(1-(Dimethylamino)-2-(diphenylphosphino)ethane)(η^3-1-arylallyl)palladium Tetrafluoroborates. Preparation, Isomeric Equilibria, and Correlations of NMR Chemical Shifts with Hammett Substituent Constants

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^{13}C NMR differences of chemical shifts ($\delta_X - \delta_H$) of allyl carbon atoms in a series of *trans*-(1-(diphenylphosphino)-2-(dimethylamino)ethane)(η^3-1-arylallyl)palladium tetrafluoroborates, X ranging from NO_2 to OMe, correlate very well with σ Hammett constants for C-1 and with σ^+ for C-3, this carbon atom being in a *trans* relationship with the positively charged nitrogen atom.

Introduction

The palladium(0)-catalyzed allylation of nucleophiles (Tsuji−Trost reaction) is a powerful synthetic method featuring cationic (η^3-allyl)palladium intermediates.[1] The knowledge of both the distribution of the positive charge density in cationic (η^3-allyl)palladium complexes and the transmission of electronic effects between the allylic framework and the ligands through the palladium atom is an important topic with regard to some aspects of the Tsuji−Trost reaction, namely the regioselectivity[1d,2] and the induction of enantioselectivity at the electrophilic allyl moiety.[1d,3] Many nucleophiles act in the Tsuji−Trost reaction by a mechanism involving two consecutive inversions (overall retention), one at the formation of the cationic (η^3-allyl)palladium intermediate and another at the attack of the nucleophile on the intermediate. Since the stabilizing ligands are placed remote to the direction of attack by the nucleophile, they can only with difficulty generate different steric environments at both termini of the allylic framework; however, some good enantioselectivities have been achieved with well designed ligands.[4,5] A more common approach involves the use of ligands featuring two bonding atoms of different chemical nature[6] that transmit different electronic effects in a *trans* fashion to the terminal carbon atoms of the allylic framework, thus generating different electrophilicities in them.

NMR data are informative with respect to the distribution of the positive charge density at these centers.[7,8] Thus, Äkermark and co-workers reported the preparation of cationic η^3-allyl complexes bearing two different ligands.[7] In them, donor−acceptor ligands (phosphines) are placed *trans* to the more substituted allylic carbon atom and induce a lower field signal to its *trans* carbon atom with respect to pure donor ligands (amines). Thus, the chemical shifts are considered as a measure of the positive charge density on the terminal carbon atoms in the allyl part of the complexes, and their results indicate that the electronic effects are indeed transmitted in a *trans* direction. We have recently described the preparation of (1,2-bis(diphenylphosphino)ethane)(η^3-1-arylallyl)palladium tetrafluoroborates (as complexes **3** with Ph_2P in the place of Me_2N), and we found good linear correlations of $\Delta\delta$ with σ constants for the three carbon atoms and for the phosphorus atom *cis* to the aryl ring whereas $\Delta\delta$ for the *trans* phosphorus atom correlated better with σ^+. We concluded that for those complexes the positive charge density is concentrated in the P−Pd−P region.[9] In spite of some theoretical limitations, linear free energy relationships (LFER) correlating NMR data with Hammett constants are a useful technique to determine the transmission of inductive and resonant electronic effects through benzene rings, and some reviews are available.[10,11] Good linear correlations have been found between differences in chemical shifts with σ constants or with dual substituent parameters ($\Delta\delta$ *vs* $\rho_I\sigma_I + \rho_R\sigma_R$)

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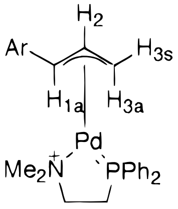


Figure 1.

Scheme 1[a]

$$\mathrm{HPPh_2} \xrightarrow{a} \underset{\mathbf{1}}{\mathrm{Ph_2PCH_2CH_2NMe_2}}$$

[a] Key: (a) tBuOK (2 equiv), THF, then $ClCH_2CH_2NMe_2$ HCl (1 equiv).

for atoms directly linked to a benzene ring: ^{1}H in *para* and in *meta* position in monosubstituted benzenes (dual correlation);[12] ^{19}F in *meta*- and *para*-substituted fluorobenzenes (dual correlation).[10,13] It can be concluded that in systems of the type 4-X-C_6H_4-(nucleus) fairly good linear correlations exist between $\Delta\delta$ for the NMR active nucleus and either σ or $\rho_I\sigma_I + \rho_R\sigma_R$ or both.[9,11] Data on carbenium ion systems is, of course, more scarce. However, good linear correlations have been described for $\Delta\delta$ (for the charged carbon atom) and σ^+ in the systems 4-X-C_6H_4-$C^+(R)(CH_3)$.[14] Finally, a correlation between σ^- (rather than σ) and $\Delta\delta$ (^{15}N NMR) for the nitrogen chemical shifts in *para*-substituted *N,N*-bis(2-chloroethyl)arylamines has been very recently reported.[15] In summary, examples of useful correlations are available covering all conceivable situations, from low electronic density to high electronic density at the studied nucleus.

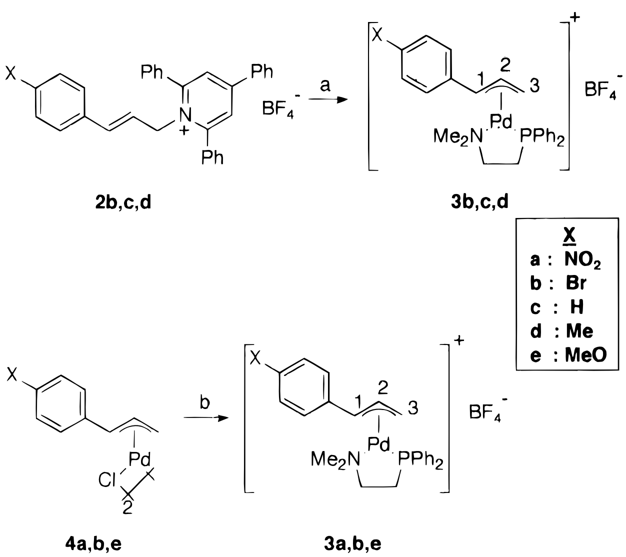
Results and Discussion

We present here the preparation of the title salts featuring two different linking atoms (N and P) at the bidentate ligand as well as results concerning the geometric isomerism and correlations of $\Delta\delta$ with Hammett substituent constants. As indicated in Figure 1, the positive charge density must be high at the donor but nonacceptor nitrogen atom (double bond Pd=P has been depicted in Figure 1 in the organic chemistry style to take account of both donation and back donation). We wish to present our results on how this fact determines the type of correlations.

The required ligand 1-(dimethylamino)-2-(diphenylphosphino)ethane, **1**,[16] was much better prepared by reaction of the potassium salt of diphenylphosphine with 2-chloro-*N,N*-dimethylethylamine (Scheme 1).

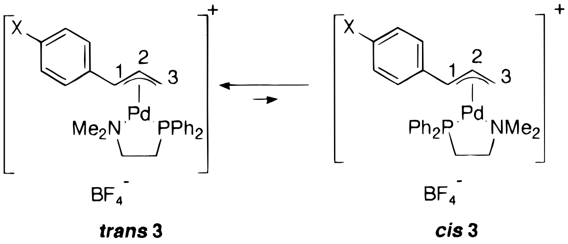
Salts **3** were prepared either by reaction of *N*-cinnamylpyridinium tetrafluoroborates **2** with Pd(dba)$_2$ in the presence of the ligand **1** (Scheme 2)[17] or by reaction of bis(μ-chloro)bis(1-aryl-η^3-allyl)dipalladium, **4**, with silver tetrafluoroborate and the ligand **1** (Scheme 2). The preparation of compounds **2** and **4** has been previously described.[9]

Scheme 2[a]



[a] Key: (a) Pd(dba)$_2$, **1**, PhH; (b) AgF$_4$B, acetone, then **1**.

Scheme 3



Trans isomers predominate in compounds **3** (Scheme 3). The ratios *trans/cis* were ca. 2 for **3a**, 4 for **3b** and >9 for **3c**−**e** as evidenced by NMR. Some ^{1}H and ^{13}C NMR signals for ***cis*-3a** could be determined. All other *cis* isomers gave no clear signals in the complex ^{1}H NMR and ^{13}C NMR spectra; however, ^{31}P NMR permitted the identification of the singlets for the minor isomers but for **3d**. The assignment of the *trans* configuration to the major isomer **3a** was made by NOE experiments. Thus, presaturation of the signal of the NMe$_2$ protons resulted in strong NOE on the signals of the *ortho* protons (with respect to the allylic chain) of the aromatic ring and smaller NOE upon the *meta* protons and H_{1a} of the allylic chain. Also, informative NOE experiments were performed for *cis*-**3a**; thus, when the signals of the NMe$_2$ protons were presaturated, NOE was observed on the signal of H_{3a}, and when the signal of H_{1a} was presaturated, NOE was detected at the distinguished *ortho* protons of one Ph-P ring.

Tables 1 and 2 show, respectively, the ^{13}C NMR chemical shifts for the allylic carbon atoms of the major isomers *trans*-**3a**−**e** and the ^{31}P NMR chemical shifts for both isomers **3a**−**e**. Table 3 contains several correlations (five points) between $\Delta\delta$ and different Hammett substituent constants or combinations thereof. In two cases we were forced to make correlations with four points, which is not advisable. However, the important point is

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Table 1. ^{13}C NMR Chemical Shifts in δ Units ($CDCl_3$) and in Hz (at 62.50 MHz) of Allyl Carbon Atoms in Compounds *trans*-3a−e

	C-1				C-2			C-3		
compd	X	δ	ν_X	ν_X-ν_H	δ	ν_X	$\nu_X-\nu_H$	δ	ν_X	ν_X-ν_H
3a	NO_2	96.08	6005	−275	117.01	7313	+194	51.23	3202	+84
3b	Br	99.32	6207	−73	114.49	7156	+37		[a]	
3c	H	100.48	6280	0	113.91	7119	0	49.89	3118	0
3d	Me	101.29	6331	+51	113.04	7065	−54	49.41	3088	−30
3e	MeO	101.95	6372	+92	111.97	6998	−121	48.94	3059	−59

[a] Spectrum too complex for safe assignments to be made.

Table 2. ^{31}P NMR Chemical Shifts in δ Units ($CDCl_3$) and in Hz (H_3PO_4 as External Standard and at 101 MHz) for P Atoms in Compounds 3a−e

		trans-**3** (*trans* P)			cis-**3** (*cis* P)		
compd	X	δ	ν_X	ν_X-ν_H	δ	ν_X	ν_X-ν_H
3a	NO_2	41.77	4230	+182	39.25	3975	+397
3b	Br	40.04	4054	+6	36.39	3685	+107
3c	H	39.98	4048	0	35.33	3578	0
3d	Me	40.26	4077	+29		[a]	
3e	MeO	38.70	3919	−129	33.98	3441	−137

[a] Undetected.

Table 3. Equations Relating $\Delta\delta$ ($\delta_X - \delta_H$) from ^{13}C NMR for Compound *trans*-3a−e and ^{31}P NMR Data with Hammett Constants for Compounds *cis*-3a−e

atom	eq	*r*	eq no.
	trans-**3a−e**		
C-1	$\Delta\delta = 0.04 - 5.38\sigma$	0.999	1
	$\Delta\delta = 0.77 - 3.82\sigma^+$	0.959	2
	$\Delta\delta = 0.08 - 5.62\sigma + 0.18\sigma^+$	0.999	3
	$\Delta\delta = 0.04 - 5.26\sigma_I - 7.07\sigma_R$	0.999	4
C-2	$\Delta\delta = -0.39 + 4.36\sigma$	0.989	5
	$\Delta\delta = -0.28 + 3.23\sigma^+$	0.989	6
	$\Delta\delta = -0.06 + 2.21\sigma + 1.65\sigma^+$	0.998	7
	$\Delta\delta = -0.08 + 3.56\sigma_I + 6.55\sigma_R$	0.996	8
C-3	$\Delta\delta = -0.21 + 1.99\sigma$	0.986	9
	$\Delta\delta = 0.09 + 1.49\sigma^+$	0.992	10
	$\Delta\delta = -0.04 + 0.85\sigma + 0.88\sigma^+$	0.999	11
	$\Delta\delta = -0.07 + 1.48\sigma_I + 3.09\sigma_R$	0.998	12
	cis **3a−e**		
P *cis*	$\Delta\delta = -0.04 + 4.82\sigma$	0.998	13
	$\Delta\delta = 0.77 + 3.34\sigma^+$	0.961	14
	$\Delta\delta = -0.06 + 4.90\sigma - 0.06\sigma^+$	0.998	15
	$\Delta\delta = 4.62\sigma_I + 6.38\sigma_R$	0.999	16

the comparison between correlations with σ and with σ^+, and we can safely assume that the conclusions to be drawn are independent of the number of points in the correlation. The following details are remarkable:

1. The absolute values of the slopes (correlations with σ and σ^+ values, Table 3, eqs 1, 5, 6, 9, and 10) for carbon atoms in the allylic framework decrease with the distance to the aryl ring, from C-1 to C-3).

2. The slope for C-1, directly attached to the aryl ring, is negative (Table 3, eq 1). This means that an electron-withdrawing substituent (i.e., nitro group, $\sigma = +0.81$) induces a high-field signal for C-1 with respect to an electron-releasing group (see Table 1). There is no intuitive explanation for this phenomenon, which has been observed previously for C-1 in 1-arylbutadienes and 1-arylacetylenes and for the terminal carbon atoms in aryl vinyl ethers and sulfides.[11] In the organometallic field we observed the same effect in complexes **3** (Ph_2P in the place of Me_2N)[9] and Rausch et al. in substituted (η^5-cyclopentadienyl)carbonyl(triphenylphosphine)-iridium.[18]

3. The *cis* percentage in the mixture increases with the electron-withdrawing character of the substituent at the aryl ring (ca. 33% of *cis*-**3a** where the pure donor group NMe_2 is placed *trans* to the acceptor NO_2Ph). Compound *trans*-**3a** (X = NO_2) exhibits broad singlets in ^1H NMR (δ 2.39) and in ^{13}C NMR (δ 50.03) for the $N(CH_3)_2$ group protons and carbon atoms, whereas *trans*-**3c−e** give different sharp signals for each methyl group. Product *trans*-**3b** (X = Br) presents a broad singlet for the $N(CH_3)_2$ protons (δ 2.31) but two signals in ^{13}C NMR. Also H-3a and H-3s of *trans*-**3a,b** present a collapsed broad singlet. NMR spectra of **3e** at 333 K did not show coalescences, and NMR spectra of **3a** at 203 K showed more broadening of signals. Thus, equilibrations fast in the NMR time scale operate in *trans*-**3a** and in *trans*-**3b**.[19−21]

4. The observed correlations for C-1 between $\Delta\delta$ and σ (Table 3, eq 1) and the dual correlation with σ_I and σ_R (Table 3, eq 4) are both much better than the correlation with σ^+ (Table 3, eq 2).

5. A good dual correlation (σ_I and σ_R) is observed for C-2 (Table 3, eq 8). Correlations with σ and σ^+ for C-2 are not so good but *both are of the same quality* (Table 3, eqs 5 and 6).

6. For C-3 again the dual correlation (σ_I and σ_R) is good (Table 3, eq 12) but now correlation with σ^+ (Table 3, eq 10) is better than with σ (Table 3, eq 9). C-3 is the carbon atom *trans* to the positive charge of the amine ligand.

7. The coefficients of the dual correlations with σ and σ^+ for C-1, C-2, and C-3 (Table 3, eqs 3, 7, and 11) indicate the relative importance of σ and σ^+. The coefficients of σ^+ can be considered as a measure of the direct connection of the corresponding carbon atom with the positive charge. Note that the coefficient of σ is much larger than the coefficient of σ^+ for C-1 (eq 3). However, the coefficient of σ^+ becomes quantitatively more important on going to C-2 (Table 3, eq 7) and to C-3 (Table 3, eq 11), this C-3 carbon atom being connected in a *trans* fashion with the positively charged nitrogen atom.

8. No good correlation is evident for the phosphorus atom of the *trans* isomers. See in Table 2 the irregularity of the values of chemical shifts for **3d** and **3e**. A similar result was observed for the related complexes featuring

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[20] For isomerizations through the apparent π-allyl-Pd rotation, see: (a) Hansson, S.; Norrby, P.-O.; Sjögren, M. P. T.; Åkermark, B.; Cucciolito, M. E.; Giordano, F.; Vitagliano, A. *Organometallics* **1993**, *12*, 4940. (b) Gogoll, A.; Örnebro, J.; Grennberg, H.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1994**, *116*, 3631.

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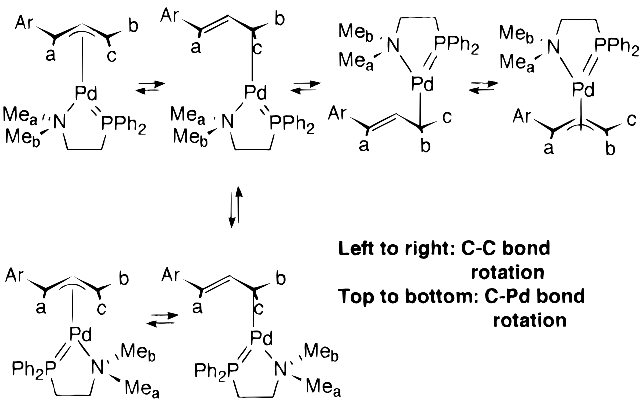
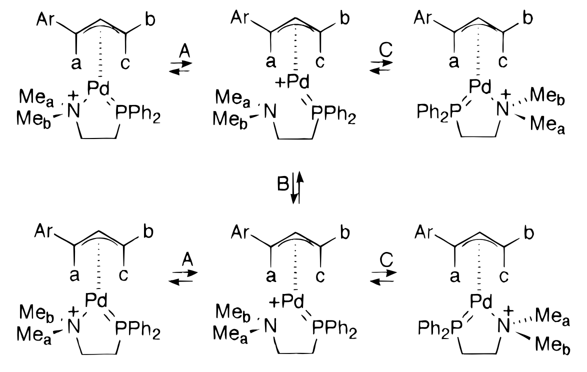
Scheme 4. Stereochemical Consequences of the π–σ–π Isomerization Mechanism



Scheme 5. Stereochemical Consequences of the Monocoordination of the Pd Atom to the Bidentate Ligand



PPh_2 in the place of Me_2N, although in that case a reasonable correlation was observed.[9]

9. For the phosphorus atom of the *cis* complexes, again a good correlation was observed for σ (Table 3, eq 13) and for the combination of σ_I and σ_R (Table 3, eq 16). Both correlations were much better than with σ^+ (Table 3, eq 14). Of course, a combination of σ and σ^+ gave a good correlation (Table 3, eq 15) with the coefficient for σ being much larger than the coefficient of σ^+.

10. Signals of C-3 appear at much higher field (16–18 ppm) than in the related complexes featuring bis(diphenylphosphino)ethane as bidentate ligand,[9] indicating a much higher electronic density in C-3 in compounds *trans*-**3**.

In summary, Hammett correlations with NMR parameters are a good tool to study the transmission of electronic effects and to determine the distribution of the positive charge density in cationic (η^3-allyl)palladium complexes. A good correlation of $\Delta\delta$ with σ^+ are observed for a center such as C-3 that supports a high electronic density but is connected in a *trans* fashion with a positively charged nitrogen donor atom.

With regard to remark 3, Scheme 4 represents the stereochemical consequences of a hypothetical π–σ–π isomerization mechanism, including a possible C–Pd bond rotation at the σ situation. Under these circumstances, any step taking place by the π–σ–π mechanism (1) interchanges the relative position of both substituents at one terminal carbon atom, (2) changes the face of the allylic framework to which the PdL_2 is attached, (3) changes the geometrical relationship of Me_a and Me_b with respect to Ar and H-a, and (4) provided C–Pd bond rotation occurs, makes *cis-trans* isomerization possible. Therefore, the π–σ–π mechanism can explain both the isomerization between stereoisomers and the equivalence of the NMR signals of the NMe_2 group in compounds **3a,b**. A tricoordinated palladium atom has been proposed by Gogoll, and Bäckvall et al. as a key feature of the so-called apparent π-allyl rotation mechanism.[20b] Scheme 5 represents the stereochemical consequences of such tricoordination on Pd. Indeed, the donor only nitrogen atoms are ideal candidates to decoordination from palladium, thus rendering the metal tricoordinated with 14 electrons in the valence shell (processes A). The resulting species can progress in two different directions: (1) fast inversion of the nitrogen atom and rotation of the $N-CH_2$ bond (process B; connection of upper and lower parts of Scheme 5), thus interchanging the positions of both Me groups, and (2) apparent π-allyl rotation mechanisms by any of the pathways suggested by Gogoll and Bäckvall (Pd–P rotation or allyl–Pd rotation, processes C), connecting the Pd-tricoordinated intermediates with the *cis* stereoisomers (right part of Scheme 5). Thus, tricoordination at Pd and apparent π-allyl-Pd rotation also accounts for both dynamic phenomena observed in **3a,b**.

Experimental Section

NMR Experiments. Structural studies were performed on a Bruker ARX400 spectrometer equipped with an inverse broad-band probe head incorporating a shielded Z-gradient coil. The exact carbon and phosphorous shifts were measured from a conventional decoupled 1D spectrum acquired on a Bruker AC250 spectrometer equipped with a triple $^1H-^{13}C-^{31}P$ probe head. Proton and carbon chemical shifts were referenced to the $CDCl_3$ signals at 7.24 and 77.0 ppm, respectively. Phosphorus chemical shifts were referenced to the signal of phosphoric acid. ^1H, ^{13}C, and ^{31}P assignments were made for compounds **3** by concerted use of gradient-enhanced COSY experiments, gradient-enhanced $^1H-^{13}C$ HMQC experiments, and gradient-enhanced $^1H-^{31}P$ HMBC experiments. NOE data were extracted from a conventional phase-cycled 2D ROESY experiment or from a gradient-enhanced 1D ROESY (GROESY) experiment when selective excitation was possible. Full details of the NMR work will be published soon. In (η^3-allyl)palladium complexes the rule is that coupling constant values between protons on a certain terminal allylic carbon atom and the phosphorus atom *cis* to that carbon atom are ca. 0 Hz, whereas coupling constants of the same protons with the phosphorus atom *trans* to the same carbon atom have significant values.[22] We have fully confirmed this tendency here and in our previous work.[9]

Magnitude-mode gradient-enhanced COSY spectra[23] resulted from a 512 × 1024 data matrix size with 1 scan per t_1 value. The recycle time was 1 s, and a 1:1 gradient combination was used. The data were zero-filled once in the t_1 dimension, and a sine bell filter was used before Fourier transformation in both dimensions.

Magnitude-mode gradient-enhanced one-bond $^1H-^{13}C$ correlation (HMQC) spectra[24] resulted from a 128 × 1024 data matrix size with 2 scans per t_1 value (no dummy scans). The delay was set to 3.5 ms, and the recycle time was 1 s. A 2:2:1 gradient combination was used. Broad-band ^{13}C decoupling with GARP-1[25] was applied during acquisition. A sine bell filter function was used prior to Fourier transformation in the t_2 and t_1 dimensions.

Magnitude-mode gradient-enhanced multiple bond $^1H-^{31}P$ shift correlation (HMBC) spectra[24] resulted from a 64 × 512

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data matrix size with 2−4 scans (no dummy scans) per t_1 value and a recycle time of 1 s. The delay was set to 50 ms. The data were zero-filled once in the t_1 dimension, and a sine bell filter was used before Fourier transformation in both dimensions. A gradient combination of 1.238:1.238:1 was used to select the desired coherence.

Phase-sensitive ROESY experiment[26] resulted from a 2 × 512 × 1024 data matrix size with 16−32 scans per t_1 value. The recycle time was 1 s. As a mixing time, a continuous off-resonance low-power pulse (2.6-KHz R_f field strength) during 500 ms was used. Quadrature detection in the t_1 dimension was achieved by the TPPI method. The data were zero-filled once in the t_1 dimension, and a cosine bell filter was used before Fourier transformation in both dimensions.

High-quality 1D GROESY spectra were obtained with a recently proposed pulse sequence[27] using a 500 ms T-ROESY mixing time.[28] Twenty and 40 ms Gaussian pulses were used as selective 90° and 180° pulses, and a 1:−1:2 gradient combination affords the desired coherence selection.

All B_0 field gradient pulses had a Gaussian shape truncated at 5% and a length of 1 ms. Only peak amplitudes were varied according to the required ratios described above.

Saturated solutions of compounds **3** in $CDCl_3$ were used throughly in NMR determinations.

Substituent Constants. Substituent constant values were taken from the textbook by March.[29]

General. Products **2** and **4** have been described[9] except for **4b**.

1-(Dimethylamino)-2-(diphenylphosphino)ethane, 1. A mixture of diphenylphosphine (0.389 g, 2.088 mmol), potassium *tert*-butoxide (0.562 g, 5.011 mmol), and anhydrous THF (65 mL) was magnetically stirred under nitrogen for 15 min at room temperature. Then 2-chloro-*N*,*N*-dimethylethylamine hydrochloride (0.361 g, 2.506 mmol) was added, and the mixture was refluxed for 6 h. Saturated aqueous ammonium chloride (100 mL) was added at room temperature, and the mixture was extracted with chloroform (3 × 70 mL). The organic layer was washed with distilled water (2 × 150 mL), dried, and evaporated to give a dense oil (0.299 g, 56%) characterized as **1** practically pure. A sample distilled at 175−180 °C/0.4 mmHg (lit.[16] bp 146−149 °C/0.08 mmHg): ^1H NMR (250MHz, $CDCl_3$) δ 2.11−2.22 (m, 8H), 2.28−2.37 (m, 2H), 7.23−7.49 (m, 10H).

4-Bromocinnamyl alcohol was prepared in 83% yield by reduction of ethyl 4-bromocinnamate with diisobutylaluminum hydride in toluene at −78 °C: oil; IR (film) 3277 (br), 969 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.77 (br s), 4.27 (d, $J = 5.5$ Hz, 2H), 6.31 (dt, $J = 15.9$ and 5.5 Hz, 1H), 6.52 (d, $J = 15.9$ Hz, 1H), 7.20 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H).

4-Bromocinnamyl chloride was prepared in 80% yield by reaction of 4-bromocinnamyl alcohol with thionyl chloride in benzene at room temperature: oil; ^1H NMR (250 MHz, $CDCl_3$) δ 4.19 (d, $J = 6.9$ Hz, 2H), 6.27 (dt, $J = 15.7$ and 6.9 Hz, 1H), 6.56 (d, $J = 15.7$ Hz, 1H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 2H).

Bis(μ-chloro)bis(1-(4-bromophenyl)-η^3-allyl)dipalladium, 4b. A degassed solution of 4-bromocinnamyl chloride (291 mg, 1.260 mmol) in anhydrous benzene (10 mL) was added under an argon atmosphere over a degassed suspension of $Pd_2(dba)_3(HCCl_3)$ (452 mg, 0.504 mmol) in anhydrous benzene (10 mL). The mixture was kept under vigorous magnetic stirring at room temperature for 22 h 30 min. The green precipitate was filtered off and washed with benzene (0.264 mg, 78%): mp 195−199 °C; IR (KBr) 3064, 2938, 1588, 1482, 1447, 1398, 1075, 1011 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 3.03 (d, $J = 12.1$ Hz, H-3a), 3.97 (d, $J = 6.6$ Hz, H-3s), 4.52 (d, $J = 11.0$ Hz, H-1a), 5.74 (dt, $J =$ ca. 12 and 6.6 Hz, H-2), 7.31 (d, $J = 8.2$ Hz, 2H), 7.37 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (62.5 MHz, C_2D_6SO) δ 64.93 (C-3), 85.70 (C-1), 113.63 (C-2), 121.27 (1C), 130.21 (2C), 131.76 (2C), 136.71 (1C). Anal. Calcd for $C_{18}H_{16}Br_2Cl_2Pd_2$: C, 31.99; H, 2.39. Found: C, 31.90; H, 2.23.

(1-(Dimethylamino)-2-(diphenylphosphino)ethane)(η^3-1-(4-nitrophenyl)allyl)palladium Tetrafluoroborate, 3a. A solution of **4a**[9] (0.175 g, 0.288 mmol) in acetone (15 mL) was added over a solution of silver tetrafluoroborate (0.112 g, 0.576 mmol) in acetone (5 mL). The mixture was magnetically stirred in the dark at room temperature. The formed precipitate was filtered off, and aminophosphine **1** (0.163 g, 0.633 mmol) was added to the solution. The mixture was stirred for 12 h at room temperature and filtered, and the solvent was evaporated to afford a foam that was digested with diethyl ether to afford **3a** (0.237 g, 68%): mp 173−178 °C; IR (KBr) 3057, 2973, 2924, 1595, 1518, 1433, 1335, 1103, 1053 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ (major *trans* isomer) 2.39 (s, $N(CH_3)_2$), 2.55−2.80 (m, 4H), 3.40−3.55 (m, H-3a and H-3s), 5.54 (dd, $J_{H\text{-}1a/H\text{-}2} = 13.2$ Hz, $J_{H\text{-}1a/P} = 9.1$ Hz, H-1a), 6.31−6.52 (m, H-2), 7.08−7.69 (m, 10H), 7.79 (d, $J = 7.7$ Hz, 2H), 8.19 (d, $J = 7.7$ Hz, 2H); δ (minor *cis* isomer, only well defined signals) 3.02 (s, NCH_3), 3.05 (s, NCH_3), 4.27 (dd, $J = 13.9$ and 9.1, H-3s), 4.80−4.86 (m, H-1a and H-3a), 6.80 (dd, $J_{HP} = 11.9$ Hz, $J_{ortho} = 7.5$ Hz, 2H *ortho* in one phenyl ring); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (major *trans* isomer) 29.04 (d, $J = 26.6$ Hz, P-CH_2), 50.03 (s, $N(CH_3)_2$), 51.23 (d, $J = 4.6$ Hz, C-3), 61.79 (d, $J = 6.5$ Hz, N-CH_2), 96.08 (d, $J = 27.7$ Hz, C-1), 117.01 (br, C-2), 123.95−146.88 (18C); δ (minor *cis* isomers, only well defined signals) 30.72 (d, $J = 26.6$, PCH_2), 52.91 (s, NCH_3), 53.52 (s, NCH_3), 61.40 (d, $J = 7.4$ Hz, NCH_2), 69.65 (d, $J = 5.5$ Hz, C-1), 80.96 (d, $J = 24.8$ Hz, C-3), 120.68 (d, $J = 5.6$ Hz, C-2). Anal. Calcd for $C_{25}H_{28}BF_4N_2O_2PPd$: C, 49.01; H, 4.61; N, 4.57. Found: C, 49.11; H, 4.69; N, 4.44.

(1-(Dimethylamino)-2-(diphenylphosphino)ethane)(η^3-1-(4-bromophenyl)allyl)palladium Tetrafluoroborate, 3b. It was obtained in 69% yield by the same method as for **3a** from **4b** (0.181 g, 0.268 mmol), silver tetrafluoroborate (0.104 g, 0.536 mmol), and **1** (0.138 g, 0.536 mmol): mp 158−161 °C; IR (KBr) 3057, 2973, 1623, 1482, 1440, 1187, 1159, 1060, 878, 751, 695 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 2.10−2.52 (br s, $N(CH_3)_2$), 2.50−2.73 (m, 4H), 3.37−3.48 (br, H-3a), 4.09 (d, $J_{H\text{-}2/H\text{-}3s} = 7.7$ Hz, H-3s), 5.48 (dd, $J_{H1\text{-}a/H\text{-}2} = 13.5$ Hz, $J_{H1\text{-}a/P} = 9.1$ Hz), 5.97−6.21 (m, H-2), 7.09−8.19 (m, 14H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 28.81 (d, $J = 24.8$ Hz, PCH_2), 49.76−50.48 ($N(CH_3)_2$ and C-3), 61.72 (d, $J = 7.3$ Hz, NCH_2), 99.32 (d, $J = 25.7$ Hz, C-1), 114.49 (C-2), 125.34−134.81 (16C).

(1-(Dimethylamino)-2-(diphenylphosphino)ethane)(η^3-1-(4-methoxyphenyl)allyl)palladium Tetrafluoroborate, 3e. It was obtained from **4e**[9] (0.155g, 0.268 mmol), silver tetrafluoroborate (0.104 g, 0.536 mmol), and **1** (0.138 g, 0.536 mmol), by the same method as for **3a**. The salt **3e** (76%) had mp 135−140 °C: IR (KBr) 3036, 2924, 2846, 1602, 1503, 1461, 1440, 1250, 1180, 1060, 878, 835 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 2.02 (s, NCH_3), 2.62 (s, NCH_3) 2.50−2.81 (m, 4H), 2.93 (d, $J_{H\text{-}3a/H2} = 13.5$ Hz, H-3a), 3.79 (s, OCH_3), 3.78−3.84 (m, H-3s), 5.51 (dd, $J_{H\text{-}1a/H2} = 13.5$ Hz, $J_{H\text{-}1a/P} = 8.8$ Hz, H-1a), 6.01−6.14 (m, H-2), 6.92 (d, $J = 8.8$ Hz, 2H), 7.44−7.67 (m, 12H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 28.56 (d, $J = 26.8$, PCH_2), 48.94 (s, NCH_3), 48.94 (d, $J = 2.8$ Hz, C-3), 49.87 (s, NCH_3), 55.33 (s, OCH_3), 61.63 (d, $J = 8.3$ Hz, NCH_2), 101.95 (d, $J = 24.9$ Hz, C-1), 111.97 (d, $J = 5.5$ Hz, C-2), 15.09 (s, 2C), 127.45−132.96 (15C), 160.36 (s, 1C). Anal. Calcd for $C_{26}H_{31}BF_4NOPPd$: C, 52.24; H, 5.23; N, 2.34. Found: C, 52.10; H, 5.30; N, 2.28.

(1-(Dimethylamino)-2-(diphenylphosphino)ethane)(η^3-1-phenylallyl)palladium Tetrafluoroborate, 3c. A solution of bis(dibenzylideneacetone)palladium(0) (0.172 g, 0.3 mmol) and **1** (0.077 g, 0.3 mmol) in anhydrous benzene (10 mL) was added to a solution of pyridinium salt **2c**[9] (0.146 g, 0.3 mmol) in anhydrous benzene (5 mL). The mixture was kept at room temperature for 6 h and filtered, the solvent was evaporated, and the residue was digested with diethyl ether to afford pure **3c** (0.148 g, 85%): mp 175−180 °C; IR (KBr) 3057, 3022, 2917, 1489, 1461, 1433, 1053, 871, 765 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.97 (br s, NCH_3), 2.58 (s, NCH_3), 2.39−2.66 (m, 4H), 2.94−3.04 (m, H-3a), 3.80−3.82 (m, H-3s),

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4.96 (dd, $J_{H\text{-}1a/H\text{-}2}$ = 13.2 Hz, $J_{H\text{-}1a/P}$ = 9.5 Hz, H-1a), 6.17 (dt, $J_{H\text{-}2/H\text{-}1a}$ = $J_{H\text{-}2/H\text{-}3a}$ = 12.9 Hz, $J_{H\text{-}2/H\text{-}3s}$ = 9.9 Hz, H-2), 7.33−7.63 (m, 15H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 28.57 (d, J = 26.8 Hz, PCH_2), 48.49 (s, NCH_3), 49.89 (d, J = 3.7 Hz, C-3), 50.05 (s, NCH_3), 61.77 (d, J = 7.4 Hz, NCH_2), 100.48 (d, J = 25.9 Hz, C-1), 113.91 (d, J = 5.5 Hz, C-2), 127.56−133.46 (18C). Anal. Calcd for $C_{25}H_{29}BF_4NPPd$: C, 52.89; H, 5.15; N, 2.47. Found: C, 52.73; H, 5.02; N, 2.31.

(1-(Dimethylamino)-2-(diphenylphosphino)ethane)(η^3-1-(4-methylphenyl)allyl)palladium Tetrafluoroborate, 3d. It was obtained from **2d**[9] (0.040g, 0.076 mmol), bis(dibenzylideneacetone)palladium(0) (0.043 g, 0.076 mmol), and **1** (0.020 g, 0.076 mmol) by the same method as for **3c**. The salt **3d** (0.035 g, 81%) had mp 162−167 °C: IR (KBr) 3057, 3022, 2924, 2860, 1616, 1595, 1440, 1103, 1053, 765, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.59 (br s, CCH_3), 2.22 (s, NCH_3), 2.01−2.35 (m, 4H), 2.62 (br s, NCH_3), 2.99 (m, H-3a), 3.25−3.50 (m, H-3s), 5.45 (dd, $J_{H\text{-}1a/H\text{-}2}$ = 13.5 Hz, $J_{H\text{-}1a/P}$ = 9.1 Hz, H-1a), 6.04−6.17 (m, H-2), 7.02−8.19 (m, 14H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 21.42 ($PhCH_3$), 28.56 (d, J = 26.8 Hz, PCH_2), 44.84 (NCH_3), 48.90 (NCH_3), 49.41 (d, J = 2.8 Hz, C-3), 61.72 (d, J = 7.4 Hz, NCH_2), 101.29 (d, J = 25.9, C-1), 113.04 (d, J = 5.5 Hz, C-2), 117.04−143.25 (18C). Anal. Calcd for $C_{26}H_{31}BF_4NPPd$: C, 53.69; H, 5.38; N, 2.41. Found: C, 53.42; H, 5.16; N, 2.33.

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Supporting Information Available: IR, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra of compounds **3** (29 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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