

Heterodimetalllic Palladium(II) Complexes with Bidentate (N,S) or Terdentate (C,N,S)[−] Ferrocenyl Ligands. The Effect of the Ligand Donor Atoms on the Regioselectivity of the Allylic Alkylation of Cinnamyl Acetate

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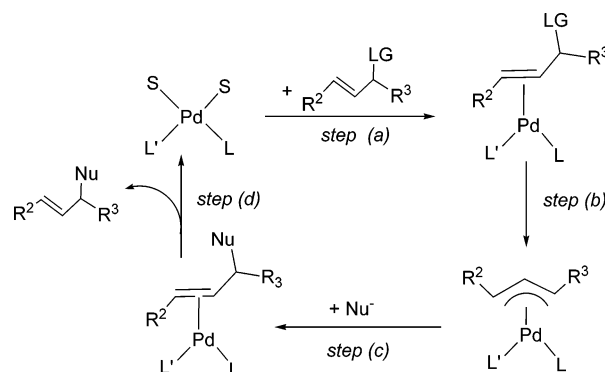
The synthesis and characterization of $[\text{Pd}(\eta^3\text{-}1\text{-R}^1\text{-C}_3\text{H}_4)\{\text{FcCH}=\text{N}-(\text{C}_6\text{H}_4-2\text{SMe})\}][\text{PF}_6]$ ($\text{R}^1 = \text{H}$ (**2a**) or Ph (**3a**)) are described. A comparative study of the catalytic activity of (a) the mixtures containing $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})]_2$ and its parent ligand (**1a**) or $\text{H}_2\text{N}-\text{C}_6\text{H}_4-2\text{SMe}$ (**4**) and (b) the palladacycles $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)-\text{CH}=\text{N}-(\text{C}_6\text{H}_4-2\text{SMe})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ (**5a**), $[\text{Pd}\{(2\text{-CH}_2\text{-}4,6\text{-Me}_2\text{C}_6\text{H}_2)-\text{CH}=\text{N}-(\text{C}_6\text{H}_4-2\text{SMe})\}\text{Cl}]$ (**5b**) in the allylic alkylation of (*E*)-3-phenyl-2-propenyl (cinnamyl) acetate with sodium diethyl 2-methylmalonate is also reported.

Introduction

Transition metal complexes containing ferrocene derivatives as ligands have attracted great interest in recent years.^{1,2} In compounds of this kind, the presence of two proximal metal centers with different environments, oxidation numbers, and spin states may influence their mutual cooperation in a wide variety of processes, including their electrochemical behavior or even their reactivity.^{1–3} Among all the examples reported so far, palladium(II) derivatives are particularly relevant due to their physical or chemical properties and their utility in several fields,^{4–10} such as homogeneous catalysis.^{1,10}

Palladium(II)-catalyzed allylic substitution is one of the most common procedures used in organic synthesis to achieve the

Scheme 1. Mechanism for the Palladium-Catalyzed Allylic Substitutions Using Soft Nucleophiles {S = Solvent, L and L' = Monodentate Ligands or (L,L') = Bidentate Ligand, LG = Leaving Group, Nu[−] = Nucleophile}



formation of C–C bonds.^{11,12} In this sort of processes the catalytic precursor is a complex containing a $(\eta^3\text{-C}_3\text{H}_5)$ group

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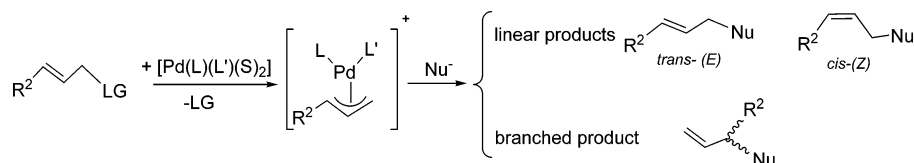
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Scheme 2. Allylic Alkylation of an Asymmetric π -allyl Complex {where LG = leaving group, L and L' = monodentate ligands or (L,L') = bidentate ligand, S = solvent, and Nu[−] = nucleophile}



and either one bidentate or two monodentate ligands. Due to the relevance of this catalytic process,^{11,12} many papers have focused on studying the influence of the nature of the donor atoms of bidentate organic ligands on the enantioselectivity of the reaction.¹³ According to the mechanism accepted for the catalytic allylic alkylation process with soft nucleophiles (Scheme 1), when the substrates used have $R^2 = R^3$, the palladium complex formed in step (b) has a symmetrically substituted allyl ligand and the nucleophilic attack produces the formation of a chiral product. However, if $R^1 \neq R^2$, the intermediates formed in step (b) are nonsymmetrically substituted palladium(II) allyl complexes, regiocontrol becomes an issue prior to enantiocontrol,¹⁴ and three different products can be formed: the nonchiral *E* and *Z* linear products and the chiral branched derivative (Scheme 2).

Many papers have focused on studying the use of ferrocene derivatives or their palladium(II) complexes in enantioselective allylic alkylation.^{13,15} However, the effect of the nature of the donor atoms of the ferrocenyl ligands on the regioselectivity has not been studied so intensively. Most of the articles deal with bidentate (P,E) ligands ($E = P', N$, or S),^{13,16} and recently Kim et al.¹⁷ described the catalytic activity of the two palladium(II) complexes shown in Figure 1 on the allylic alkylation of cinnamyl acetate. In view of this, and due to the increasing interest in palladium(II) complexes derived from thioethers,^{16,18,19} we were prompted to prepare and characterize $[Pd(\eta^3\text{-}1\text{-}R^1\text{-}C_3H_4)\{FcCH=N-(C_6H_4-2SMe)\}][PF_6]$ [$R^1 = H$ (**2a**) or Ph (**3a**)]. A comparative study of the catalytic activity of **2a**, its parent ligand **1a**, [(2,4,6- $Me_3C_6H_2$)- $CH=N-(C_6H_4-2SMe)$] (**1b**), the amine $H_2N-C_6H_4-2SMe$ (**4**), and the palladacycles **5a**^{7a} and **5b**^{18a} (Figure 2) in the allylic alkylation of (*E*)-3-phenyl-2-propenyl (cinnamyl) acetate with sodium diethyl 2-methylmalonate is also reported.

Results and Discussion

The reaction of $[FcCH=N-(C_6H_4-2SMe)]$ (**1a**)^{7a} with the corresponding $[Pd(\eta^3\text{-}1\text{-}R^1\text{-}C_3H_4)(\mu\text{-}Cl)_2]$ ($R^1 = H$ or Ph) complex in a 2:1 molar ratio and an excess of $K[PF_6]$ gave $[Pd(\eta^3\text{-}1\text{-}R^1\text{-}C_3H_4)\{FcCH=N-(C_6H_4-2SMe)\}][PF_6]$ [$R^1 = H$ (**2a**) or Ph (**3a**)] (Scheme 3). Compounds **2a** and **3a** are garnet red and air-stable solids at 298 K. Their IR spectra showed the absorption due to the $[PF_6]^-$ anion²⁰ and a sharp and intense band due to the stretching of the imine group. The shift of this band to lower frequencies is consistent with the binding of the ligand to palladium(II) through the imine nitrogen.^{7,9,18a,19}

The crystal structure of **2a** contains equimolar amounts of $[Pd(\eta^3\text{-}C_3H_5)\{FcCH=N-(C_6H_4-2SMe)\}]^+$ and $[PF_6]^-$. The palladium(II) is bound to the two heteroatoms of the ferrocenyl ligand and to the allyl group in a η^3 -fashion. The five-membered chelate ring has an envelope-like conformation in which the palladium(II) is out of the main plane defined by the atoms N, C(12), C(17), and S. The Pd–N and Pd–S bond lengths agree with those of related palladium(II) complexes with (N,S) ligands.^{7a,18,21,22} The differences between the Pd–C(19) and the Pd–C(21) bond distances {2.14(2) and 2.11(2) Å, respectively} do not exceed 3σ , but the N–Pd–C(19) bond angle [105.8-(5)°] is larger than that of S–Pd–C(21) [101.5(5)°]. A similar variation has been found in $[Pd(\eta^3\text{-}1,3\text{-}Ph_2C_3H_3)\{(2\text{-}Cl\text{-}C_6H_4)\text{-}CH=N\text{-}CH(CH_3)_2\}](ClO_4)$,²² which also contains a (N,S) bidentate ligand. The imine adopts the *anti-E* conformation, and the C(11)–N bond length is similar to the value reported for most ferrocenylimines.^{7a,19,21,23} The methyl group of the –SMe moiety, the central “–CH–” unit of the allyl group, and the “Fe($\eta^5\text{-}C_5H_5$)” unit are located on the same side of the coordination plane of the palladium(II).

The crystal structure of **3a**·H₂O is formed by two nonequivalent units of $[Pd(\eta^3\text{-}1\text{-}Ph\text{-}C_3H_4)\{FcCH=N-(C_6H_4-2SMe)\}]^+$ (**I** and **II**, respectively), $[PF_6]^-$ anions, and H₂O molecules. In **I** and **II** (Figure 3), **1a** binds to the Pd(II) through the N and S atoms. For this distribution of groups, the hydrogen atoms on the *ortho* site of the C₅H₄ ring and one of the –CH₂– moiety, in a *cis*-arrangement to the nitrogen, are close {distances between these atoms: 2.44 (in **I**) and 2.77 Å (in **II**)}.

In cations **I** and **II** (a) the sulfur is in a *cis*-arrangement to the substituted carbon of the allyl unit; (b) the phenyl ring of the allyl ligand is in a *syn*-position in relation to the central hydrogen of this group; and (c) the five-membered chelates have an envelope-like conformation.

In **3a** the presence of the phenyl produces a larger twist of the C₅H₄ ring in relation to the C_{ipso}–CH=N– moiety {angles between planes = 29.7° (for **I**) and 23.1° (for **II**)} than for **2a** (where the angle is 20.3°). A similar distortion has also been found in $[Pd(\eta^3\text{-}1,3\text{-}Ph_2C_3H_3)\{(2\text{-}Cl\text{-}C_6H_4)\text{-}CH=N\text{-}CH-$

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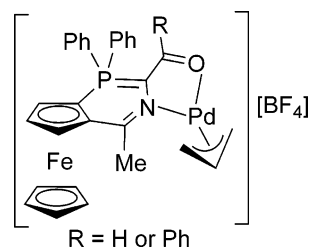


Figure 1. Palladium(II)-allyl complexes containing (N,O) ferrocenyl ligands used as precursors in allylic alkylation processes.¹⁷

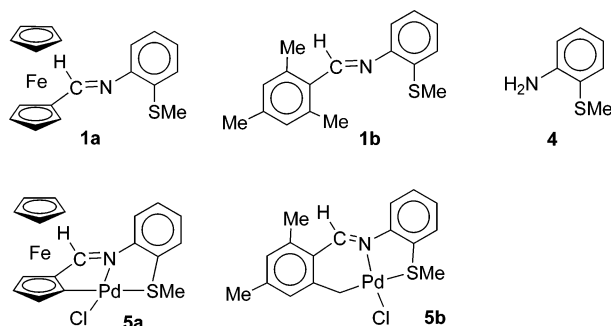
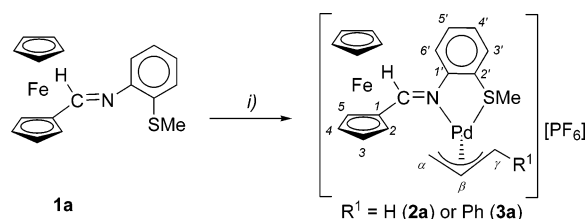


Figure 2. Ligands and cyclopalladated complexes used in this work.

Scheme 3^a



^a (i) In acetone followed by the addition of $[\text{Pd}(\eta^3\text{-}1\text{-R}^1\text{-C}_3\text{H}_4)(\mu\text{-Cl})_2]$ {in a **1a**:Pd(II) molar ratio of 1} and a slight excess (20%) of $\text{K}[\text{PF}_6]$.

$(\text{CHMe}_2)\text{-CH}_2\text{SPh}\}(\text{ClO}_4)$,²² where the 2-chlorophenyl ring is out of conjugation with the imine unit by ca. 40.9°.

In order to clarify whether the nature of the substituent on the allyl group could affect the electronic environment of the Fe(II) center, ⁵⁷Fe Mössbauer studies were performed. In both cases, the spectra consisted of a single quadrupole doublet, thus indicating that there was a single iron site.²⁴ It is well-known that in ferrocene derivatives the presence of electron-donating groups produces an increase in the quadrupole splitting (ΔE_q) relative to that of ferrocene, whereas electron-withdrawing substituents have the opposite effect.²⁵ For **2a** and **3a**, the ΔE_q ²⁴ was smaller than that of Fc-H^{26} ($\Delta E_q = 2.41$ mm/s at 80 K), thus indicating that the “ $\text{Pd}(\eta^3\text{-}1\text{-R}^1\text{-C}_3\text{H}_4)\{\text{-CH=N-(C}_6\text{H}_4\text{-2SMe)}\}$ ” moieties have a somewhat stronger electron-withdrawing effect. The differences between the ΔE_q values for **2a** and **3a**²⁴ indicate that the replacement of the hydrogen in **2a** by a phenyl in **3a** increases the electron-pulling ability of the substituent bound to the ferrocenyl unit.

The ¹H NMR spectrum of **2a** in acetone-*d*₆ at 298 K had broad signals. This could be indicative of the existence of

dynamic processes between different isomeric forms. Several isomers of the cation of **2a** could in principle be expected (Scheme 4), due to (a) the prochirality of the sulfur atom; (b) the presence of the allyl group; and (c) the asymmetry of the (N,S) ferrocenyl ligand. The methyl group of the -SMe moiety and the central carbon of the allyl group (C^β) could be located on the same side of the coordination plane of the palladium(II) (**A** and **D** in Scheme 4) or on opposite sides (**B** and **C** in Scheme 4).¹⁸ Thus, the two pairs of cations (**A**, **C**) and (**B**, **D**) differ in the configuration of the sulfur center. In addition, it should be noted that the imine may adopt the *anti-E* or the *syn-Z* conformation. Moreover, if the free rotation around the $\text{C}_{\text{ipso}}\text{-C}_{\text{imine}}$ bond of the ligand is inhibited, different rotameric species could also be present in solution. This should be especially relevant at low temperatures.

The ¹H NMR spectrum of **2a** in acetone-*d*₆ at 203 K suggested the presence of two isomers (**2a_I** and **2a_{II}**) of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{-}\{\text{FcCH=N-(C}_6\text{H}_4\text{-2SMe)}\}]^+$ in solution in a molar ratio 10.0:2.2. The $\{\text{H}^1\text{-H}^1\}$ -NOESY spectrum showed (a) that the ligand adopted the *anti-E* conformation in **2a_I** and **2a_{II}** and (b) a NOE interaction between the -SMe protons and the $\text{H}^{\gamma}_{\text{anti}}$ of **2a_I**. This is only possible if they are on the same side of the coordination plane of the Pd(II).

The differences detected in the chemical shifts of the signals due to **2a_I** and **2a_{II}** are very similar to those reported for the two isomers (*endo* and *exo*) of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L},\text{L}')^+]$ (Figure 4).¹⁶ On this basis, we tentatively postulate that **2a_I** and **2a_{II}** may differ in the conformation of the allyl group. Furthermore, the $\{\text{H}^1\text{-H}^1\}$ -NOESY spectrum of **2a** showed interchange peaks between the signals of the methyl groups of **2a_I** and **2a_{II}**, suggesting that this process mainly affects the Me units of the two isomers. Dynamic processes involving the cleavage of the $\sigma(\text{M-SMe})$ bond have also been reported for $[\text{M}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2SMe)}]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]\text{Cl}$ ($\text{M} = \text{Pd}$ or Pt).^{7b}

Due to the asymmetry of the $(\eta^3\text{-}1\text{-Ph-C}_3\text{H}_4)$ unit and the presence of two different donor atoms (N and S) on **1a**, the number of possible isomers of **3a** is greater than for **2a**. For **3a** the substituted carbon of the allyl group (C^γ) could be in a *cis*- or in a *trans*-arrangement to the sulfur and the phenyl group attached to C^γ may be located in the *syn*- or *anti*-position.

NMR spectra of **3a** in acetone-*d*₆ at 193 K suggested the coexistence of four isomers (**3a_I**–**3a_{IV}**, respectively) in molar ratios of 10.0:1.5:1.6:0.4. $\{\text{H}^1\text{-H}^1\}$ -NOESY experiments indicated that in **3a_I** the imine had the *anti-E* conformation and that the phenyl ring bound to C^γ was in the *syn*-position. The upfield shift of the signals due to the SMe units of **3a_I** and **3a_{II}**, compared with the values of **2a_I** and **2a_{II}**, is similar to that reported for $[\text{M}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2SMe)}]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]\text{Cl}$ ($\text{M} = \text{Pd}$ or Pt),^{7b} in which the ligand acts as a terdentate group and the PPh_3 is in a *cis*-arrangement to the sulfur atom. These findings suggest that the C^γ and S atoms were in a *cis*-arrangement.

The comparison of the ¹H NMR at 298 and 223 K in $\text{CD}_2\text{-Cl}_2$ and acetone-*d*₆ suggests that the isomeric processes and interconversion rates were strongly dependent on the solvent.²⁷ The $\{\text{H}^1\text{-H}^1\}$ -NOESY spectrum of **3a** in CD_2Cl_2 at 188 K indicated that the ligand had the *anti-E* conformation in **3a_I**–**3a_{III}**. For **3a_{III}** and **3a_{IV}** the resonances of the Me protons appeared at lower fields than for **3a_I** and **3a_{II}**. This can be

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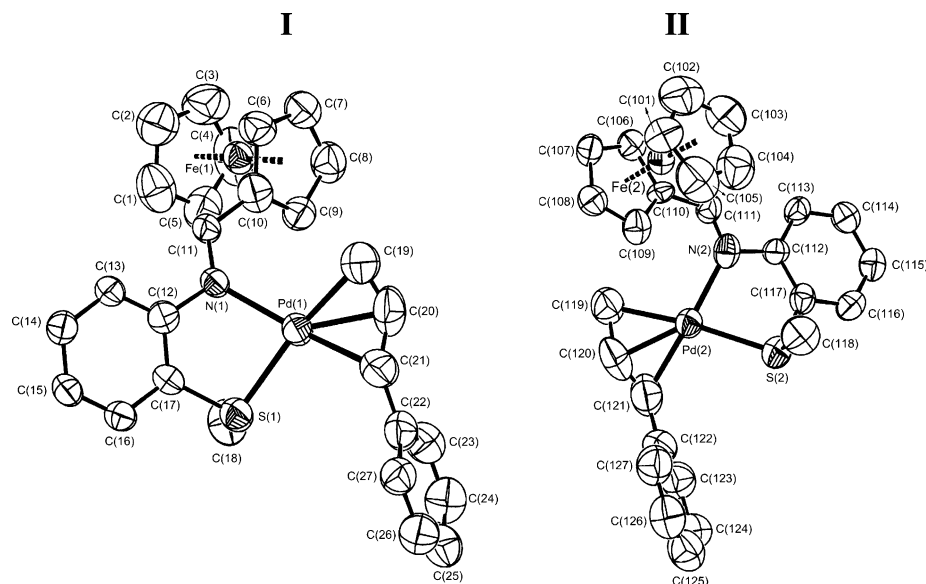
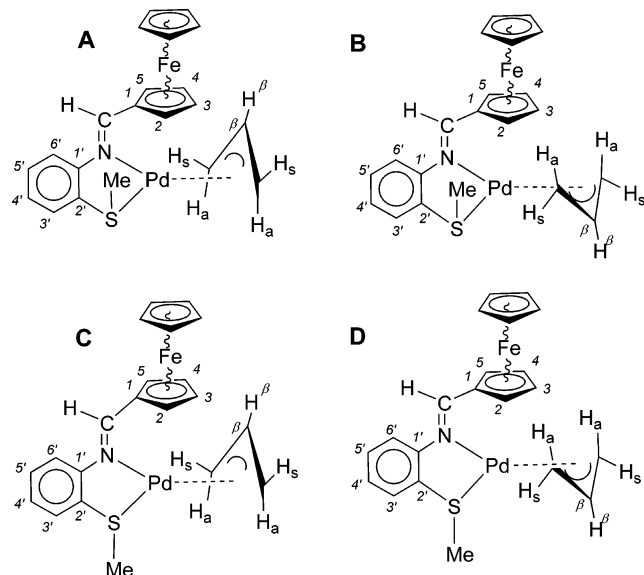


Figure 3. ORTEP plots of the two nonequivalent cations (**I** and **II**) found in the crystal structure of $[\text{Pd}(\eta^3\text{-1-Ph-C}_3\text{H}_4)\{\text{FcCH=N-(C}_6\text{H}_4\text{-2SMe)}\}][\text{PF}_6] \cdot 3\mathbf{a} \cdot \text{H}_2\text{O}$. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)–N(1), 2.118(9); Pd(1)–S(1), 2.351(4); Pd(1)–C(19), 2.128(14); Pd(1)–C(20), 2.121(14); Pd(1)–C(21), 2.127(13); C(11)–N(1), 1.270(12); Pd(2)–N(2), 2.078(10); Pd(2)–S(2), 2.367(4); Pd(2)–C(119), 2.159(16); Pd(2)–C(120), 2.088(14); Pd(2)–C(121), 2.184(16); C(110)–C(111), 1.508(13); C(111)–N(2), 1.217(13); N(1)–Pd(1)–S(1), 83.0(2); N(1)–Pd(1)–C(19), 105.6(5); N(1)–Pd(1)–C(21), 168.3(5); C(20)–Pd(1)–C(21), 35.1(5); N(2)–Pd(2)–S(2), 81.0(3); N(2)–Pd(2)–C(119), 104.7(5); N(2)–Pd(2)–C(121), 161.7(5); C(120)–Pd(2)–C(121), 37.5(5).

Scheme 4. Schematic View of Some of the Isomeric Forms Expected for the Cation of Compound **2a**^a



^a The wavy lines indicate that the “ $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ ” moieties may be located in an upper (or in a lower) plane in reference to that defined by the C_5H_4 ring of the ferrocenyl unit.

explained if we assume that in **3a_{III}** and **3a_{IV}** the C^γ carbon is in a *cis*-arrangement to the nitrogen, while in **3a_I** and **3a_{II}** these atoms are in a *trans*-disposition.

The variations detected in the $\delta(\text{SMe})$ values for **3a_I** and **3a_{II}** could be explained in terms of the relative arrangement between the phenyl and the Me units. Molecular models revealed that if the $\text{C}^\beta\text{--H}^\beta$ bond and SMe unit are on the same side of the coordination plane, the phenyl ring (which is in a *syn*-position) should be close to the Me protons. NMR experiments indicated that in **3a_{II}** the Ph and the Me groups are on the same side of the coordination plane, while in **3a_I** they are on opposite sides. The existence of cross-peaks between the four singlets due to

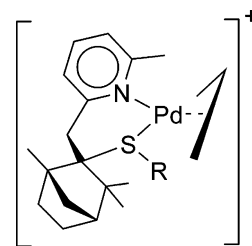


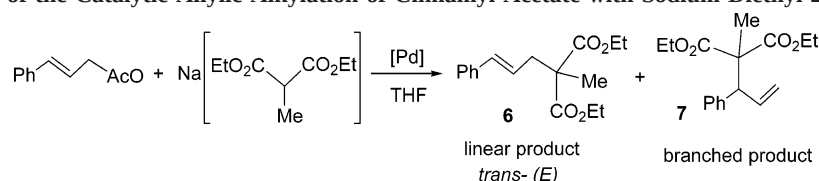
Figure 4. Palladium(II) allyl complex described by Kellogg et al.¹⁶ (with $\text{R} = \text{}^i\text{Pr}$).

the methyl protons of the --SMe unit suggests that the four isomeric forms of **3a** interchange in solution.

In a first attempt to clarify the proclivity of the coordinated allyl group to undergo nucleophilic attacks, **3a** was treated with an excess of sodium diethyl 2-methylmalonate in THF at 298 K (stoichiometric reaction). The reaction was instantaneous and gave, after workup, a mixture of the linear *trans-E* derivative (**6**) and the branched compound (**7**) in a molar ratio of **6**:**7** = 96.3:3.7.

The crystal structure of **3a** showed that the substituted carbon of the allyl unit (C^γ) was in a *cis*-arrangement to the sulfur and the phenyl was in a *syn*-position. This arrangement is the same as that found for **3a_I**. Thus, the formation of **6** arises from the attack of the nucleophile on C^α , which is in a *trans*-arrangement to the sulfur in **3a_I**.

There is increasing interest in the study of the utility of ferrocene derivatives with two different donor atoms and their Pd(II) complexes in the allylic alkylation and in elucidating the effects induced by these heteroatoms or the ferrocenyl unit on the regio- and stereoselectivity of the process.^{14a,17,18b} Therefore, we decided to study the alkylation of cinnamyl acetate with sodium diethyl 2-methylmalonate using catalytic amounts of **1a**, **1b^{18a}** (Figure 2) or **2a** (Table 1, entries I–IV). In all cases the formation of **6** is strongly preferred over that of the branched product (**7**). The use of **1b** compared to **1a** results in a slight decrease in the regioselectivity (entry II). When **2a** was used

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 6:7
I	1a and [Pd(η^3 -C ₃ H ₅)(μ -Cl)] ₂	20	100.0	96.5:3.5
II	1b and [Pd(η^3 -C ₃ H ₅)(μ -Cl)] ₂	20	100.0	95.8:4.2
III	2a	3	90.5	94.8:5.2
IV	2a	20	100.0	93.4:6.6
V	4 and [Pd(η^3 -C ₃ H ₅)(μ -Cl)] ₂	20	87.8	99.0:1.0
VI	4 and [Pd(η^3 -C ₃ H ₅)(μ -Cl)] ₂	44	98.0	98.9:1.1
VII	5a ^c	44	90.5	98.6:1.4
VIII	5b ^c	44	90.7	98.8:1.2

^a Experimental conditions: mixtures containing 2.5×10^{-3} mmol of [Pd(η^3 -C₃H₅)(μ -Cl)]₂ and 5.0×10^{-3} mmol of ligand **1a**, **1b**, or **4** (entries I, II, V, and VI) or 5.0×10^{-3} mmol of **2a**, **5a**, or **5b** (entries III, IV, VII, and VIII); 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. ^bDetermined by GC. ^cSee text.

(Table 1, entries III and IV), the regioselectivity decreased in comparison to that obtained in entry I.

In order to ascertain the influence of the electronic properties of the nitrogen in this process, a parallel study was carried out using H₂N-C₆H₄-2SMe (**4**). In this case, the regioselectivity (Table 1, entries V and VI) was a bit higher but the process was slower than that of **1a** or **1b**.

There may be several reasons for the differences in the regioselectivity of experiments I–III presented in Table 1. Previous studies on the reactivity of imines with Pd(II) or Pt(II) have shown that in the presence of a base these imines may hydrolyze, giving the aldehyde and the amine.^{7a,28} Since these catalytic studies are performed in basic medium, the formation of small amounts of **4** cannot be ruled out. The presence of traces of **4** in the reaction medium would produce a slight increase in the molar ratio 6:7.

It should be noted that **1a** and **1b** are also active in the catalytic alkylation of other substrates such as cinnamyl chloride or even *rac*- α -vinylbenzylacetate.²⁹

There has been considerable recent interest in the utility of palladacycles in homogeneous catalysis.^{10,11,30} For this reason, and to evaluate whether the mode of binding of the ferrocenyl ligand could affect the effectiveness of the palladium(II) complex, the regioselectivity, or the rate of the catalytic process, we also performed a parallel study with **5a** and **5b** (Figure 2). Compounds **5** are also active in the allylic alkylation of the cinnamyl acetate (Table 1, entries VII and VIII). These reactions were slower than those of the catalytic systems formed by [Pd-(η^3 -C₃H₅)(μ -Cl)]₂ and **1a** or **1b**, and the molar ratios 6:7 were somewhat higher. The yield was smaller (50%) for **5b** than for **5a** (76.4%).

All these observations suggest that the nature of the N-donor atom {sp² (in **1** or **2a**) or sp³ (in **4**)} plays a crucial role. This could be due to several factors such as the different *trans*-influences of the N(sp²) and N(sp³) donor atoms or the steric

effects derived from the presence of the bulky (ferrocenyl or mesityl) groups bound to the nitrogen in **1** or **2a** when compared with **4**.

The results presented here have shown the potential utility of compounds **1a**, **1b**, **2a**, **4**, **5a**, and **5b** as precursors in the allylic alkylation of cinnamyl acetate. In general terms, for **1a**, **1b**, and **2a** the reactions are faster than for **4**. However, the regioselectivity toward the linear *trans*-E product decreases.

Cyclopalladated complexes have been used in several catalytic processes (i.e., Heck, Suzuki, Stille, Sonogashira reactions, aza-Claisen rearrangements, etc.),^{10,11,30} but their utility in allylic alkylations has not been studied in detail. Only two cyclopalladated complexes with pincer [P,C,E] ligands have been tested.^{30,31} Therefore, the results obtained with **5** constitute the first step toward further work in this area. Such work could provide additional information on the role of the palladacycles in this catalytic process and on the influence of the nature of the donor atoms of the terdentate ligand on the regioselectivity and the rate of these reactions. We realize that the metallacycles may not be present in the active catalytic species. However, this is also true for the metalated Suzuki and Heck catalysts, for which the cyclometalated species are excellent precursors or perhaps resting states.

Experimental Section

Material and Methods. Compounds **1a,b**, **5a,b**, and [Pd(η^3 -1-R¹-C₃H₄)(μ -Cl)]₂ (R¹ = H or Ph) were synthesized as described previously.^{7a,18a,32,33} Sodium diethyl 2-methylmalonate (0.5 M in THF) was prepared from diethyl-2-methyl malonate and NaH in THF at 273 K. The remaining reagents were obtained from Aldrich and used as received. The solvents were distilled and dried before use.³⁴ Elemental analyses were carried out at the Serveis de Recursos Científics i Tècnics (Univ. Rovira i Virgili). FAB⁺ mass spectra were performed at the Servei d'Espectrometria de Masses (Univ. Barcelona) with a VG-Quattro Fisions instrument and using

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(29) For cinnamyl chloride: conversion = 100% (t = 20 h) and molar ratios 6:7 = 98.9:1.1 (for **1a**) and 95.9:4.1 (for **1b**). For *rac*- α -vinylbenzylacetate: conversion (t = 20 h) = 61.2% (for **1a**) and 51.7% (for **1b**), and the molar ratios of the final products linear:branched were 86.3:13.7 (for **1a**) and 80.5:19.5 (for **1b**).

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3-nitrobenzylalcohol as matrix. IR spectra were obtained with a Nicolet 400-FTIR instrument using KBr pellets. Routine ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained with a Gemini-200 MHz and a Bruker 250-DXR or a Mercury-400 instrument, respectively. High-resolution ^1H NMR spectra and the $\{^1\text{H}-^1\text{H}\}$ -NOESY, COSY, $\{^1\text{H}-^{13}\text{C}\}$ -HSQC, and HMBC NMR experiments were recorded with a Varian VRX-500 or a Bruker Advance-DMX 500 instrument at 298 K. The latter equipment was also used to perform the VT-NMR experiments. The chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz. The product distribution of the alkylation experiments was measured on an Interscience Mega2 or Trace-DQS apparatus. The Interscience Mega2 was equipped with a DB1 column, length 30 m, inner diameter 0.32 mm, a film thickness of 3.0 μm , and a flame ionization detector. The Trace-DQS instrument had a HP-5 column (25 m in length, 0.5 μm film thickness, and 0.2 mm inner diameter) and was equipped with an electron impact mass detector.

Synthesis of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\{\text{FcCH}=\text{N}-(\text{C}_6\text{H}_4-2\text{SMe})\}][\text{PF}_6]$ (2a**).** Ligand **1a** (183 mg, 5.46×10^{-4} mol) and $\text{K}[\text{PF}_6]$ (120 mg, 6.52×10^{-4} mol) were added to a solution of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})_2]$ (100 mg, 2.73×10^{-4} mol) in acetone (20 mL). The mixture was stirred at 298 K for 1 h and then filtered. The filtrate was concentrated to dryness on a rotary evaporator. The garnet residue was treated with CH_2Cl_2 (ca. 5 mL), and the undissolved materials were removed by filtration and discarded. The filtrate was concentrated to dryness on a rotary evaporator. The isolated solid was dried in vacuum for 24 h and then collected (yield: 262 mg, 76%). Crystals of **2a** were grown by slow evaporation of a solution of **2a** in a CH_2Cl_2 /hexane (1:1) mixture.

Synthesis of $[\text{Pd}(\eta^3\text{-1-Ph-C}_3\text{H}_4)\{\text{FcCH}=\text{N}-(\text{C}_6\text{H}_4-2\text{SMe})\}][\text{PF}_6]$ (3a**) $\cdot\text{H}_2\text{O}$.** This product was prepared according to the procedure described for **2a**, but $[\text{Pd}(\eta^3\text{-1-Ph-C}_3\text{H}_4)(\mu\text{-Cl})_2]$ (109 mg, 2.72×10^{-4} mol) was used as the starting material. In this case, the filtrate obtained after the removal of the inorganic salts was treated with Et_2O . Slow evaporation of the solution produced the formation of microcrystals of **3a**. These were collected, air-dried, and then dried in vacuum for 24 h (yield: 323 mg, 82%).

Alkylation Reactions. These studies were performed under nitrogen. The stoichiometric alkylation reaction of **3a** was performed at 298 K by adding an excess of sodium diethyl-2-methylmalonate (0.8 mL of a 0.5 M solution in THF) to a solution containing **3a** (80 mg, 1.1×10^{-4} mol). 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 H_2O . The organic phase was dried over MgSO_4 , and the filtrate was concentrated to dryness on a rotary evaporator. The residue was dissolved in a minimum amount of Et_2O and passed through a short SiO_2 column (4.0 cm $\times$ 0.6 cm). The band released was collected and concentrated to dryness. The oily residue contained {according to ^1H NMR (500 MHz) and GC} **6** and **7** in a molar ratio **6**:**7** = 96.3:3.7.

The catalytic reactions were performed at 298 K in THF (5 mL) using 5.0×10^{-3} mmol of **2a**, **5a**, or **5b** {or mixtures of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})_2]$ (2.5×10^{-3} mmol) and **1a**, **1b**, or **4** (5.0×10^{-3}

mmol)}, cinnamyl acetate (0.5 mmol), and sodium diethyl 2-methylmalonate (1.0 mmol). The reaction was monitored by taking samples from the reaction mixture. Each aliquot was diluted with Et_2O , washed with water, and dried over MgSO_4 . Aliquots then were analyzed by GC using decane (0.258 mmol) as the internal standard.

Crystallographic Data. For **2a**: orthorhombic, space group $P2_12_12_1$, $a = 9.780(1)$ Å, $b = 10.513(1)$ Å, $c = 22.371(1)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 2300.1(3)$ Å³, $T = 293(2)$ K, $Z = 4$, $D_c = 1.813$ g cm⁻³, $\mu = 1.630$ mm⁻¹, MAR345 diffractometer, and 5433 reflections were collected {1712 were unique ($R_{\text{int}} = 0.0302$)}. The structure was solved by direct methods (SHELXS)³⁵ and refined by full-matrix least-squares (SHELX93).³⁶ Final R indices: $R1 = 0.0390$ and $wR2 = 0.1059$ [$I > 2\sigma(I)$] and $R1 = 0.0441$ and $wR2 = 0.1334$ (all data), and the Flack coefficient³⁷ was 0.0(6). For **3a** $\cdot\text{H}_2\text{O}$: triclinic, space group $P1$, $a = 10.075(1)$ Å, $b = 15.148(4)$ Å, $c = 19.533(7)$ Å, $\alpha = 84.67(3)^\circ$, $\beta = 79.20(5)^\circ$, $\gamma = 83.55(4)^\circ$, $V = 2902(3)$ Å³, $T = 293(2)$ K, $Z = 4$, $D_c = 1.652$ g cm⁻³, $\mu = 1.307$ mm⁻¹, Enraf-Nonius-CAD4 diffractometer, and 16 857 reflections were collected and used ($R_{\text{int}} = 0.0028$). The structure was solved by direct methods (SHELXS)³⁵ and refined by full-matrix least-squares (SHELX97).³⁸ Final R indices: $R1 = 0.0508$ and $wR2 = 0.1243$ [$I > 2\sigma(I)$] and $R1 = 0.2259$ and $wR2 = 0.1657$ (all data).

^{57}Fe Mössbauer Studies. Mössbauer spectra were recorded using powdered solid samples. The samples were placed in liquid N_2 , quenched to 80 K, and transferred to an Oxford Instrument cryostat. Spectra were collected at 80 K using a constant acceleration Mössbauer spectrometer with a $^{57}\text{Co}/\text{Rh}$ source. The source was moved via a triangular velocity wave, and the γ -counts were collected in a 512 multichannel analyzer. The velocity calibration was undertaken using a 25 μm thick metallic iron foil. The Mössbauer spectral parameters are given to this standard at room temperature.

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Supporting Information Available: Characterization data {elemental analyses and spectroscopic data (MS, IR, and NMR data)} for **2a** and **3a**, ORTEP plot of the cationic array of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\{\text{FcCH}=\text{N}-(\text{C}_6\text{H}_4-2\text{SMe})\}][\text{PF}_6]$ (**2a**) with a selection of bond lengths and angles (Figure S1), ^{57}Fe Mössbauer spectra of solid samples of **2a** and **3a** $\cdot\text{H}_2\text{O}$ at 80 K (Figure S2), and full details of crystallographic analyses of **2a** and **3a** $\cdot\text{H}_2\text{O}$ in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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