$-(C_4H_3S)] {with $n = 1$(**2a**) or 2(**2b**)} under study together with the labelling scheme of the atoms.

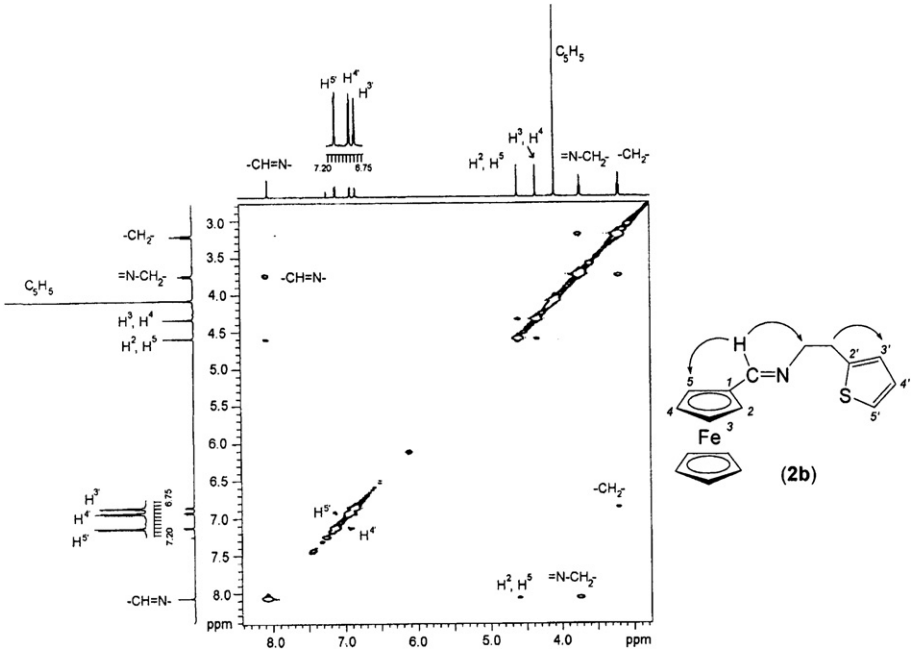


Fig. 2. {^{1}H–^{1}H} NOESY spectrum of **2b** in $CDCl_3$ at 298 K. In the chemical formula, the arrows indicate the most relevant NOE contacts.

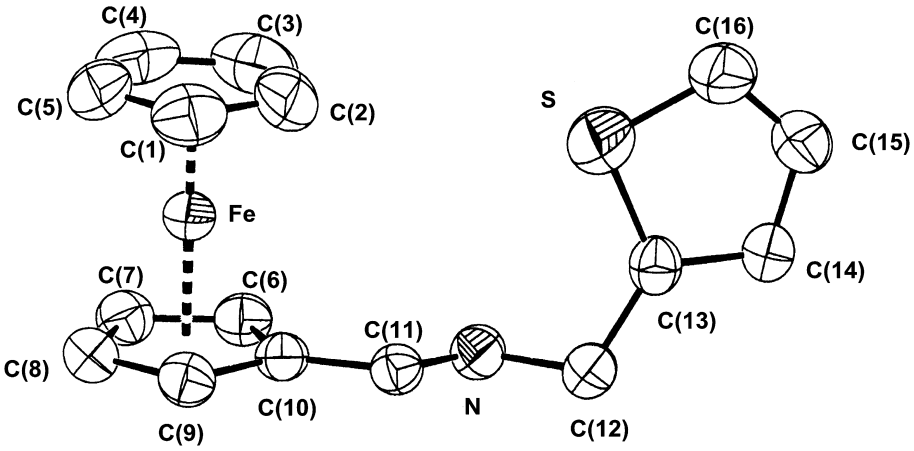


Fig. 3. ORTEP plot of the crystal structure of [Fc-CH=N-(CH_2)-(C_4H_3S)] (**2a**). Selected bond lengths (in Å) and bond angles (in °): C(6)–C(10), 1.429(4); C(9)–C(10), 1.445(4); C(10)–C(11), 1.463(3); C(11)–N, 1.263(4); N–C(12), 1.481(3); C(12)–C(13), 1.495(4); C(13)–C(14), 1.409(4); C(14)–C(15), 1.404(4); C(15)–C(16), 1.336(5); S–C(13), 1.711(3); S–C(16), 1.691(4); C(6)–C(10)–C(11), 128.2(2); C(9)–C(10)–C(11), 123.2(2); C(10)–C(11)–N, 121.7(2); C(11)–N–C(12), 116.0(2); N–C(12)–C(13), 111.2(2); C(12)–C(13)–C(14), 127.3(3); C(13)–C(14)–C(15), 111.0(3); C(14)–C(15)–C(16), 114.4(3); C(15)–C(16)–S, 111.8(3) and C(16)–S–C(13), 92.7(17).

2.2. Catalytic studies

In view of the recent interest of sulphur containing ligands as precursors for palladium-catalyzed allylic alkylation [12,17,18], and in order to elucidate the effects induced by the length of the $-(CH_2)_n-$ chain and the electronic properties of the heterocyclic sulphur on the viability of the process, we decided to study the alkylation of cinnamyl acetate with sodium diethyl 2-methyl malonate using catalytic amounts of ligands **2** (Fig. 1) and $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$. The results obtained from these studies are presented in Table 1 (entries I–IV). For comparison purposes the results published for ligands [Fc-CH=N-(C_6H_4–2SMe)] (**1a**) and [(2,4,6-Me_3–C_6H_2)–CH=N-(C_6H_4–2SMe)] (**1b**) under identical experimental conditions are also included (entries V and VI).

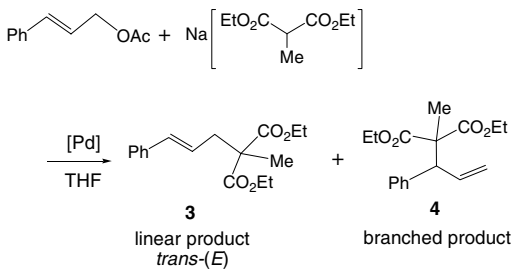
As shown in Table 1 (entries I–IV), **2a** and **2b** catalyze the reaction and the formation of the linear *trans*-(*E*) product (**3**) is strongly preferred over that of the branched product (**4**). The similar regioselectivities obtained when using **2a** (88%) and **2b** (89%) suggest that there is no big influence of the ring size (a five- or a six-membered ring, for **2a** and **2b**, respectively) on the catalytic active species formed when going from five to six membered rings.

The comparison of the results obtained for **2** and for the Schiff bases [Fc-CH=N-(C_6H_4–2SMe)] (**1a**) or [2,4,6-$Me_3C_6H_2$-CH=N-(C_6H_4–2SMe)] (**1b**) [12], which contain the same heteroatoms (N and S), (entries V and VI of Table 1) indicate that for ligands **2**, both activity and selectivity to linear **3** are lower those reported for the thioimines **1a** or **1b**. Furthermore, comparison of the results obtained for **2a** and **1a** (which would both generate five-membered chelate rings) suggest that the replacement of the $-C_6H_4-$2SMe moiety (in **1a**) by the more flexible backbone $-(CH_2)-(C_4H_3S)$ (in **2a**) reduces the regioselectivity of the catalytic process as well as its rate. Whether this effect is due to increased ligand flexibility or to the nature of the S donor atom remains unclear.

2.3. Palladium allylic intermediates

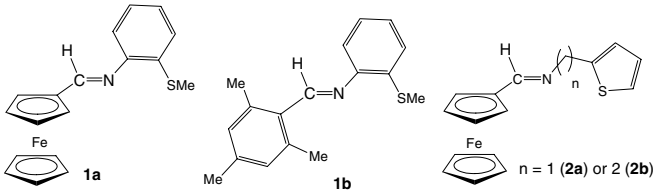
It is well-known that regioselectivity of the allylic alkylation is dependent on a wide variety of factors including the number of isomers of the intermediates formed after the oxidative addition {Scheme 1, step (**b**)} present in solution, their relative abundances, their interconversion rates, the relative arrangement between the non-substituted carbon atom of the allyl group and the two donor atoms of the ligand, the rate of the nucleophilic attack and the position where it takes place. For the catalytic process under study these intermediates are the cationic species $[Pd(\eta^3\text{-}1\text{-}Ph\text{–}C_3H_4)\{Fc\text{-}CH{=}N\text{–}(CH_2)_n\text{–}(C_4H_3S)\}]^+$. In order to rationalize the results obtained from the catalytic studies we decided to prepare and characterize the palladium(II) complexes containing these cations and to study their behaviour in solution.

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



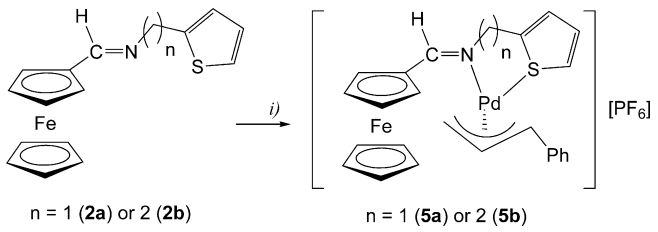
Entry	L	*t* (h)	Conversion (%)	Molar ratio[b] (**3**:**4**)
I	**2a**	20	86.7	89:11
II	**2a**	44	95.0	88:12
III	**2b**	20	87.3	89:11
IV	**2b**	44	97.8	89:11
V[c]	**1a**	20	100.0	96.5:3.5
VI[c]	**1b**	20	100.0	95.8:4:2

[a] *Experimental conditions:* mixtures containing 2.5×10^{-3} mmol of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$, 5.0×10^{-3} mmol of **2a** (or **2b**); 0.5 mmol of cinnamyl acetate, 1.0 mmol of sodium diethyl 2-methylmalonate, THF (5.0 mL), and decane (0.258 mmol) at 298 K.
[b] Determined by GC.
[c] Data from Ref. [12].



Treatment of **2a** (or **2b**) with $[Pd(\eta^3\text{-}1\text{-}Ph\text{–}C_3H_4)(\mu\text{-}Cl)]_2$ (in a 2:1 molar ratio) and in the presence of a slight excess (12%) of $K[PF_6]$ in acetone gave orange solids (herein after referred to as **5a** and **5b**) (Scheme 3). Their elemental analyses agreed with those expected for: $[Pd(\eta^3\text{-}1\text{-}Ph\text{–}C_3H_4)\text{-}\{Fc\text{-}CH{=}N\text{–}(CH_2)_n\text{-}(C_4H_3S)\}][PF_6]$ {with $n = 1$(**5a**) or 2(**5b**), respectively} and their mass spectra showed a peak at $m/z = 532$ (for **5a**) or at $m/z = 546$ (for **5b**), which is consistent with those of the cations $[Pd(\eta^3\text{-}1\text{-}Ph\text{–}C_3H_4)\{Fc\text{-}CH{=}N\text{–}(CH_2)_n\text{–}(C_4H_3S)\}]^+$ ($n = 1$ or 2, respectively).

Proton NMR spectra of **5** in $CDCl_3$ or CD_2Cl_2 at 298 K showed broad signals (Fig. 4a). This could be indicative of the existence of dynamic processes between different isomeric forms. Several isomers of the cations of **5** could be expected in principle due to: (a) the conformation adopted by ligands **2** in the complexes {*anti*-(*E*) (Fig. 5) or *syn*-(*Z*)}; (b) the conformation of the allyl group {*endo*- or *exo*-, Fig. 5(a–d) or (e–h), respectively}, (c) the relative arrangement between the substituted carbon of the allyl group (hereafter referred to as C^γ) and one of the two heteroatoms (N or S) of the ferrocenyl ligand [i.e. the C^γ and the sulphur atom could be in a *cis*- or a *trans*- arrangement



Scheme 3. (i) $[Pd(\eta^3\text{-}1\text{-}Ph\text{–}C_3H_4)(\mu\text{-}Cl)]_2$ {in a **2**:Pd(II) molar ratio of 1} and a slight excess (12%) of $K[PF_6]$ in acetone at 298 K.

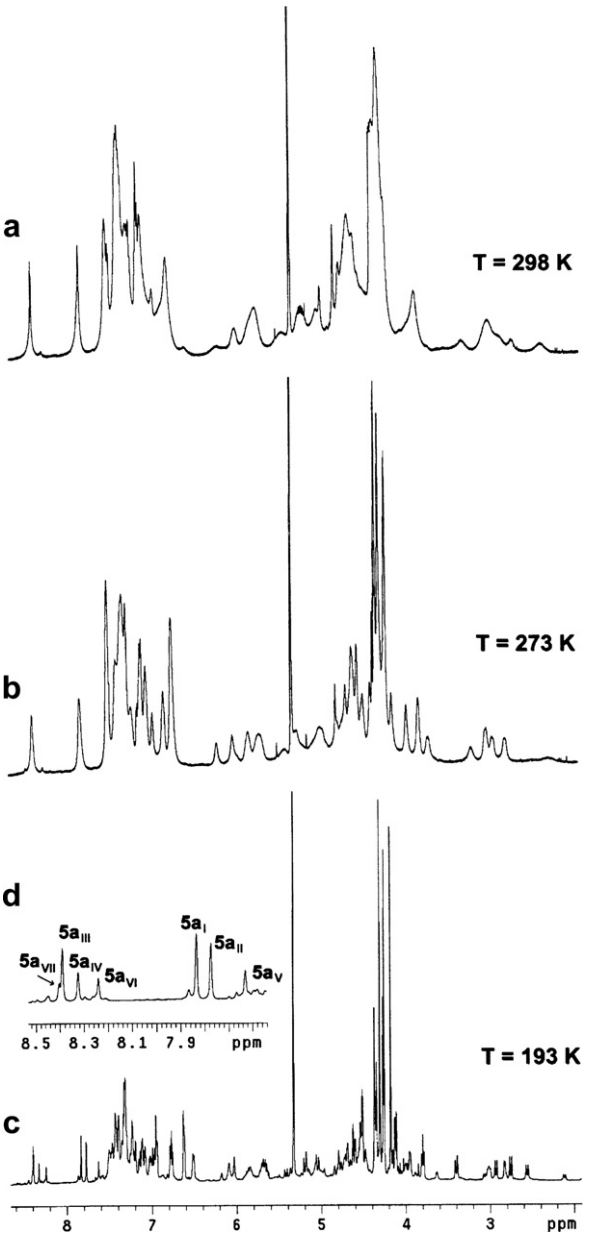


Fig. 4. ^1H NMR spectra (500 MHz) of $[Pd(\eta^3\text{-}1\text{-}Ph\text{–}C_3H_4)\{Fc\text{-}CH{=}N\text{–}(CH_2)\text{-}(C_4H_3S)\}][PF_6]$ (**5a**) in CD_2Cl_2 at 298 K (a), 273 K (b) and 193 K (c), together with an expansion of the spectrum at 193 K in the range 7.55 ppm $< \delta <$ 8.52 ppm (d).

{Fig. 5(a–b, e–f) or (c–d, g–h), respectively}] and (d) the position occupied by phenyl group attached to C^{γ} in relation to the hydrogen bound to the central carbon of the allyl unit {*syn*- (Fig. 5a,c,e or g) or *anti*- (Fig. 5b,d,f or h)}. Besides that, the non-planar chelates formed by the binding of the S and N atoms to the palladium(II) may adopt different conformations. Moreover, if the free rotation around the C_{ipso}–C_{imine} bond of the ligands is inhibited, different rotameric species could also be present in solution. This should be especially relevant at low temperatures.

The resolution of the ^1H NMR spectra of **5** improved upon cooling (Fig. 4a–c). In particular, the spectrum of **5a** in CD_2Cl_2 at 273 K showed two sets of resonances of relative intensities 10.0:6.3 (Fig. 4b). At 193 K the number of resonances increased but their width decreased (Fig. 4c) and the analyses of the sets of signals suggested the coexistence of at least seven isomers (here after referred to as $\mathbf{5a_I}$–$\mathbf{5a_{VII}}$) in a relative abundance of 10.0:8.5:7.7:4.9:3.9:3.4:1.2.

The solution behaviour of **5b** was similar to that of **5a**, its ^1H NMR spectra at 193 K suggested the coexistence of six distinguishable isomers ($\mathbf{5b_I}$–$\mathbf{5b_{VI}}$), but in this case their relative ratios were 10.0:5.5:3.9:2.1:1.6:1.4. The $\{^1H\text{–}^1H\}$-NOESY spectra of the major isomers of **5**{$\mathbf{5a_I}$–$\mathbf{5a_{III}}$ and $\mathbf{5b_I}$–$\mathbf{5b_{II}}$} showed NOE contacts between the imine proton and those of the "=N–CH_2–" moiety; thus, indicating that in these isomers the imine adopted the *anti*-(*E*) conformation. Furthermore, for $\mathbf{5a_I}$–$\mathbf{5a_{III}}$ and $\mathbf{5b_I}$–$\mathbf{5b_{II}}$, the values of the coupling constant $^3J(H^{\gamma}\text{–}H^{\beta})$ suggest that the proton attached to the C^{γ} carbon is located in an *anti*- position in relation to the central proton of the allyl unit (H^{β}). These findings reduce the number of possible isomers to four and more specifically to types a,c,e or g depicted in Fig. 5.

The use of molecular models for cations where the C^{γ} carbon of the allyl ligand is in a *trans*- arrangement to the sulphur (types c and g) reveals that in these isomers, the phenyl ring would be too close to the C_5H_4 ring to the ferrocenyl unit. Consequently, this distribution of the substituents would introduce significant steric effects. In fact the $\{^1H\text{–}^1H\}$-NOESY and ROESY spectra of **5** {($\mathbf{5a_I}$ and $\mathbf{5a_{II}}$) and ($\mathbf{5b_I}$ and $\mathbf{5b_{II}}$)} at 193 K showed NOE peaks between the doublet due to the $H^{5'}$ proton of the thienyl unit and one aromatic proton. This is only possible if the heterocycle and the phenyl group are proximal, which is indicative of a *cis*- arrangement between the C^{γ} carbon and the sulphur atom. All these findings suggests that the pairs of isomers {($\mathbf{5a_I}$ and $\mathbf{5a_{II}}$) and ($\mathbf{5b_I}$ and $\mathbf{5b_{II}}$)} correspond to the types a and e shown in Fig. 5, which differ in the conformation of the allyl group (*endo*- and *exo*-, respectively).

The complexity of the ^1H and the two dimensional [$\{^1H\text{–}^1H\}$-NOESY, $\{^1H\text{–}^1H\}$-ROESY and $\{^1H\text{–}^{13}C\}$-HSQC] NMR spectra of **5** at 193 K together with the low abundance of $\mathbf{5a_{IV}}$–$\mathbf{5a_{VII}}$ and $\mathbf{5b_{III}}$–$\mathbf{5b_{VI}}$ and the partial overlapping of the resonances due to these isomers and those of the major components did not allow us to assign the resonances due these minor isomers.

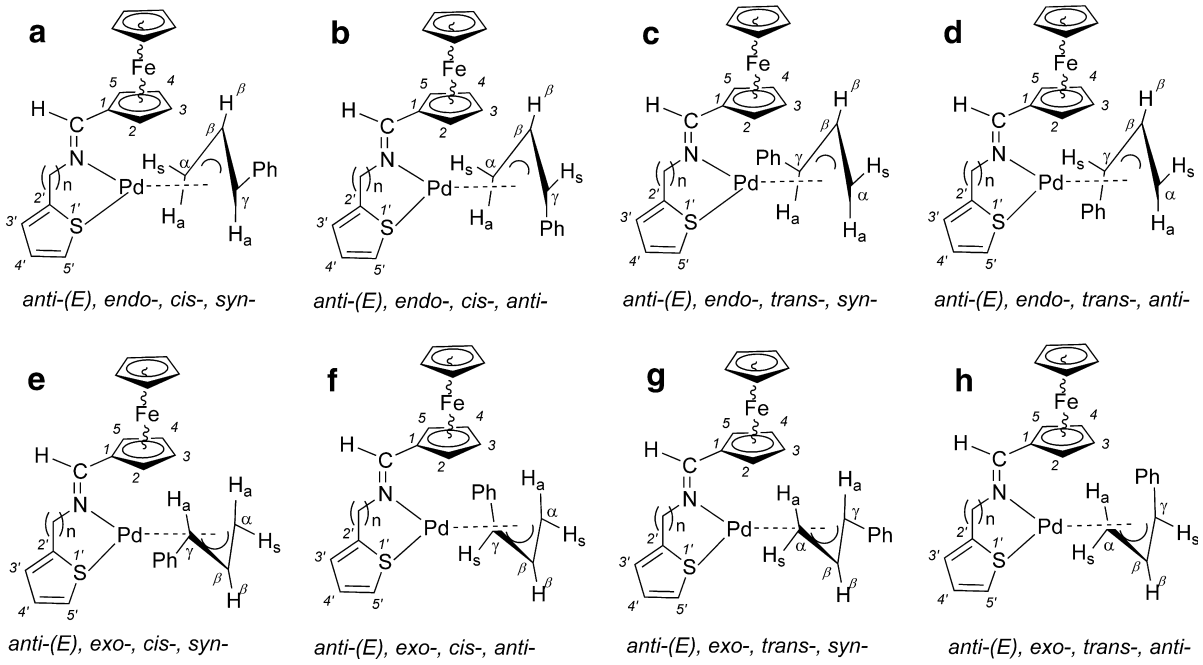


Fig. 5. Schematic view of some of the isomeric forms expected for the cations of compounds $[Pd(\eta^3\text{-}1\text{-}Ph\text{–}C_3H_4)\{Fc\text{-}CH{=}N\text{–}(CH_2)_n\text{–}(C_4H_3S)\}][PF_6]$ $\{n = 1(\mathbf{5a})$ or $2(\mathbf{5b})\}$, in which the ligand adopts the *anti*-(*E*) conformation (see text). The wavy lines indicate that the "$Fe(\eta^5\text{-}C_5H_5)$" moieties may be situated in an upper (or in a lower) plane in reference to that of the C_5H_4 ring of the ferrocenyl unit. An additional set of isomers could also be formed if the ligand exhibits the *syn-(Z)* conformation.

2.4. Stoichiometric reactions

We also studied the reactions between compounds **5** and an excess of sodium diethyl 2-methylmalonate in THF at 298 K (*stoichiometric reaction*). The reaction gave after work up a mixture of the linear *trans*-(*E*) derivative (**3**) and the branched product (**4**) in molar ratios **3**:**4** of 94.1:5.9 (for **5a**) and 93.0:7.0 (for **5b**).

The study of the solution behaviour of **5** (described above) showed that in the two major isomers of **5a**($\mathbf{5a_I}$ and $\mathbf{5a_{II}}$) and **5b** ($\mathbf{5b_I}$ and $\mathbf{5b_{II}}$) differ in the conformation of the "(1-Ph–C_3H_4)", but in all cases: (a) the ligand adopts the *anti*-(*E*) conformation, (b) the phenyl ring is located on the *syn*-position and (c) the substituted carbon of the allyl group (C^{γ}) is in a *cis*-arrangement to the sulphur of the thienyl unit.

In addition, the results obtained from the stoichiometric and catalytic studies indicate that the formation of the linear product **3** is preferred over that of the branched product **4**. This could be due to several factors such as the smaller steric hindrance on the non-substituted carbon (C^{α}) or its higher electrophilic character when compared with that of the C^{γ} carbon atom.

2.5. Conclusions

The results presented here have shown the potential utility of ligands $[Fc\text{-}CH{=}N\text{–}(CH_2)_n\text{–}(C_4H_3S)]$ (**2**), that contain two different donor atoms (N and S), in the palladium catalyzed allylic alkylation of cinnamyl acetate under mild experimental conditions. The comparison of the results obtained for **2** and those reported recently for $[Fc\text{-}CH{=}N\text{–}(C_6H_4\text{–}2SMe)]$ (**1a**), has allowed us to establish the relevancy of the electronic properties of the sulphur atom and the flexibility of the chain connecting these two donor atoms on the regioselectivity and rate of the catalytic process. The presence of the thienyl unit (in **2a** and **2b**) slows down the reaction and produces a significant decrease (*ca.* 9%) in the regioselectivity towards the linear product (**3**) in comparison with data obtained for **1a**, where the sulphur belongs to a thioether group. Besides that, data presented in Table 1 also indicate that this factor has greater influence on the regioselectivity of the catalytic process than that due to the length of the $\text{–}(CH_2)_n\text{–}$ chain. Several factors such as the different *trans*-influence of the sulphur atom and the lability of the Pd–S bond in the intermediate species formed in the catalytic process, may also be important to determine the number of isomers present in solution {i.e. four in $[Pd(\eta^3\text{-}1\text{-}Ph\text{–}C_3H_4)(\mathbf{1a})]$ [12] or seven (in **5a**) at 193 K}, their interconversion rates or the preferential position for the nucleophilic attack in each one of the isomeric species. Further experimental work on this field is required to clarify the relative weight of each one of these factors.

3. Experimental

3.1. Materials and methods

Ferrocenecarboxaldehyde and the amines $H_2N\text{–}(CH_2)_n\text{–}(C_4H_3S)$ (with $n = 1$ or 2) were purchased from Aldrich and used as received. Compound $[Pd(\eta^3\text{-}1\text{-}Ph\text{–}C_3H_4)(\mu\text{-}Cl)]_2$

was prepared as described previously [19]. Sodium diethyl 2-methylmalonate (0.5 M) was synthesized from diethyl 2-methyl malonate and NaH in THF at 273 K. Solvents (except benzene) were distilled and dried before use [20]. Some of the preparations described below require the use of highly hazardous reagents (such as benzene) that should be handled with *Caution*.

Elemental analyses were carried out at the Serveis de Recursos Cientifics i Tècnics (*Universitat Rovira i Virgili*). FAB^+ mass spectra were performed at the Servei d'Espectrometria de Masses (*Universitat de Barcelona*) with a VG-Quatro Fissions instrument and using 3-nitrobenzylalcohol (NBA) as matrix. IR spectra were obtained with a Nicolet 400-FTIR instrument using KBr pellets. Routine ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Gemini-200 MHz or a Mercury-400 MHz instruments, respectively. High resolution ^1H NMR spectra and the two-dimensional [$\{^1H$–$^1H\}$-NOESY and ROESY and $\{^1H$–$^{13}C\}$-HSQC and HMBC] NMR experiments were registered with a Varian VRX-500 or a Bruker Avance DMX-500 MHz instruments at 298 K. The latter equipment was also used to perform the variable temperature (VT) NMR experiments. The chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz. Except where quoted, the NMR spectra were recorded using $CDCl_3$ (99.9%) as solvent and $SiMe_4$ as internal reference.

The product distribution of alkylation experiments was measured on a Trace-DQS instrument equipped with a HP-5 column, length 25 m, inner diameter 0.2 mm, film thickness 0.5 μm, and an electron impact mass detector.

3.2. Preparation of the compounds

3.2.1. Synthesis of [Fc-CH=N–$(CH_2)_n$–(C_4H_3S)] [n = 1(**2a**) or 2(**2b**)]

Ferrocenecarboxaldehyde (1.00 g, 4.67×10^{-3} mol) was dissolved in 20 mL of benzene. The reaction mixture was stirred at 298 K for 10 min and then filtered out. The undissolved materials were discarded, the filtrate was transferred to an erlenmeyer flask and then equimolar amount (4.80×10^{-3} mol) of the corresponding amine $\{H_2N$–$(CH_2)_n$–(C_4H_3S) ($n = 1$ or 2)$\}$ was added. The flask was introduced in an ethyleneglycol bath and it was connected to a Dean-Stark apparatus and to a condenser. The reaction mixture was refluxed until *ca.* 10 mL had condensed on the Dean-Stark apparatus. The hot reaction mixture was filtered out and the deep-red filtrate was concentrated to dryness on a rotary evaporator. The solids formed were collected and dried. [Yield: 1.17 g (80%) and 1.08 g (72%) for **2a** and **2b**, respectively]. Characterization data for **2a**: Anal. Calc. for $C_{16}H_{15}NFeS$: C, 62.15; H, 4.89; N, 4.53; S, 10.37. Found: C, 62.1; H, 5.0; N, 4.6; S, 11.3%. MS (FAB^+): $m/z = 309$, $[M]^+$. IR-data: 1629 cm^{-1} {ν(>C=N–)}. ^1H NMR data [21]: $\delta = 8.21$ (s, 1H, –CH=N–), 4.20 (s, 5H, C_5H_5), 4.46 (t, 2H, $^3J = 1.5$, H^3 and H^4), 4.77 (t, 2H, $^3J = 1.5$, H^2 and H^5), 4.83 (s, 2H, =N–CH_2–), 7.02 (br s, 2H, $H^{3'}$ and $H^{4'}$) and 7.26 (d, 1H, $^3J = 4.0$, $H^{5'}$). $^{13}C\{^1H\}$ NMR-data [21]: $\delta = 163.3$(–CH=N–), 69.2 (C_5H_5), 79.3 (C^1), 69.0 (C^2 and C^5), 71.4 (C^3 and C^4), 58.3 (=N–CH_2–), 141.2 ($C^{2'}$), 125.7 ($C^{3'}$), 127.1 ($C^{4'}$) and 125.3($C^{5'}$). For **2b**: Anal. Calc. for $C_{17}H_{17}NFeS$: C, 63.17; H, 5.30; N, 4.33; S, 9.92 Found: C, 63.3; H, 5.5; N, 4.4; S, 10.2%. MS (FAB^+): $m/z = 323$, $[M]^+$. IR-data: 1645 cm^{-1} {ν(>C=N–)}. ^1H NMR data [21]: $\delta = 8.05$ (s, 1H, –CH=N–), 4.07 (s, 5H, C_5H_5), 4.33 (t, 2H, $^3J = 1.5$, H^3 and H^4), 4.58 (t, 2H, $^3J = 1.5$, H^2 and H^5), 3.73 (t, 2H, $^3J = 6.0$, =N–CH_2–), 3.18 (t, 2H, $^3J = 6.0$, –CH_2–), 6.84 (br., 1H, $H^{3'}$), 6.92 (dd, 1H, $^3J = 5.0$ and $^4J = 3.0$, $H^{4'}$) and 7.12 (d, 1H, $^3J = 5.0$, $H^{5'}$). $^{13}C\{^1H\}$ NMR-data [21]: $\delta = 161.9$ (–CH=N–), 69.1 (C_5H_5), 80.4 (C^1), 70.6 (C^2 and C^5), 68.6 (C^3 and C^4), 63.1 (=N–CH_2–), 31.5 (–CH_2–), 142.7 ($C^{2'}$), 125.0 ($C^{3'}$), 126.8 ($C^{4'}$) and 123.5 ($C^{5'}$).

3.2.2. Synthesis of [Pd(η^3-1-Ph–C_3H_4){Fc-CH=N–$(CH_2)_n$–(C_4H_3S)}][PF_6] {n = 1(**5a**) or 2(**5b**)}

A 0.150 g (2.89×10^{-4} mol) amount of [Pd(η^3-1-Ph–C_3H_4)(μ-Cl)]$_2$ and 5.78×10^{-4} mol of the corresponding ligand [Fc-CH=N–$(CH_2)_n$–(C_4H_3S)] {$n = 1$(**2a**) or 2(**2b**)} were dissolved in 20 ml of acetone. Then, 0.123 g (6.68×10^{-4} mol) of K[PF_6] was added. The reaction mixture was stirred at 298 K for 1.5 h and then filtered. The filtrate was concentrated to dryness on rotatory evaporator. The orange residue was treated with the minimum amount of CH_2Cl_2 and the undissolved materials were removed by filtration and discarded. The addition of Et_2O to the filtrate produced the formation of an orange solid, which was collected by filtration and dried in vacuum for 24 h. [Yield: 0.150 g, (38%) for **5a** and 0.209 g, (52%) for **5b**]. *Characterization data for* **5a**: Anal. Calc. for $C_{25}H_{24}F_6FeNPPdS$: C, 44.31; H, 3.57; N, 2.07; S, 4.73. Found: C, 44.5; H, 3.7; N, 2.15; S, 4.95%. MS (FAB^+): $m/z = 532$, $\{M-[PF_6]\}^+$. IR-data: 1645 {ν(>C=N–)} and 839 cm^{-1} {$[PF_6]^-$}. ^1H NMR data in CD_2Cl_2 at 273 K: two isomeric forms (**5a$_I$** and **5a$_{II}$**) coexisted in a molar ratio **5a$_I$**:**5a$_{II}$** 10.0:6.3. For **5a$_I$** [22,23]: 7.82 (s, 1H, –CH=N–), 4.33 (s, 5H, C_5H_5), 4.54 (s, 2H, H^2 and H^5), 4.39 (s, 2H, H^3 and H^4), 5.29 and 4.63 (m, 2H, =N–CH_2–), 5.71 (br s, 1H, H^β), 3.97 (br s, 1H, H^α_s) and 3.03 (br s, 1H, H^α_a). For **5a$_{II}$** [22,23]: 8.38 (s, 1H, –CH=N–), 4.28 (s, 5H, C_5H_5), 4.73 and 4.48 (br s, 2H, =N–CH_2–), 5.84 (br s, 1H, H^β), 3.83 (br s, 1H, H^α_s) and 2.80 (br s, 1H, H^α_a). The resonances of the H^γ_a protons (for **5a$_I$** and **5a$_{II}$**) were overlapped by the signals due to the =N–CH_2– and C_5H_4– protons of the two species. At 193 K: **5a$_I$**–**5a$_{VII}$** coexisted in a ratio 10.0:8.5:7.7:4.9:3.9:3.4 and 1.2. Due to the low abundance of **5a$_{IV}$**–**5a$_{VII}$** only the assignment of the signals due to **5a$_I$**–**5a$_{III}$** was possible. For **5a$_I$** [22,23]: 7.83 (s, 1H, –CH=N–), 4.31 (s, 5H, C_5H_5), 4.51 (s, 2H, H^2 and H^5), 4.35 (s, 2H, H^3 and H^4), 5.21 and 4.53 (m, 2H, =N–CH_2–), 7.23 (br s, 1H, $H^{3'}$), 6.94 (br s, 1H, $H^{4'}$), 6.52 (d, 1H, $^3J = 7$, $H^{5'}$), 3.41(d, 1H, $^3J = 11.5$, H^γ_a), 5.67 (m, 1H, $^3J = 11.5$ and 6.5, H^β), 3.79 (d, 1H, $^3J = 6.5$, H^α_s) and 2.76 (d, 1H, $^3J = 11.5$, H^α_a). For **5a$_{II}$** [22–24]: 7.77 (s, 1H, –CH=N–), 4.18 (s, 5H,

C_5H_5), 4.71 and 4.35 (m, 2H, =N–CH_2–), 4.13 (d, 1H, $^3J = 12.0$, H^{γ}_a), 5.86 (m, 1H, $^3J = 12.0$ and 6.5, H^{β}), 3.81 (d, 1H, $^3J = 6.5$, H^{α}_s) and 2.93 (d, 1H, $^3J = 12.0$, H^{α}_a). For **5a$_{III}$** [22–24]: 8.39 (s, 1H, –CH=N–), 4.25 (s, 5H, C_5H_5), 5.05 and 4.61(m, 2H, =N–CH_2–), 4.38 (d, 1H, $^3J = 12.0$, H^{γ}_a), 5.16(m, 1H, $^3J = 12.0$ and 6.0, H^{β}), 2.84 (d, 1H, $^3J = 6.0$, H^{α}_s) and 2.56 (d, 1H, $^3J = 12.0$, H^{α}_a). ^{13}C NMR data [25] in CD_2Cl_2 at 193 K, for **5a$_I$** [22,23]: 164.6 (–CH=N–), 70.3 (C_5H_5), 72.5 (C^2 and C^5), 72.6 (C^3 and C^4), 60.2 (=N–CH_2–), 72.9 (C^{γ}), 107.4 (C^{β}), 56.0 (C^{α}), 129.7 ($C^{3'}$), 127.5 ($C^{4'}$) and 127.0 ($C^{5'}$). For **5a$_{II}$** [22,23]: 164.7(–CH=N–), 70.0 (C_5H_5), 58.4 (=N–CH_2–), 79.4 (C^{γ}), 107.1 (C^{β}) and 55.3 (C^{α}). For **5b$_{III}$** [22,23]: 166.7 (–CH=N–), 70.2 (C_5H_5), 61.4 (=N–CH_2–), 76.5 (C^{γ}), 107.1 (C^{β}) and 56.8 (C^{α}). For **5b**: Anal. Calc. for $C_{26}H_{26}F_6FeNPPdS$: C, 45.14; H, 3.79; N, 2.02; S, 4.63. Found: C, 45.2; H, 3.6; N, 2.1; S, 4.8%. MS (FAB^+): $m/z = 546$ $\{M\text{-}[PF_6]\}^+$. IR-data: 1629 $\{\nu(\text{>C=N–})\}$ and 840 $cm^{-1}\{[PF_6]^-\}$. ^{1}H NMR data in CD_2Cl_2 at 193 K: six isomeric forms (**5b$_I$**–**5b$_{VI}$**) coexisted in solution in molar ratios 10.0:5.5: 3.9:2.1:1.6:1.4. Due to the low abundance of **5b$_{III}$**–**5b$_{VI}$** only the assignment of the signals due to **5b$_I$** and **5b$_{II}$** was possible. For **5b$_I$** [22]: 7.78 (s, 1H, –CH=N–), 4.14 (s, 5H, C_5H_5), 4.61 (s, 2H, H^2 and H^5), 4.52 (s, 2H, H^3 and H^4), 3.96 and 3.00 (m, 2H, =N–CH_2–), 3.26 (m, 2H, –CH_2–), 7.54 (br s, 1H, $H^{3'}$), 6.91 (t, 1H, $^3J = 8.0$, $H^{4'}$), 6.84 (br s, 1H, $H^{5'}$), 4.31 (d, 1H, $^3J = 12.0$, H^{γ}_a), 6.02 (m, 1H, $^3J = 12.0$ and 6.5, H^{β}), 3.90 (d, 1H, $^3J = 6.5$, H^{α}_s) and 3.04 (d, 1H, $^3J = 12.0$, H^{α}_a). For **5b$_{II}$** [22,23]: 7.50 (s, 1H, –CH=N–), 4.03 (s, 5H, C_5H_5), 4.74 (s, 1H, H^2), 4.37 (s, 1H, H^3), 4.49 (s, 1H, H^4), 4.57 (s, 1H, H^5), 3.75 (br s, 2H, =N–CH_2–), 3.21 and 2.48 (m, 2H, –CH_2–), 4.26 (d, 1H, $^3J = 11.5$, H^{γ}_a), 5.77 (m, 1H, $^3J = 11.5$ and 7.0, H^{β}), 3.84 (d, 1H, $^3J = 7.0$, H^{α}_s) and 2.90 (d, 1H, $^3J = 11.5$, H^{α}_a). The resonances due to the protons $H^{3'}$, $H^{4'}$ and $H^{5'}$ were partially masked by those due to the aromatic protons of the phenyl ring. ^{13}C NMR data [25] in CD_2Cl_2 at 193 K, for **5b$_I$** [22,23]: 171.8 (–CH=N–), 75.2 (C_5H_5), 77.8 (C^2 and C^5), 77.7 (C^3 and C^4), 65.6 (=N–CH_2–), 36.4 (–CH_2–), 133.1 ($C^{3'}$), 132.7 ($C^{4'}$), 132.4 ($C^{5'}$), 83.2 (C^{γ}), 111.9 (C^{β}) and 61.8 (C^{α}). For **5b$_{II}$** [22,23]: 171.7 (–CH=N–), 75.1 (C_5H_5), 77.8 (C^2), 77.3 (C^3), 77.9 (C^4), 78.1 (C^5), 70.5 (=N–CH_2–), 35.3 (–CH_2–), 84.3 (C^{γ}), 111.8 (C^{β}) and 61.5 (C^{α}).

3.3. Allylic alkylation reactions

3.3.1. Catalytic reactions

These reactions were performed under nitrogen at 298 K in THF (5 mL), using 2.5×10^{-3} mmol of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$, 5.0×10^{-3} mmol of **2a** or **2b**, 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 mixture. Each aliquot was diluted with Et_2O, washed with water, and dried over Na_2SO_4. Aliquots then were analyzed by GC using decane (0.258 mmol) as the internal standard.

3.3.2. Stoichiometric reaction

The stoichiometric alkylation of **5** was performed under nitrogen atmosphere at 298 K by adding an excess of sodium diethyl 2-methylmalonate (0.7 mL of a 0.5 M solution in THF) to a solution containing 70 mg, (1.03×10^{-4} mol) of **5a** (or 1.01×10^{-4} mol of **5b**). The reaction was instantaneous and H_2O was added after 10 min. The reaction mixture was filtered over Celite. The filtrate was then treated with Et_2O (≈15 mL) and the organic layer was washed three times with water. The organic layer was then dried over Na_2SO_4 and the filtrate was concentrated to dryness on a rotary evaporator. The residue was dissolved in the minimum amount of Et_2O and passed through a short SiO_2 column (4.0 cm × 0.6 cm). The band released was collected and concentrated to dryness. The oily residue contained {according to ^{1}H NMR (500 MHz) and GC} **3** and **4** in a molar ratios **3**:**4** = 94.1:5.9 (for **5a**) and 93.0:7.0 (for **5b**).

3.4. Crystallography

A prismatic crystal of **2a** (0.1 mm × 0.1 mm × 0.2 mm) was selected and mounted on a MAR345 diffractometer with a image plate detector. Unit-cell parameters were determined from 250 reflections in the range $3° < \Theta < 31°$ and refined by least-squares method. Intensities were collected with a graphite monochromatized Mo Kα radiation. The number of reflections measured in the range $3.52° \leqslant \Theta \leqslant 29.32°$ was 4901 of which 2622 were non-equivalent by symmetry $\{R_{int}(\text{on } I) = 0.022\}$ and 2542 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz-polarization corrections were made but absorption corrections were not. The structure was solved by Direct methods using SHELXS computer program [26] and refined by full-matrix least-squares method with the SHELX97 computer program [27] using 4910 reflections. The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0710P)^2 + 0.3514P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f' and f'' were obtained from the literature [28]. All hydrogen 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 atoms linked to it.

Appendix A. Supplementary material

CCDC 648588 contains the supplementary crystallographic data for **2a**. 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.2007.07.027.

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[21] Labelling of the atoms refers to that depicted in Fig. 1.

[22] Labelling of the atoms corresponds to those shown in Fig. 5.

[23] Selected data.

[24] The signals due to the protons of the C_5H_4 ring were partially overlapped by those of the =N–CH_2– moiety and those of the thienyl group were masked by the resonances of the aromatic protons of the (1-Ph–C_3H_4) ligand.

[25] These data were obtained from two dimensional {^{1}H–^{13}C}-HSQC NMR experiments at 193 K.

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