Preparation of Ferrocene-Containing Phosphinamine Ligands Possessing Central and Planar Chirality and Their Application in Palladium-Catalyzed Asymmetric Allylic Alkylation

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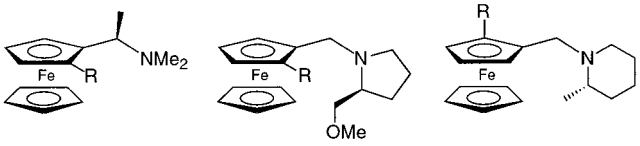
The preparation of {2-(S_p)-[(*trans*-(2*R*,5*R*)-2,5-dialkylpyrrolidinyl)methyl]}ferrocenyldiphenyl phosphines, new ferrocenylphosphinamine ligands possessing one site of planar and two stereogenic centers, is described. *trans*-(2*R*,5*R*)-2,5-Dialkyl-1-(ferrocenylmethyl)pyrrolidines were diastereoselectively lithiated and quenched with chlorodiphenylphosphine. For the dimethyl ligand, chemical yields of up to 65% and des of up to 90% were obtained whereas the diethyl ligand afforded lower chemical yields (10%) and des of 78%. Diastereomerically pure material was obtained in both cases after a single recrystallization from ethanol. (*S*)-Planar chirality was confirmed by X-ray crystallographic analysis of the dimethyl ligand. The palladium complexes of the new ligands were applied in the allylic alkylation of 1,3-diphenylprop-2-enyl acetate with reasonable chemical yields and moderate ees of up to 36% and 38% when dimethyl malonate and dimethyl methyl malonate were employed as nucleophiles, respectively. Importantly, it was found that the new ligands possessing the combination of planar and central chirality gave the opposite enantiomeric alkylation products compared to ligands which possess only the central chirality of the *trans*-2,5-dimethylpyrrolidinyl moiety. Solution NMR studies of the 1,3-diphenylallyl palladium complex of the dimethyl ligand revealed the presence of only the *exo*-configured allyl diastereomer.

Introduction

The ability of enantiopure ligands to induce asymmetry in reactions occurring within the coordination sphere of the transition metal to which they are bound, has led to the development of an active area of research in their design and application in asymmetric catalysis.[1,2] A range of diphosphine and phosphinamine ferrocene-containing ligands possessing planar chirality have been prepared and applied with success in a variety of processes.[3,4] The initial example of Kumada and Hayashi **1**, and subsequent related examples from Togni, have as their key precursor (*R*)-*N*,*N*-(dimethyl-1-ferrocenyl)ethylamine **2**.[5,6] Amine **2**, and a range of other *ortho*-metalating groups, including sulfoxides,[7] acetals,[8] oxazolines,[9−11] azepines,[12] sulfoximines[13] and hydrazones,[14] promote highly diastereoselective *ortho*-metalations, thus allowing for the preparation of planar chiral ferrocene compounds. A further example is (*S*)-(2-methoxymethylpyrrolidin-1-yl)-ferrocene **3**, developed by Ganter, which directs lithiation through the ether oxygen to afford phosphinamine ligand **4**.[15] The asymmetric lithiation of (*S*)-(2-methyl)piperdin-1-yl)ferrocene **5** was initially claimed by Aratani to afford up to 94% diastereoselectivity.[16] However, this was corrected to 67% diastereoselectivity favoring (*S*) planar chirality in subsequent work by Ugi.[17] Although the phosphinamine ligand **6** was not prepared, ligands **4** and **6** do not contain a symmetrically substituted pyrrolidine or piperidine ring, respectively, which limits their potential application in asymmetric catalysis.



1; R = PPh_2
2; R = H
3; R = H
4; R = PPh_2
5; R = H
6; R = PPh_2

We have recently reported the preparation of phosphinamine ligands **7**−**10**,[18] bearing an enantiopure C_2-

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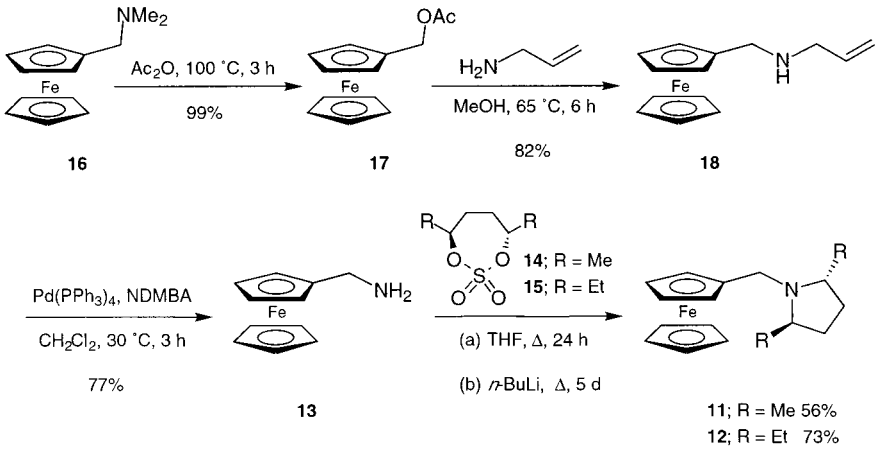
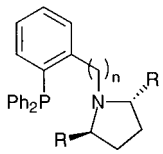
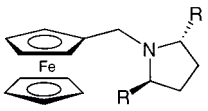
Scheme 1. Synthesis of Pyrrolidines 11 and 12



symmetric *trans*-2,5-disubstituted pyrrolidine unit and have described their application in palladium-catalyzed allylic substitution,[19] iridium-catalyzed enantioselective imine reduction,[20] the palladium-catalyzed asymmetric intermolecular Heck reaction,[21] and a mechanistic study of their palladium η^3-allyl species.[22]



7: n = 1; R = Me; **8**: R = Et.
9: n = 0; R = Me; **10**: R = Et.



11; R = Me
12; R = Et

It was therefore of interest to prepare the analogous *trans*-(2*R*,5*R*)-2,5-dialkyl-1-(ferrocenylmethyl)pyrrolidines **11** and **12** and to study their ability to direct diastereoselective metalation as a route to ferrocenylphosphinamine ligands possessing both planar chirality and stereogenic centers. We now report the preparation of two such ligands and the determination of the absolute configuration of the *trans*-(2*R*,5*R*)-2,5-dimethyl-substituted example by X-ray crystallography. In addition, the application of these ligands in palladium-catalyzed allylic substitution and a spectroscopic study of their palladium η^3-allyl species will be presented.

Results and Discussion

The key step in the synthesis of **11** and **12** was the cyclocondensation of ferrocenylmethylamine **13** with enantiopure 2,5-dimethyl- or 2,5-diethyl-1,4-diol cyclic sulfate **14** and **15** and similar, successful routes to *trans*-2,5-disubstituted pyrrolidines have used appropriately substituted 1,4-dimesylates[23−25] or 1,4-diacetates.[26,27] The required ferrocenylmethylamine **13** was prepared in three steps from *N*,*N*-(dimethylamino)methylferrocene **16**, Scheme 1.

The first step converted **16** into ferrocenyl(methyl)-acetate **17** in 99% yield using Hayashi's acylation procedure.[5] The reaction of **17** with allylamine afforded (ferrocenylmethyl)prop-2-enylamine **18** in 82% yield and subsequent deprotection,[28] in a modification of literature procedures for deallylation using palladium(0) catalysis and *N*,*N*′-dimethylbarbituric acid as the allyl scavenger, gave ferrocenylmethylamine **13** in 77% yield.[29,30] Using the standard procedure for pyrrolidine ring formation, **13** was reacted with (2*S*,5*S*)-hexanediol cyclic sulfate **14** to give *trans*-(2*R*,5*R*)-2,5-dimethyl-1-(ferrocenylmethyl)-pyrrolidine **11** in an optimized 56% yield. Similarly, *trans*-(2*R*,5*R*)-2,5-diethyl-1-(ferrocenylmethyl)pyrrolidine **12** was formed in 73% yield from the reaction of **13** with (3*S*,6*S*)-octanediol cyclic sulfate **14**.

The directed diastereoselective *ortho*-lithiation of *trans*-(2*R*,5*R*)-2,5-dialkyl-1-(ferrocenylmethyl)pyrrolidines **11** and **12** and subsequent treatment with chlorodiphenylphosphine was then investigated. The process was found to be sensitive to the 2,5-dialkyl substituent, the alkyllithium reagent used, the reaction temperature, and the solvent (Scheme 2 and Table 1). The yields quoted refer to the overall yields obtained and not those for the major diastereomers formed.

With **11**, use of *n*-butyllithium in either ether or hexane at −78 °C or ambient temperature, conditions previously successful for the directed lithiation of amine **16**,[31] failed to afford any product. A change to *sec*-butyllithium in ether gave a 65% yield in 80% de which was optimized

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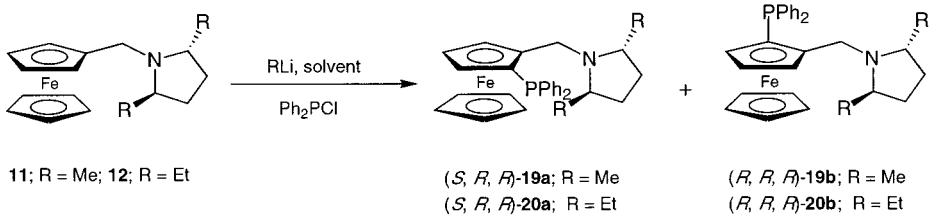
Scheme 2. Diastereoselective Lithiation of Pyrrolidines 11 and 12



11; R = Me; **12**; R = Et

(*S*, *R*, *R*)-**19a**; R = Me
(*S*, *R*, *R*)-**20a**; R = Et

(*R*, *R*, *R*)-**19b**; R = Me
(*R*, *R*, *R*)-**20b**; R = Et

Table 1. Diastereoselectivity of *Ortho*-lithiation of *trans*-(2*R*,5*R*)-2,5-Dialkyl-1-(ferrocenylmethyl)pyrrolidines 11 and 12

amine	RLi	*T* [°C]	time [h]	yield [%]	de [%]
11	*n*-BuLi[a]	−78	1	–	–
11	*n*-BuLi[a]	25	1	–	–
11	*s*-BuLi[b]	25	1	65	80[c]
11	*s*-BuLi[b]	25	5	37	80
11	*s*-BuLi[b]	0	1	20	90
11	*t*-BuLi[b]	25	1	30	82
11	*t*-BuLi[b]	0	1	10	90
12	*n*-BuLi[b]	25	1	10	78[c]

[a] Hexane or Et_2O as solvent. [b] Et_2O as solvent. [c] >100:1 after a single recrystallization from EtOH.

to >100:1 de after a single recrystallization from ethanol. The key resonances for de determination by ^{1}H NMR were the unsubstituted cyclopentadienyl ring of the major diastereomer at δ 4.01 and of the minor diastereomer at δ 3.97. Alternatively, the de could be determined using ^{31}P NMR as the major diastereomer resonated at δ −22.32 and the minor diastereomer at δ −16.5. A longer reaction time of 5 h led to a decreased chemical yield of 37% and lowering of the reaction temperature to 0 °C gave a de of 90% but a lower yield of 20%. Lithiation with *tert*-butyllithium at 25 °C gave a yield of 30% and 82% de and lowering the reaction temperature to 0 °C gave a 90% de in a poor 10% yield. The lithiation of **12** proved much more difficult and only use of *n*-butyllithium in ether at 25 °C gave **20** in 10% yield and a 78% de, which was increased to >100:1 de after a single recrystallization from ethanol. In this case the de was calculated by ^{1}H NMR spectroscopy as the unsubstituted cyclopentadienyl ring of the major diastereomer occurred at δ 4.01 and in the minor diastereomer appeared at δ 3.96.

Crystals of the major diastereomer obtained from the directed phosphinylation of **11** were suitable for X-ray structure determination and the result of this analysis is summarized in Figure 1.[32] The compound crystallizes in the chiral space group $P2_1$ with two independent molecules in the asymmetric unit. Despite their different crystal environments the two molecules adopt almost identical conformations (rms deviation for non-H atoms 0.200 Å) in which the open face of the pyrrolidinyl group lies approximately parallel to one of the phenyl rings of the phosphine. The intramolecular distance of the N atom from the mean plane through the C atoms of the phenyl group is 3.39(2) Å (mean).

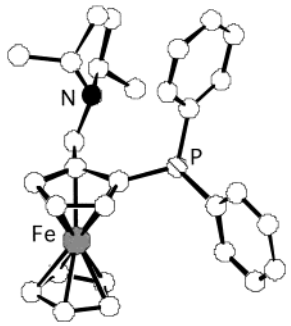


Figure 1. X-ray crystal structure of (S_P,*R*,*R*)-**19a**.

Figure 2. Proposed interactions of alkyllithium reagent with amines **11** and **12**. [The lower cyclopentadienyl ring has been omitted for clarity].

The major product was therefore assigned (*S*) planar chirality, which was suggested by comparison of its optical rotation with known ferrocenyl compounds.[5,33] We propose that (*S*)-planar chirality is preferred due to the orientation of the pyrrolidinyl methyl groups and their interaction with the incoming lithiating reagent. If the lithium reagent coordinates in the position leading to the favored diastereomer by approaching the substituted Cp ring from above, then the 2-methyl of the pyrrolidine is oriented away from the alkyllithium approach, structure **21**, Figure 2. However, if the lithium reagent coordinates to the nitrogen to remove the proton to give the (*R*)-planar product, the 5-methyl causes a repulsive interaction with the approaching alkyllithium reagent, structure **22**. These are similar arguments to those made by Ganter in the lithiations of **3**[15] and by Uemura in the lithiation of ferroceneoxazolines.[11]

This is the first example of a diastereoselective *ortho*-metalation directed by a *trans*-2,5-dialkyl-substituted pyrrolidine nitrogen atom. It is clear that there is a subtle interplay between the steric bulk of the alkyllithium reagent and that of the 2,5-dialkyl group. The more hindered 2,5-diethyl-substituted pyrrolidine fails to afford any product with *sec*- or *tert*-butyllithium. The less sterically hindered 2,5-dimethyl-substituted pyrrolidine gives product with both *sec*- and *tert*-butyllithium, although the latter proceeds in poorer yield but with higher de.

(32) Crystal data for (S_P,*R*,*R*)-**19**: $C_{29}H_{32}FeNP$, M_w = 481.4, orange plate 0.02 × 0.08 × 0.64 mm, monoclinic $P2_1$ [No. 4], a = 7.4699(7), b = 33.466(3), c = 9.8599(9) Å, β = 95.349(3)°, U = 2454.1(4) Å^3, T = 100 K, Z = 4, D_x = 1.303 g cm^{-3}, λ = 0.71073 Å, μ(Mo−K$_\alpha$) = 0.696 mm^{-1} Nonius KappaCCD diffractometer, 2.07 < θ < 32.23°, Gaussian absorption correction (T_{min} 0.83473, T_{max} 0.98593), 10074 measured reflections, 7518 independent, 4147 with $I > 2(I)$. Structure refined by least-squares using Chebyshev weights on F_o^2 to R_1 = 0.081 [$I > 2\sigma(I)$], wR_2 = 0.260, absolute configuration determined [Flack parameter −0.02(4)], 581 parameters, H atoms riding, S = 1.004, residual electron density +0.761/−1.320 e Å^{-3}.

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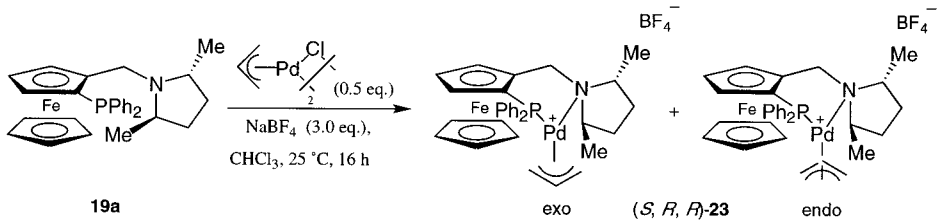
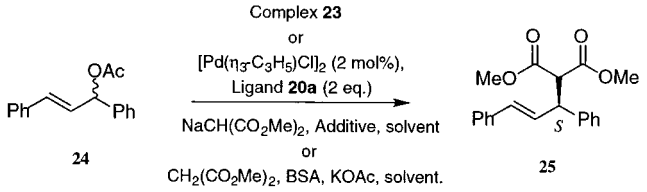
Scheme 3



19a exo (*S*, *R*, *R*)-**23** endo

Scheme 4. Palladium Catalyzed Allylic Alkylation of Acetate 22



24 **25**

The application of these new ferrocenylphosphinamine ligands in enantioselective palladium-catalyzed allylic alkylation allowed for a direct comparison with ligands **7** and **8** and the influence of the planar element of chirality was determined.

In performing allylic substitutions it is possible to use as the catalyst either preformed palladium (η^3-allyl) complexes of the ligand or to assume that such complexes are formed when a slight excess of ligand is added to either $Pd_2(dba)_3$ or a η^3-allyl palladium chloride dimer. The latter approach was used for (S_P,*R*,*R*)-**20** whereas the air-stable η^3-allyl palladium tetrafluoroborate salt of ligand (S_P,*R*,*R*)-**19** was prepared in quantitative yield, Scheme 3. [Hereafter for clarity, (S_P,*R*,*R*)-**19** will be referred to as **19a** and (S_P,*R*,*R*)-**20** as **20a**.]

The structure of palladium{(2-[(*trans*-(2*R*,5*R*)-2,5-dimethylpyrrolidinyl)methyl]}ferrocenyl diphenylphosphine(η^3-allyl)tetrafluoroborate **23** was confirmed by spectroscopic methods. The high field ^{1}H NMR spectrum was broad at room temperature, but the ^{31}P NMR spectrum showed two peaks at 16.3 and 15.1 ppm in a ratio of 8:1, indicating the existence of both diastereomeric *endo*- and *exo*-intermediates in solution. [Nomenclature note: the *endo*-isomer is defined here as that allyl configuration in which the central allyl proton points above the plane of the P−Pd−N chelate].

Once prepared, the asymmetry-inducing abilities of the palladium complexes of **19a** and **20a** were tested in what has become one of the standard reactions in allylic alkylation, namely that between dimethylmalonate and racemic 1,3-diphenylprop-2-enyl acetate **24** to afford enantioenriched malonate product **25**, Scheme 4. The results obtained are summarized in Table 2.

The malonate nucleophile can be preformed as its sodium salt (NaMal) or prepared in situ by Trost's procedure using *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and catalytic quantities of potassium acetate.[35] Using the malonate procedure, the highest enantioselectivity for ligand **19a** was found to be a moderate 36% (*S*) when dichloromethane was employed as solvent (entry 1). When 15-crown-5, which is generally used to enhance the solubility of the sodium salt, was employed as an additive, it resulted in both a lower ee and chemical yield (entry 2). Changing solvent to acetonitrile or dimethylformamide gave lower ees (26 and 14%, respectively), and the chemical yield in the latter case was poor (25%, entries 3 and 4). Dichloromethane and acetonitrile were used as solvents for the BSA procedure, but in all cases, despite investigating a variety of reaction conditions, the yields and ees were lower than those observed using the malonate procedure. Palladium complexes of **20a** afforded higher chemical yields but gave disappointingly low ees of 18−20%, again favoring the (*S*)-product **25**. For comparative purposes the yields and ees obtained in a previous study using palladium complexes of **7** and **8** are included in Table 2 (entries 11 and 12).[19] A direct comparison of **19a** with **7** shows that the latter gave a higher ee of 55% but of the *opposite* enantiomer. Similarly, **20a** gave a 90% ee favoring (*R*)-**25** while **8** gave an optimum ee of 20% favoring (*S*)-**25**. This indicates that in the case of the ferrocene-containing P,N ligands **19a** and **20a**, the planar element of chirality influences the stereoselectivity to a greater extent than the two stereogenic centers of the *trans*-2,5-disubstituted pyrrolidine moiety. This leads to a mismatch of the chiral elements present in ligands **19a** and **20a**.

Table 2. Application of 19a and 20a to the Palladium-Catalyzed Asymmetric Allylic Alkylation of 1,3-diphenylprop-1-enyl Acetate 22[a]

entry	ligand	method	solvent	temp [°C]	yield [%][b]	ee [%][c] (config)[d]
1	**19a**	NaMal	CH_2Cl_2	25	69	36 (*S*)
2	**19a**	NaMal[e]	CH_2Cl_2	25	53	12 (*S*)
3	**19a**	NaMal	DMF	25	25	14 (*S*)
4	**19a**	NaMal	CH_3CN	25	70	26 (*S*)
5	**19a**	BSA	CH_2Cl_2	25	49	24 (*S*)
6	**19a**	BSA	CH_3CN	25	22	14 (*S*)
7	**19a**	BSA	CH_2Cl_2	0	41	12 (*S*)
8	**19a**	BSA	CH_3CN	0	23	24 (*S*)
9	**20a**	BSA	CH_2Cl_2	25	71	20 (*S*)
10	**20a**	BSA	CH_3CN	25	64	18 (*S*)
11	**7**	BSA	DMF	0	62	55 (*R*)[19]
12	**8**	BSA	CH_3CN	25	89	90 (*R*)[19]

[a] The reaction was carried out over 24 h in the presence of 1 mol % of preformed catalyst **21** or in situ formed catalyst from ligand **20a** using either NaMal or BSA method. [b] Isolated yield after silica gel chromatography. [c] Enantiomeric excesses were determined by ^{1}H NMR using Eu(hfc)$_3$ as the chiral shift reagent. [d] Assignment is based on the sign of the optical rotation and comparison with the literature.[34] [e] 15-Crown-5 added to reaction.

In an attempt to increase the enantioselectivites induced by catalyst **23** we also examined the influence of increasing the size of nucleophile. Thus, the reaction of acetate **24** with dimethyl methyl malonate was studied, Scheme 5. The results of these investigations are given in Table 3.

The yields in all cases were higher than those observed when dimethyl malonate was the nucleophile. The malonate procedure gave low to moderate enantioselectivities (16−38%) and even lower (10−16%) enantioselectiv-

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Scheme 5

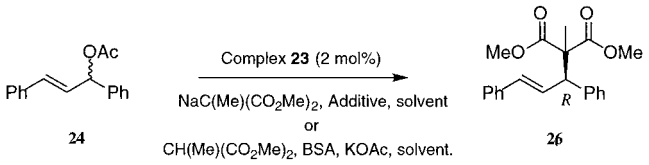

Table 3. Application of Palladium Complex 23 to the Asymmetric Allylic Alkylation of Acetate 22 with Dimethyl Methyl Malonate[a]

entry	method	solvent	temp [°C]	yield [%][b]	ee [%][c] (config)[d]
1	NaMal	CH_2Cl_2	25	72	36 (*R*)
2	NaMal	CH_3CN	25	79	38 (*R*)
3	NaMal	DMF	25	37	34 (*R*)
4	NaMal	THF	25	58	16 (*R*)
5	BSA	CH_2Cl_2	25	85	12 (*R*)
6	BSA	CH_3CN	25	79	16 (*R*)
7	BSA	THF	25	83	10 (*R*)
8	BSA	DMF	25	70	16 (*R*)

[a] The reaction was carried out over 24 h in the presence of 1 mol % of preformed catalyst **23** using either NaMal or BSA method. [b] Isolated yield after silica gel chromatography. [c] Enantiomeric excesses were determined by ^{1}H NMR using Eu(hfc)$_3$ as the chiral shift reagent. [d] Assignment is based on the sign of the optical rotation and comparison with the literature.[34]

ities when the BSA procedure was employed. In all cases the (*R*)-enantiomer of **26** was the favored enantiomer formed indicating the same sense of asymmetric induction as for the dimethyl malonate case. [Note: the assignment of configuration is opposite for **25** and **26** as the malonate substituent priority changes.]

In an attempt to explain the enantioselectivities observed with palladium complexes of ligand **19a**, solution NMR studies were carried out on its cationic palladium(II) 1,3-diphenylallyl intermediates. The information thus garnered could be useful for future rational ligand design. For palladium complexes of phosphinamine ligands, the generally accepted mechanism of allylic alkylation involves the initial association of a palladium(0) phosphinamine species to the olefinic fragment of racemic 1,3-diphenylprop-2-enyl acetate **24** to give diastereomeric η^2-palladium(0) species **27** which undergo oxidative addition to give cationic palladium(II) η^3-intermediates **28**-*endo* and **28**-*exo*, Scheme 6 [note: only two of the four possible η^2-palladium(0) species **27** are shown for clarity]. Intermediates **28** interconvert, thus allowing racemic material the possibility to afford enantiomerically enriched product. Carbon−carbon bond formation with soft nucleophiles then occurs outside the coordination sphere to afford, after olefin dissociation from **29**, the allylated product as either the (*R*)-**25** or (*S*)-**25** enantiomer (when the nucleophile is dimethyl malonate).[36]

A considerable effort has been made to understand this critical enantiodifferentiating carbon−carbon bond-forming step from the initial investigations of Bosnich[37,38] employing diphosphine ligands to the more recent work of Brown, Pfaltz, Togni, and Helmchen employing phosphinamine ligands.[39−43] The key findings from the latter studies suggest that the ground state of complex **28** contains an allyl group which has reoriented itself into a product-like geometry, thus facilitating nucleophilic attack on that allyl terminal carbon *trans* to the phosphorus donor atom. The lability of the diastereomeric 1,3-diphenylallyl complexes is influenced by such electronic factors and also by intra-complex steric clashes between the ligand and the allyl. Solution NMR studies on these key intermediates would allow us to determine the ratio of *endo*- to *exo*-diastereomers and to gain some insight as to the influence of the planar chiral element of the 1,2-disubstituted ferrocene and the alkyl groups at the stereogenic centers of the pyrrolidine. In the present study it would allow for a direct comparison between the solution behavior of the 1,3-diphenylallyl complexes of the *trans*-2,5-dialkylpyrrolidinyl-containing phosphinamine ligands **7**−**10** and **19a**.[22]

Hence the η^3-1,3-diphenylallyl palladium tetrafluoroborate salt **30** was prepared in quantitative yield following literature precedent by the reaction of **19a** with di-μ-chloro-bis(1,3-diphenyl-π-allyl)dipalladium, Scheme 7.[44]

The ^{31}P spectrum of the resultant complex showed a single peak at 34.4 ppm, indicating the presence of only one diastereomeric intermediate. At room temperature the ^{1}H NMR spectrum was broad, and it was necessary to reduce the temperature until sharp peaks were observed at −55 °C, Figure 3.

The pyrrolidine methyl groups were inequivalent and appear as doublets at 1.18 and 1.41 ppm with coupling constants of 6.35 Hz. To distinguish the methyl groups ($Me_{2'}$ and $Me_{5'}$) required the examination of the ^{1}H NOESY spectrum to determine which methyl showed a cross-peak to one of the Fc-CH_2 peaks. It was found that the methyl at 1.41 ppm showed such a cross-peak to one of protons of the Fc-CH_2, which appears as a double doublet at 4.38−4.42 ppm. With the aid of ^{1}H−^{1}H COSY, all of the pyrrolidine proton peaks were subsequently identified, the CH_2 multiplets were observed at 1.66−1.70 ppm for $H_{3b'}$ and $H_{4a'}$ and at 1.95−2.03 pm for $H_{3a'}$ and $H_{4b'}$. The methine protons appeared at 3.47−3.50 ppm for $H_{5'}$ and at 3.69−3.72 ppm for $H_{2'}$. The remaining proton of the Fc-CH_2 appeared as a multiplet at 4.74−4.78 ppm. The unsubstituted cyclopentadienyl ring appeared as a singlet at 4.01 ppm, and the protons of the substituted ring at 4.32−4.35 ppm for H_5, 4.63−4.65 ppm for H_4, and 5.13−5.16 ppm for H_3. Full assignment of the allyl protons was facilitated by DQF−COSY experiments. In this fashion, the central allyl proton was determined to be a broad multiplet at 8.87−8.92 ppm, the allyl proton *trans* to nitrogen was under the methine multiplet for $H_{5'}$ at 3.47−3.50 ppm and the allyl proton *trans* to phosphorus appeared under one of the Fc-CH_2 multiplets at 4.74−4.78. With these peaks assigned, it was then necessary to further examine the ^{1}H NOESY spectrum to decide whether the major enantiomer was of *endo* or *exo* configuration.

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(41) Togni, A.; Bruckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031.
(42) Sprinz, J.; Kiefer, M.; Helmchen, G.; Huttner, G.; Walter, O.; Zsolnai, L.; Reggelin, M. *Tetrahedron Lett.* **1994**, *35*, 1523.
(43) Kollmar, M.; Goldfuss, B.; Reggelin, M.; Rominger, F.; Helmchen, G. *Chem. Eur. J.* **2001**, *7*, 4913.
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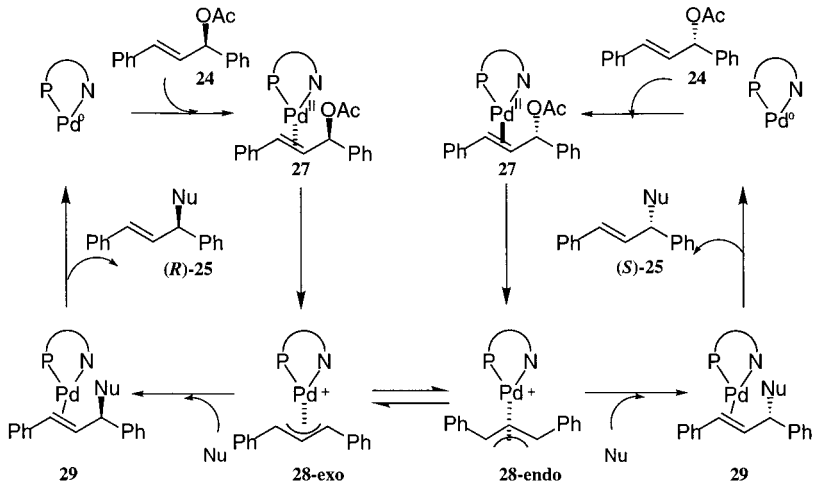
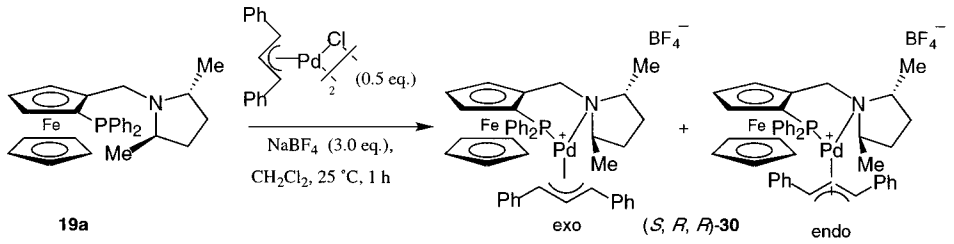
Scheme 6



Scheme 7



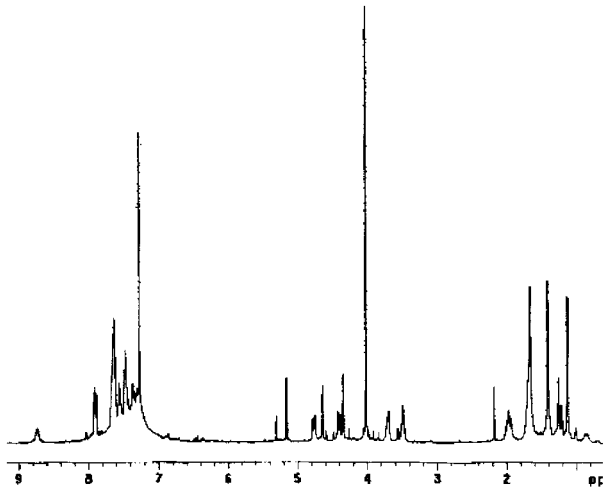


Figure 3. ^{1}H NMR of 1,3-diphenylallyl palladium complex **30** at −55 °C.

There were two critical NOEs which allowed its unambiguous assignment, and the side view of the X-ray structure of the palladium dichloride complex of **7**[18] is given to aid in the visualization of the relevant NOEs, Figure 4(a). The central allyl proton showed a NOE to the methine proton ($H_{2'}$) and the $Me_{5'}$, which is only possible if the allyl complex adopts the *exo* configuration and rolls slightly in a counterclockwise direction, Figure 4b. The methine proton $H_{2'}$ also shows a weak NOE to the aromatic region, possibly to an *ortho*-proton of the allyl phenyl *trans* to phosphorus. Hence, the major diastereomer is assigned the *exo* configuration of the π-allyl which gives rise to the preferred (*S*)-enantiomer of **25**. This is in contrast to the intermediates observed in the corresponding 1,3-diphenylallyl palladium complex

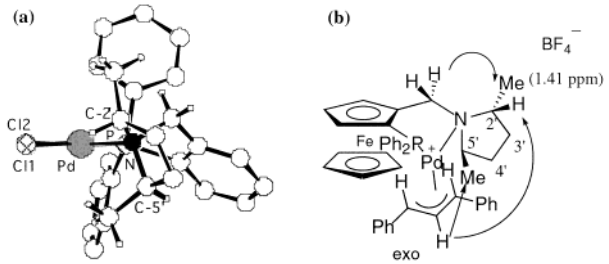


Figure 4. (a) Side view of X-ray structure of Pd dichloride complex of **7**. (b) Important NOEs allowing assignment of diastereomer.

of ligand **7** where a 5:2 ratio of *endo*:*exo* diastereomers was observed.[22] This comparison highlights the influence that planar chirality exerts on the 1,3-diphenylallyl orientation, presumably through interactions between the diphenylphosphinoferrocene unit and the allyl fragment.

The implication of the current NMR study is that the nucleophile attacks *trans* to phosphorus in the major diastereomer. The ground state favors one diastereomer exclusively and the low ees observed could be due to the flexibility at the Fc-CH_2 position as observed by other workers with ferrocenyl ligands lacking a stereogenic center at the α-methyl position. In addition, it could be that the six-membered chelate is strongly bent and that this leads to further, rapidly interconverting isomers. We are currently testing metal complexes of ligand **19a** and related ferrocene-containing P,N ligands in other asymmetric transformations and the results of these investigations will be reported from these laboratories in due course.[45]

(45) Farrell, A.; Meaney, K.; Guiry, P. J. Unpublished results.

Conclusion

In conclusion, two new ferrocene-containing phosphinamine ligands possessing both planar chirality and stereogenic centers were prepared in five steps from (*N*,*N*-dimethylamino)methylferrocene. The key and final step was a directed diastereoselective phosphinylation which proceeded in 80% de and 65% yield for the *trans*-(2*R*,5*R*)-2,5-methyl-1-(ferrocenylmethyl)pyrrolidine **11** and in 78% de but poor chemical yield for *trans*-(2*R*,5*R*)-2,5-diethyl-1-(ferrocenylmethyl)pyrrolidine **12**. A single recrystallization from ethanol afforded diastereomerically pure material in both cases. Their palladium complexes were applied in the allylic alkylation of 1,3-diphenylprop-2-enyl acetate with reasonable chemical yields and moderate ees of up to 36% when dimethyl malonate and 38% when dimethyl methyl malonate was employed as the nucleophile. Importantly, it was found that use of the new ligands, possessing both planar chirality and the two stereogenic centers in the *trans*-2,5-dialkylpyrrolidine groups, resulted in alkylation products that were enantiomeric to those obtained using palladium complexes of the **7** and **8**, containing the chiral *trans*-2,5-dialkylpyrrolidine groups alone. Clearly, the planar chirality of the ferrocenyl unit plays an important role in the stereoselectivity. Moreover, its influence appears to be contrary to that of the two stereogenic centers. Solution NMR studies enabled the results of the catalytic studies to be elucidated and reveal that the 1,3-diphenylallyl unit in the palladium complex of (S_P,*R*,*R*)-**19** exists in solution solely as the *exo*-configured allyl diastereomer.

Experimental Section

General Remarks. ^{1}H (270 or 400 MHz), ^{13}C (67.5 or 125 MHz), and ^{31}P (109.3 MHz) spectra were recorded at room temperature in $CDCl_3$. Chemical shifts (δ) are given in parts per million relative to $CHCl_3$ (7.26, ^{1}H), $CDCl_3$ (77.0, ^{13}C), and 85% aqueous phosphoric acid (0.0, ^{31}P). Coupling constants are given as absolute values expressed in hertz. Low resolution electron-impact MS spectra were measured at an ionization potential of 70 eV. Isomers were assumed to have the same response factors. Elemental analyses were performed by Ms Anne Connolly, Department of Chemistry, University College Dublin. Infrared spectra were recorded on a Perkin-Elmer infrared FT spectrometer. Optical rotation values were measured on a Perkin-Elmer polarimeter. Melting points were determined in open capillary tubes in a Gallenkamp melting point apparatus and are uncorrected. Thin-layer chromatography (TLC) was carried out on aluminum sheets precoated with silica gel 60 F 254 (0.25 mm, Macherey-Nagel). Column chromatography separations were performed using Merck Kieselgel 60 (Art. 7734), Merck Alumina (Art. 1097) or Merck Alumina (Art. 1104) as stated. Solvents were dried immediately before use by distillation from standard drying agents.[46] Dimethylaminomethylferrocene, chlorodiphenylphosphine, *N*,*N*-dimethylbarbituric acid, allylamine and (+)-(3*S*,6*S*)-2,5-octanediol were used as received from commercial sources. Ferrocenylmethyl acetate (**17**) was prepared according to a procedure developed by Hayashi.[5] Palladium(tetrakis(triphenylphosphine)) was prepared by literature procedures.[47]

(Ferrocenylmethyl)prop-2-enylamine (18). To a solution of ferrocenylmethyl acetate (1 g, 3.8 mmol) and methanol (14 mL) was added freshly distilled allylamine (3.14 mL, 4.6 mmol), and the mixture was refluxed for 6 h under a nitrogen atmosphere. The solvent was evaporated, crude product was dissolved in diethyl ether, and an excess of 1 M HCl was added (2 × 30 mL). The combined aqueous layers were basified using 1 M NaOH, and the product was extracted with diethyl ether (3 × 30 mL), dried (Na_2SO_4), and concentrated to yield 1 g of crude **18** as a red brown oil. This oil was purified using column chromatography, alumina, diethyl ether/hexane 2:1 yielding **18** (809 mg, 82%): Found: C, 65.70; H, 6.72; N, 5.29; $C_{14}H_{17}$FeN requires C, 65.85; H, 6.69; N, 5.05; ^{1}H NMR (270 MHz): δ 1.46 (br.s, 1H), 3.27 (dd, *J* 1.3, 6.0, 2H), 3.51 (s, 2H), 4.08 (app. t, *J* 1.74, 2H), 4.12 (s, 5H), 4.19 (app. t, *J* 1.65, 2H), 5.15 (dq, *J* 17.2, 10.3, 1.5, 2H), and 5.84−5.99 (m, 1H); ^{13}C NMR (67.8 MHz): δ 48.3, 52.1, 67.8, 68.4, 70.2, 86.8, 115.9, and 136.7; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1642 and 1270; MS (EI, 70 eV): *m*/*z* (%): 254 [M^+] (10), 199 (100), 134 (17), 121 (71), and 56 (30).

Ferrocenylmethylamine (13). Palladium(tetrakis(triphenylphosphine)) (136 mg, 10 mol %) and *N*,*N*-dimethylbarbituric acid (NDMBA) (550 mg, 3 equiv) were placed in a dry Schlenk under nitrogen. To this was added a solution of **18** (300 mg, 1 mmol) in dry degassed dichloromethane (2.5 mL per mmol of amine). The solution was stirred at 40 °C for 3 h. Hexane was added to remove the palladium byproducts and unreacted *N*,*N*-dimethylbarbituric acid. The remaining solid was dissolved in diethyl ether (100 mL) and extracted with 1 M HCl (4 × 20 mL). The combined aqueous layers were basified with 1 M NaOH and extracted with diethyl ether to yield **13** (192 mg, 77%) as an orange oil: Found: C, 61.17; H, 6.09; N, 6.21; $C_{11}H_{13}$FeN requires C, 61.43; H, 6.09; N, 6.04; ^{1}H NMR δ 1.60 (br. s, 2H), 3.54 (s, 2H), 4.11 (app. t, *J* 1.83, 2H), 4.14 (s, 5H), and 4.16 (app. t, *J* 1.83, 2H); ^{13}C NMR δ 41.4, 67.1, 67.8, 68.4, and 91.1; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3100 and 1244; MS (EI, 70 eV): *m*/*z* (%): 215 [M^+] (47), 199 (18), 121 (41), and 56 (100).

***trans*-(2*R*,5*R*)-2,5-Dimethyl-1-(ferrocenylmethyl)pyrrolidine (11).** Amine **13** (400 mg, 1.86 mmol) and (*S*,*S*)-2,5-dimethyl cyclic sulfate (334 mg, 1 equiv) were refluxed in dry tetrahydrofuran for 16 h. The resulting precipitate indicated the presence of the zwitterionic amine-sulfate species. The Schlenk was evacuated under nitrogen and cooled to −78 °C and *n*-butyllithium (1.27 mL, 1.1 equiv) added. The mixture was warmed to room temperature and then refluxed for 72 h. Diethyl ether was added to the solution which was then washed with 10% ammonium chloride, water, and brine and extracted into diethyl ether. This extract was dried ($MgSO_4$) and concentrated to yield 359 mg of crude material which was purified using column chromatography, alumina, hexane/diethyl ether 2:1, to yield **11** (309 mg, 56%) as an orange oil which crystallized on cooling: Found: C, 68.69; H, 7.08; N, 4.71; $C_{17}H_{23}$FeN requires C, 68.69; H, 7.01; N, 4.66; $[\alpha]_D^{20} = -82.2$ (c = 0.5, $CHCl_3$); ^{1}H NMR δ 0.99 (d, *J* 6.22, 6H), 1.25−1.36 (m, 2H), 1.94−2.02 (m, 2H), 2.96−3.01 (m, 2H), 3.34 (d, *J* 13.01, 1H), 3.54 (d, *J* 13.00, 1H), 4.06−4.09 (m, 2H), 4.11 (s, 5H), 4.22 (app. t, *J* 1.28, 2H), and 4.26 (app. t, *J* 1.28, 2H); ^{13}C NMR δ 16.9, 30.6, 47.2, 55.1, 67.5, 67.9, 68.5, 69.5, 70.0, 85.9; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1365; MS (EI, 70 eV): *m*/*z* (%): 298 [M^+] (22%), 199 (100), 121 (63), and 56 (58).

***trans*-(2*R*,5*R*)-2,5-Diethyl-1-(ferrocenylmethyl)pyrrolidine (12).** Amine **13** (272 mg, 12 mmol) and (2*S*,2*S*)-2,5-diethyl cyclic sulfate (263 mg, 1 equiv) were refluxed in dry tetrahydrofuran for 48 h. The resulting precipitate indicated the presence of the zwitterionic amine-sulfate species. The Schlenk was evacuated under nitrogen, cooled to −78 °C and *n*-butyllithium (0.545 mL, 1.1 equiv) added. The mixture was warmed to room temperature and then refluxed for 72 h. Diethyl ether was added to the solution which was then washed with 10% ammonium chloride, water, and brine and extracted into diethyl ether. This extract was dried ($MgSO_4$) and concentrated to yield 300 mg of crude *trans*-(2*R*,5*R*)-2,5-diethyl-1-(ferrocenylmethyl)pyrrolidine. This was purified using column chromatography, alumina, hexane/diethyl ether 2:1, to yield **12** (298 mg, 73%) as an orange oil: Found: C, 69.98; H, 8.26; N, 4.25; $C_{19}H_{27}$FeNP requires C, 70.15; H, 8.37; N, 4.30; $[\alpha]_D^{20} = -47.2$ (c = 0.5, $CHCl_4$); ^{1}H NMR δ 0.81 (t, *J* 7.5, 6H), 1.06−1.10 (m, 2H), 1.41−1.48 (m, 2H), 1.63−1.69 (m, 2H), 1.80−1.85 (m, 2H), 2.69−2.76 (m, 2H), 3.45 (d, *J* 13.00, 1H), 3.55 (d, *J* 13.01, 1H), 4.04−4.07 (m, 2H), 4.10 (s, 5H),

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(47) Hegedus, L. S. In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: New York, 1994; p 448.

4.15−4.18 (m, 1H), and 4.21−4.25 (m, 1H); ^{13}C NMR δ 10.9, 22.9, 27.5, 46.8, 62.2, 67.5, 67.8, 68.5, 69.5, 70.0, and 86.1; ν_{max} (CH_2Cl_2)/cm^{-1} 2312; MS (EI, 70 eV): *m*/*z* (%): 325 [M$^+$] (20%), 199 (100), and 121 (25).

{2*S*$_P$-[(*trans*-(2*R*,5*R*)-2,5-Dimethylpyrrolidinyl)methyl]}-ferrocenyldiphenyl phosphine (19). To a solution of *trans*-(2*R*,5*R*)-2,5-dimethyl-1-(ferrocenylmethyl)pyrrolidine (143 mg, 78 mmol) in dry diethyl ether under nitrogen at room temperature was added *sec*-butyllithium (0.40 mL, 1.1 equiv) and stirred for 5 h. Chlorodiphenylphosphine (0.086 mL, 1 equiv) was added, and the solution was refluxed for 1 h. The solution was diluted with diethyl ether, washed with 10% ammonium chloride, water, and brine, and extracted with diethyl ether. The solution was dried ($MgSO_4$) and concentrated to yield 205 mg of crude product. This was purified using column chromatography, alumina, hexane/diethyl ether 4:1 to yield 83 mg of a mixture of diastereomeric products as a yellow solid which, after a single recrystallization from hot ethanol, yielded **19** as a single diastereomer (63 mg, 27%): mp 107−110 °C; Found: C, 72.37; H, 6.58; N, 2.78; $C_{29}H_{32}FeNP$ requires C, 72.36; H, 6.70; N, 2.91; $[\alpha]_D^{20} = -32.2$ (c = 0.25, $CHCl_3$); ^{1}H NMR δ 0.86 (d, *J* 6.22, 6H), 0.83−0.89 (m, 2H), 1.39−1.45 (m, 2H), 2.62−2.69 (m, 2H), 3.24 (d, *J* 10.69, 1H), 3.65−3.67 (m, 1H), 3.98 (d, *J* 10.44, 1H), 4.01 (s, 5H), 4.17−4.20 (m, 1H), 4.40−4.43 (m, 1H), 7.07−7.10 (m, 4H), 7.37−7.39 (m, 2H), and 7.56−7.59 (m, 4H); ^{13}C NMR δ 16.2, 30.1, 44.9, 53.8, 68.3, 69.6, 71.6, 72.4, 91.7, 127.2−129.0, 130.8−132.7, 135.3, 138.1, and 140.4; ^{31}P NMR δ −22.32; ν_{max} (CH_2Cl_2)/cm^{-1} 3045, 2983 and 1264; MS (EI, 70 eV): *m*/*z* (%): 481 [M$^+$] (100%), 383 (36), 121 (99), and 55 (85).

{2*S*$_P$-[(*trans*-(2*R*,5*R*)-2,5-Diethylpyrrolidinyl)methyl]}-ferrocenyldiphenylphosphine (20). To a solution of *trans*-(2*R*,5*R*)-2,5-diethyl-1-(ferrocenylmethyl)pyrrolidine (111 mg, 64 mmol) in dry diethyl ether under nitrogen at room temperature was added *n*-butyllithium (0.40 mL, 1.1 equiv) and stirred for 1 h. Chlorodiphenylphosphine (0.012 mL, 1 equiv) was added, and the solution was refluxed for 1 h at 35 °C. The solution was diluted with diethyl ether, washed with 10% ammonium chloride, water, and brine, and extracted with diethyl ether. The solution was dried ($MgSO_4$) and concentrated to yield 126 mg of crude product. This was purified using column chromatography, alumina, hexane/diethyl ether 4:1 to yield a mixture of diastereomeric products as a yellow solid (9 mg). Successful recrystallization from ethanol yielded **20** as a single diastereomer (7 mg, 10%): mp 80−83 °C; Found: C, 72.96; H, 7.16; N, 2.53; $C_{31}H_{37}FeNP$ requires C, 72.94; H, 7.30; N, 2.74; $[\alpha]_D^{20} = -82.5$ (c = 0.2, $CHCl_3$); ^{1}H NMR δ 0.71 (t, *J* 7.32, 6H), 0.85−0.88 (m, 2H), 1.07−1.10 (m, 2H), 1.27−1.31 (m, 2H), 1.68−1.75 (m, 2H), 2.42−2.48 (m, 2H), 3.40 (d, *J* 12.96, 1H), 3.67−3.69 (m, 1H), 3.99 (s, 5H), 4.02 (m, 1H), 4.19−4.21 (m, 1H), 4.38−4.41 (m, 1H), 7.17−7.21 (m, 4H), 7.36−7.39 (m, 2H), and 7.17−7.21 (m, 4H); ^{13}C NMR δ 10.9, 22.1, 26.9, 44.9, 61.3, 68.6, 69.5, 71.6, 72.6, 91.9, 127, 132, 135, 138.2, and 140.48; ^{31}P NMR δ −22.40; ν_{max}(CH_2Cl_2)/cm^{-1} 3032, 2984, and 1271; MS (EI, 70 eV): *m*/*z* (%): 509 [M$^+$] (100%), 383 (78), 324 (68), 199 (14), and 183 (63).

Palladium{2*S*-[(*trans*-(2R,5R)-2,5-dimethylpyrrolidinyl)methyl]}ferrocenyl diphenylphosphine(allyl)-tetrafluoroborate (23). Di-μ-chloro-bis(π-allyl)dipalladium (12.6 mg, 0.5 equiv), {2S_P-[(*trans*-(2*R*,5*R*)-2,5-dimethylpyrrolidinyl)methyl]}ferrocenyldiphenyl phosphine (33 mg, 6.86 mmol), and sodium tetrafluoroborate (22.6 mg, 3 equiv) were placed in a Schlenk under nitrogen. Degassed chloroform (1.5 mL) was added via syringe to give a yellow suspension which was stirred for 24 h. The solid was removed by filtration and the solvent removed in vacuo to yield **23** (44 mg, 100%) as a brown solid: mp 176−178 °C (dec); Found: C, 53.85; H, 5.49; N, 1.73; $C_{32}H_{37}BF_4FeNPPd$ requires C, 53.70; H, 5.21; N, 1.96; ^{1}H NMR δ 1.31−1.39 (m, 6H), 1.98−2.09 (m, 1H), 3.39−3.43 (m, 4H), 3.47−3.55 (m, 1H), 3.64 (s, 5H), 3.76−3.81 (m, 1H), 4.35−3.40 (m, 2H), 4.38−4.45 (m, 2H), 4.42−4.44 (m, 1H), 4.52−4.55 (m, 1H), 4.76−4.78 (m, 1H), 5.05−5.11 (m, 1H), 6.07−6.10 (m, 1H), 7.05−7.09 (m, 4H), 7.19−7.25 (m, 2H), and 7.59−7.68 (m, 4H); ^{31}P NMR δ 16.3 and 15.1; MS (ES): 629 [M − BF_4].

Allylic Alkylation Procedures. Malonate Ion Procedure. Sodium dimethyl malonate (0.042 g, 0.275 mmol) was placed in a dry Schlenk which had previously been flushed with nitrogen, and dry degassed acetonitrile (0.3 mL) was added to form a white suspension. To this was added a solution of either palladium{2S_P-[(*trans*-(2*R*,5*R*)-2,5-dimethylpyrrolidinyl)-methyl]}ferrocenyldiphenylphosphine(allyl)tetrafluoroborate (1.8 mg, 0.0025 mmol) or in situ prepared catalyst [di-μ-chloro-bis(π-allyl)dipalladium (0.0025 mmol) and {2S_P-[(*trans*-(2*R*,5*R*)-2,5-diethylpyrrolidinyl)methyl]}ferrocenyldiphenylphosphine (0.005 mmol)] and (*E*)-1,3-diphenylprop-2-enyl acetate (0.063 g, 0.250 mmol) in dry degassed solvent (0.4 mL) to form a pale orange suspension. Reaction progress was monitored by TLC (petroleum ether 40−60 °C:diethyl ether: 2:1 as the eluent). After stirring under nitrogen at room temperature for 24 h, acetic acid (0.1 mL) was added, and the solvent was removed in vacuo. Water (25 mL) was added, and the reaction was extracted into diethyl ether (25 mL) and then washed with water (25 mL) and brine (25 mL). The solution was dried with $MgSO_4$, filtered, and the solvent removed in vacuo to give an orange oil. This was purified on silica gel plates (eluent = petroleum ether 40−60 °C:diethyl ether; 2:1) to afford **25** [when dimethyl malonate was the nucleophile], (*S*)-methyl-2-carbomethoxy-3,5-diphenylpent-4-enoate as a colorless oil: R_f = 0.37; ^{1}H NMR δ 3.51 (s, 3H), 3.70 (s, 3H), 3.95 (d, *J* 11.2, 1H), 4.26 (dd, *J* 8.8, J 11, 1H), 6.33 (dd, *J* 8.8, 5.6, 1H), 6.47 (d, *J* 15.6, 1H), and 7.33−7.18 (m, 10H); ν_{max} (Nujol)/cm^{-1} 1733 and 1600; MS (EI, 70 eV): *m*/*z* (%) 324 (M$^+$, 5), 193 (20), 105 (100), and 91 (27).

Similarly, this procedure afforded [when dimethyl methyl malonate was the nucleophile], (*R*)-ethyl-2-carbomethoxy-3,5-diphenylpent-4-enoate **26** as a colorless oil: ^{1}H NMR δ 1.48 (s, 3H), 3.62 (s, 3H), 3.70 (s, 3H), 6.43−6.49 (d, *J* 15.75, 1H), 6.67−6.72 (m, 1H), and 7.29−7.45 (m, 10H); ν_{max}(Nujol)/cm^{-1} 1735 and 1600.

BSA Procedure. A solution of palladium{2S_P-[(*trans*-(2*R*, 5*R*)-2,5-dimethylpyrrolidinyl)methyl]}ferrocenyldiphenylphosphine(allyl)tetrafluoroborate (1.8 mg, 0.0025 mmol) in dry degassed solvent (0.5 mL) was added to potassium acetate (0.005 mmol), under a nitrogen atmosphere to form a suspension. To this suspension were then added 1,3-diphenylprop-2-enyl acetate (0.063 g, 0.250 mmol), dimethylmalonate (0.275 mmol), and *N*,*O*-bis(trimethylsilyl)acetamide (BSA), (0.275 mmol) by syringe. The yellow suspension was allowed to stir under nitrogen at ambient temperature, the reaction rate monitored by TLC and the reaction mixture purified as for the Malonate Ion procedure.

Determination of Enantiomeric Excess. The ee was found by ^{1}H NMR spectroscopy from the spectrum obtained after adding 20−30 μL of a 0.2 M solution of tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium (III) to 10−15 mg of methyl 2-carbomethoxy-3,5-diphenylpent-4-enoate in $CDCl_3$ (0.5 mL). The methoxy groups of methyl 2-carbomethoxy-3,5-diphenylpent-4-enoate resonate at 3.51 and 3.70 ppm. Following the addition of the chiral shift reagent and subsequent formation of diastereomers, four methoxy peaks are present in the ^{1}H spectrum. The methoxy peak originally at 3.70 ppm is changed to two peaks at 3.74 and 3.76 ppm, and the relative integration of these peaks gives the ee value. If the right-hand peak of these two is larger than this is typical of the (*S*)-enantiomer in excess which was confirmed by comparing the optical rotation obtained with literature values.[35]

Palladium{2*S*$_P$-[(*trans*-(2*R*,5*R*)-2,5-dimethylpyrrolidinyl)methyl]}ferrocenyldiphenylphosphine(diphenylallyl)tetrafluoroborate (30). Di-μ-chloro-bis(1,3-diphenyl-π-allyl)dipalladium (24 mg, 0.5 equiv), {2S_P-[(*trans*-(2*R*,5R)-2,5-dimethylpyrrolidinyl)methyl]}ferrocenyldiphenylphosphine (28 mg, 5.82 mmol) and sodium tetrafluoroborate (19 mg, 3 equiv) were placed in a Schlenk under an atmosphere of nitrogen. Degassed dichloromethane (1.5 mL) was added via syringe to give a red suspension which was stirred for 1 h. The solvent was removed in vacuo to yield **30** (54.9 mg, 100%) as an orange powder: mp 163−165 °C (dec); Found: C, 53.85; H, 5.49; N, 1.73; $C_{32}H_{37}BF_4FeNPPd$ requires C, 53.70; H, 5.21;

N, 1.96; ^{1}H NMR δ 1.18 (d, *J* 6.83, 3H), 1.41 (d, *J* 6.35, 3H), 1.66−1.70 (m, 2H), 1.95−2.03 (m, 2H), 3.47−3.50 (m, 1H), 3.69−3.72 (m, 2H), 4.01 (s, 5H), 4.32−4.35 (m, 1H), 4.38−4.42 (d, *J* 13.67, 1H), 4.63−4.65 (m, 1H), 4.74−4.78 (m, 2H), 5.13−5.16 (m, 1H), 7.29−7.63 (m, 18H), 7.79−7.89 (m, 2H), and 8.87−8.92 (m, 1H); ^{31}P NMR δ 34.4; ν_{max} (CH_2Cl_2)/cm^{-1} 3054, 2973, and 1079; *m*/*z* (ESI $^+$) 781.51 (M − BF_4).

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Supporting Information Available: Tables of X-ray crystal data, atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for **19a**, relevant spectra for compounds **11**, **12**, **18**, **19a**, **20a**, **23**, and **30**. This material is available free of charge via the Internet at http://pubs.acs.org.

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