Preparation and NMR Spectroscopy of (1,2-Bis(diphenylphosphino)ethane)(η^3-1,3-diarylallyl)-palladium Tetrafluoroborates. Correlation of Chemical Shifts with Hammett Substituent Constants and with the Regioselectivity of Nucleophilic Attack

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^{13}C NMR chemical shifts of the terminal allyl carbon atoms C-1 and C-3 of (1,2-bis-(diphenylphosphino)ethane)(η^3-1,3-diarylallyl)palladium tetrafluoroborates correlate with σ Hammett substituent constants. For each complex the chemical shift at lower field indicates the site of preferred attack by soft nucleophiles in the Tsuji−Trost reaction.

The palladium(0)-catalyzed allylation of nucleophiles (the Tsuji−Trost reaction) is a synthetic method of high acceptance due to its broad scope and easy experimental procedure.[1] The catalytic cycle (Figure 1) involves the formation of the η^3-allylpalladium complex, **1**, as the key intermediate which can be attacked by nucleophiles at both termini of the allylic system. It is generally accepted that nucleophiles attack preferentially at the less hindered allylic terminus; thus product **2** is predominantly formed, mainly if R = alkyl and aryl. However, exceptions have been described and corresponding explanations have been advanced. Thus, for a given nucleophile regioselectivity depends on the electronic nature of the stabilizing ligand, acceptor ligands favoring attack at the more substituted terminus.[2] Also, for a given allylpalladium system regioselectivity can depend on the nucleophile, nonstabilized nucleophiles presenting some propensity to attack at the more substituted terminus.[3] Important electronic effects are evident when R in Figure 1 is a polar group attached directly to the allylic framework, although in

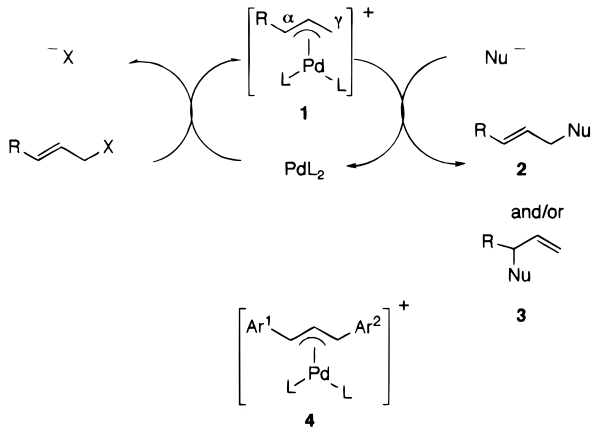

Figure 1.

these cases both electronic and steric effects are important. Thus, strong electron-withdrawing groups, as defined by positive σ_p values, direct the attack on complexes **1** at the more remote side (γ attack: R′CO− and R′OCO−,[4] NC−,[4d,e,5] $PhSO_2$−,[6] $(R'O)_2P(O)$−,[7] PhS−[8]), whereas electron-donating groups placed on one allylic terminal carbon atom favor the attack at the same position (α attack: R′O−,[9] anomeric oxygen atom

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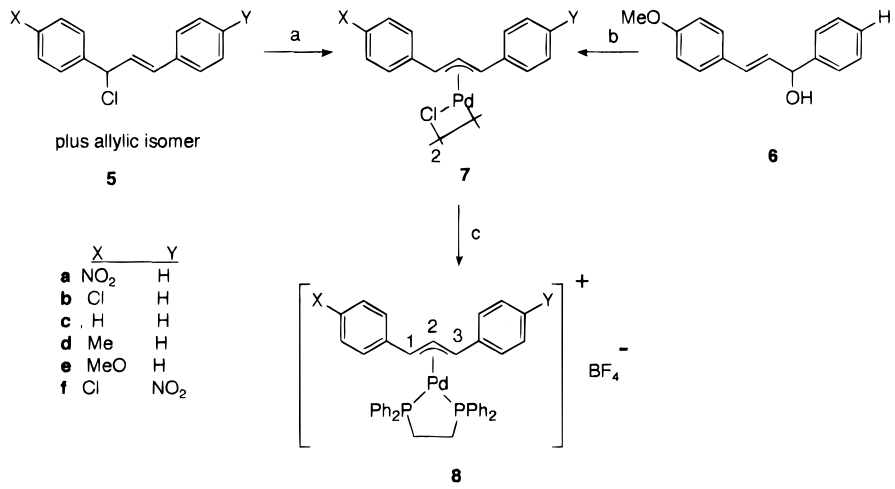
Scheme 1[a]



[a] Key: (a) $Pd_2(dba)_3 \cdot HCCl_3$, PhH (for **7a−d,f**); (b) Pd(dba)*n* or $Pd_2(dba)_3 \cdot HCCl_3$, LiCl, aq HCl, THF, EtOH (for **7e**); (c) AgF_4B, acetone and then dppe, acetone.

in unsaturated carbohydrates[10]). The influence of other groups has been also described: In general acetoxy (MeCOO−) induces α attack[11] although steric effects can reverse this propensity.[11a,b,d,12] The regioselectivity when R = fluorine depends on the nature of the nucleophile.[13] The trimethylsilyl group induces clearly γ attack,[14,15] although it is considered to be neither electron-withdrawing nor electron-donating (σ_p in the range 0.00 to −0.07), and the same applies to the tributyltin group.[15]

In summary, apart from steric effects, the regioselectivity depends on the relative charge at both termini of the allylic framework, and this can be modulated by the substituents at the carbon skeleton and by the ligands at palladium. On the other hand, it is well-known that ^{13}C NMR chemical shifts are an indication of the relative positive charge distribution[2f,16] at the allylic termini.

In order to clarify the role of the isolated electronic effects on the regioselectivity we studied some years ago the palladium(0)-catalyzed allylations of soft nucleophiles with 1,3-diarylallyl acetates.[17] These reactions involved (η^3-allyl)palladium complexes **4** (L = PPh_3) featuring aryl rings differently substituted at *para* positions (Figure 1). These aryl rings confer equal steric requirements but different electronic requirements at both ends of the allylic system. Complexes **4**, with Ar^1 = 4-ClPh or 4-MeOPh and Ar^2 = 4-NO_2Ph, were studied,

Table 1. ^{13}C NMR Chemical Shifts in δ Units ($CDCl_3$) of Allyl Carbon Atoms in Compounds 8a−f

8	X	Y	δ(C-1)	δ(C-2)	δ(C-3)
8a	NO_2	H	84.70	113.11	93.95
8b	Cl	H	88.17	111.78	91.14
8c	H	H	90.10	111.60	90.10
8d	Me	H	90.72	111.04	89.54
8e	MeO	H	91.45	110.32	88.90
8f	Cl	NO_2	91.84	113.75	85.41

and the results indicated that the nucleophilic attacks occur preferentially at the terminus remote from the most electron-withdrawing group.[17] Previous work on systems involving cations of type **4** was not conclusive[18] with regard to the regioselectivity problem as discussed in our previous paper.[17] We now have prepared (1,2-bis(diphenylphosphino)ethane)(η^3-1,3-diarylallyl)palladium tetrafluoroborates, **8** (Scheme 1), and fully assigned their ^{13}C NMR spectra. We find that the ^{13}C NMR chemical shifts of C-1 and C-3 at the allylic moiety and, indirectly, the σ_p Hammett constants of the substituents at the aryl rings are correct indicators to anticipate the site of attack by soft nucleophiles.

Complexes **8** were prepared by standard methods as indicated in Scheme 1. Allyl chlorides **5**, prepared from the corresponding alcohols, were transformed into the bis(μ-chloro)bis(1,3-diaryl-η^3-allyl)dipalladium **7a−d,f** by treatment with $Pd_2(dba)_3 \cdot HCCl_3$ in benzene. Since complex **7e** could not be prepared by this method, we adopted and adapted a different procedure described by Bosnich and co-workers.[19] Thus, **7e** was prepared by reaction of alcohol **6** with Pd(0) species, aqueous HCl and LiCl as indicated in Scheme 1. Treatment of compounds **7** with silver tetrafluoroborate and then with 1,2-bis(diphenylphosphino)ethane in acetone afforded cationic complexes **8a−f**.

The ^{13}C NMR data for the allylic part of the cationic complexes **8** are given in Table 1. C-1 and C-3 have different responses to the electronic character of the group X. Thus, the chemical shift of C-1 is displaced

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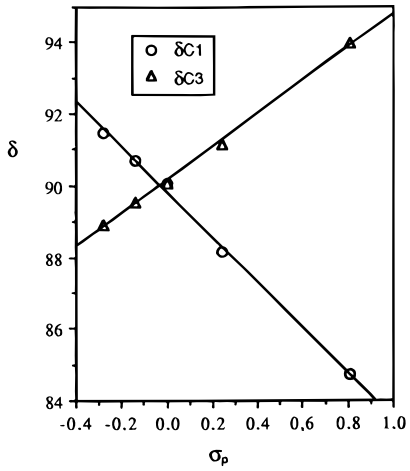

Figure 2. Plot of ^{13}C NMR chemical shifts of C-1 and C-3 vs σ_p for compounds **8a**−**e**.

at higher field by electron-withdrawing substituents, whereas the chemical shifts of C-2 and C-3 are displaced at lower fields by the same substituents. Moreover, for Y = H (compounds **8a**−**e**) $\Delta\delta$ for C-1 and for C-3 correlate well with the σ_p substituent constants ($\Delta\delta$(C-1) = − 0.28 − 6.32σ_p (r = 0.998, sd = 0.196) and $\Delta\delta$-(C-3) = 0.04 + 4.63σ_p (r = 0.999, sd = 0.088)). Similar correlations with σ_p^+ are much worse for these two carbon atoms. Figure 2 represents plots of δ vs σ_p for C-1 and C-3. On the contrary, $\Delta\delta$ for C-2 correlates much better with σ_p^+ ($\Delta\delta$(C-2) = 0.04 + 1.78σ_p^+ (r = 0.998, sd = 0.072)). In spite of theoretical limitations the correlation of differences in chemical shifts with Hammett substituent constants has been proposed as an experimental tool to determine the distribution of the positive charge in (η^3-allyl)palladium cations, good correlations with σ_p^+ rather than with σ_p at a given atom being interpreted as an indication of the presence of a substantial density of positive charge on it.[16c,d] The correlation data, together with the much lower field chemical shifts of the signals of the C-2 carbon atoms (Table 1), point to a concentration of positive charge at C-2. In fact palladium-catalyzed attacks at C-2 by hard nucleophiles to afford cyclopropyl derivatives is well precedented for substituted allyl systems in general[20] and for the 1,3-diphenyl system in particular.[20c,e] However, soft nucleophiles attack at the terminal carbon atoms of the allylic system when the palladium is stabilized by phosphines.[20e]

It is reasonable to assume that both triphenylphosphine or 1,2-bis(diphenylphosphino)ethane should lead to the same regioselection. However, since our previous experiments were performed with triphenylphosphine and with the nitro group as the common aryl substituent,[17] we have now studied the reaction of the acetylacetone conjugate base with a mixture of isomeric acetates **9** in the presence of 1,2-bis(diphenylphosphino)-ethane. This reaction is supposed to occur through the cation of salt **8e**. The results (Scheme 2) show that compounds **10a** and **11a**, arising from attack at C-1, proximal to the phenyl ring substituted with the most electron-donating methoxy group, are predominant to an extent of 69% with respect to isomers **10b** and **11b**, in agreement with our hypothesis. A blank experiment in the absence of the catalytic system showed only possible traces of reaction after a much extended refluxing time (47 h).

Assignment of structures to isomers **10** was based on the positive NOE between the olefinic proton −CHCH=C*H*− and aromatic *ortho* protons of the phenyl ring (C_6H_5) observed in the major isomer, therefore formulated **10a**, and the positive NOE between the olefinic proton −C*H*=CHCH− and aromatic protons MeOCCHC*H*− observed in the minor isomer, therefore formulated **10b**. Similarly, for isomers **11** a positive NOE was observed between the CH_2 protons and the aromatic *ortho* protons of the phenyl ring (C_6H_5) in the major isomer formulated **11a** and between the CH_2 protons and the aromatic protons MeOCCHC*H*− for the minor isomer **11b**.

In summary, ^{13}C NMR chemical shifts of the isolated salts **8** give good support to understand the regioselectivity of nucleophilic attacks of stabilized carbanions on (η^3-1,3-diarylallyl)palladium cations when steric effects cancel out. The different response of chemical shifts for C-1 and C-3 to the electronic character of the *para* substituent is not intuitively clear, but it has precedents.[16c,d]

Experimental Section

NMR Experiments. The complete signal assignments for products **8**, **10**, and **11** were made on a 400 MHz machine, by concerted use of several gradient-enhanced experiments such as 2D COSY,[21] $^1H-^{13}C$ 2D HMQC,[22] and $^1H-^{13}C$ 2D HMBC.[22,23] Required NOE data were extracted from phase-cycled 2D NOESY spectra[24] or from gradient-enhanced 1D ROESY (GROESY) experiments.[25] Full technical details will be published elsewhere. Proton and carbon chemical shifts are referenced to the $CDCl_3$ signals at 7.24 and 77.0 ppm, respectively. Phosphorus chemical shifts are referenced to the signal of phosphoric acid.

Substituent Constants. Substituent constant values for correlations were taken from ref 26.

Bis(μ-chloro)bis(1-(4-nitrophenyl)-3-phenyl-η^3-allyl)dipalladium, 7a. General Method. A degassed solution of 3-chloro-3-phenyl-1-(4-nitrophenyl)-1-propene and its allylic isomer, **5a** (0.075 g, 0.28 mmol), in benzene (10 mL) was added under inert atmosphere to a degassed suspension of $Pd_2(dba)_3$·$HCCl_3$ (0.100 g, 0.10 mmol) in benzene (10 mL). The mixture was magnetically stirred at room temperature for 52 h. The formed solid was filtered out, washed throughly with benzene, and dried to afford **7a** (0.071 g, 97%): Mp 310 °C (d); IR (KBr) 1597, 1518, 1488, 1343, 690 cm^{-1}; ^1H NMR (250 MHz, C_2D_6SO) δ 5.22 (d, J = 11.0 Hz, 1H), 5.36 (d, J = 12.1 Hz, 1H), 7.12 (t, J ca. 12 Hz, 1H), 7.24−7.45 (m, 3H), 7.75 (d, J = 7.7 Hz, 2H), 7.95 (d, J = 8.6 Hz, 2H), 8.15 (d, J = 8.6 Hz, 2H); ^{13}C NMR (62.9 MHz, C_2D_6SO) δ 79.50, 85.15, 108.80, 123.45, 128.08,

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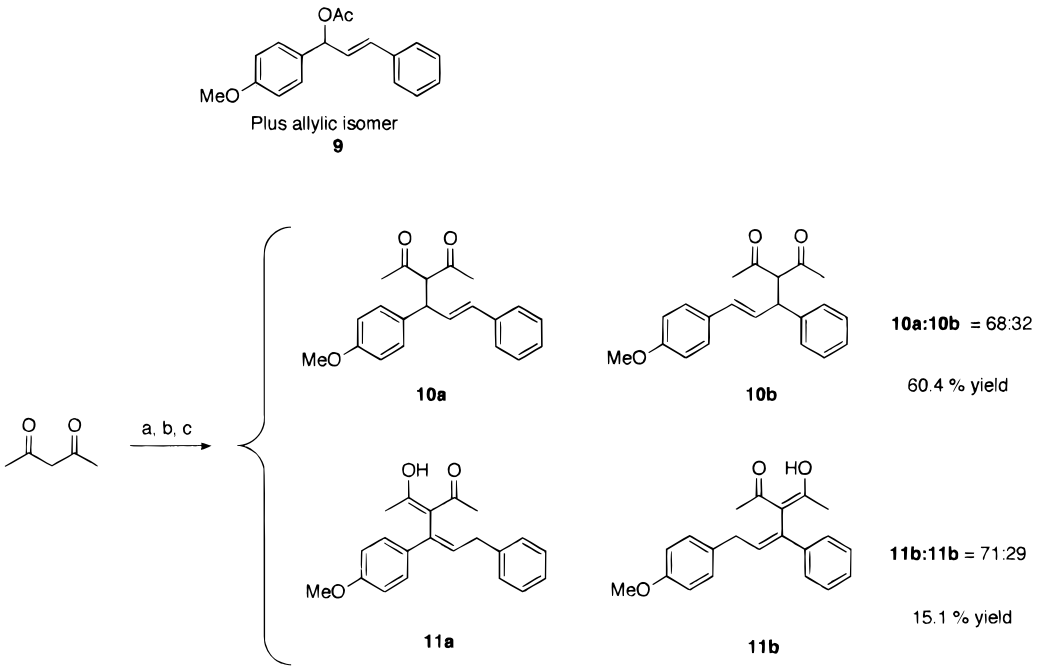
Scheme 2[a]



[a] Key: (a) HNa, THF; (b) $Pd(dba)_n$ (n = 1.5−2), 1,2-bis(diphenylphosphino)ethane; (c) **9**, refluxing THF.

128.47, 128.74, 129.22, 136.56, 145.23, 146.06. Anal. Calcd for $C_{30}H_{24}Cl_2N_2O_4Pd_2$: C, 47.41; H, 3.18; N, 3.69. Found: C, 47.10; H, 3.14; N, 3.39.

Bis(μ-chloro)bis(1-(4-chlorophenyl)-3-phenyl-η³-allyl)-dipalladium, 7b. This compound was obtained in 80% yield: Mp 222−226 °C; IR (KBr) 1596, 1488, 822, 753, 689 cm^{-1}; ^1H NMR (250 MHz, C_2D_6SO) δ 5.22 (d, J = 11.3 Hz, 2H), 6.97 (t, J ca 11 Hz, 1H), 7.38 (s, 5H), 7.74 (s, 4H); ^{13}C NMR (62.9 MHz, C_2D_6SO) δ 82.30, 83.72, 107.77, 128.57, 128.75, 128.87, 129.03, 130.41, 132.70, 136.63, 137.36. Anal. Calcd for $C_{30}H_{24}Cl_4Pd_2$: C, 48.75; H, 3.27. Found: C, 48.65; H, 3.29.

Bis(μ-chloro)bis(1,3-diphenyl-η³-allyl)dipalladium, 7c. It was obtained in 87% yield: Mp 208−210 °C (lit.[27] mp 230−235 °C); IR (KBr) 1521, 1488, 1459, 754, 693 cm^{-1}; ^1H NMR (250 MHz, C_2D_6SO) δ 5.25 (d, J = 11.6 Hz, 2H), 6.98 (t, J = 11.6 Hz, 1H), 7.32−7.48 (m, 6H), 7.74 (dd, J = 6.2 and 2.1, 4H) (this spectrum is coincident with that described in the literature);[28] ^{13}C NMR (62.9 MHz, C_2D_6SO) δ 83.60, 107.50, 128.40, 128.69, 128.92, 137.42.

Bis(μ-chloro)bis(1-(4-methylphenyl)-3-phenyl-η³-allyl)-dipalladium, 7d. This compound was obtained in ca. 100% yield: mp 224 °C; IR (KBr) 1511, 1492, 811, 755, 689 cm^{-1}; ^1H NMR (250 MHz, C_2D_6SO) δ 3.32 (s, 3H), 5.20 (d, J = 12.2 Hz, 1H), 5.25 (d, J = 12.2 Hz, 1H), 6.91 (t, J ca 12.2 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.28−7.45 (m, 3H), 7.65 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H); ^{13}C NMR (62.9 MHz, C_2D_6SO) δ 21.26, 83.17, 84.34, 107.02, 128.34, 128.69, 128.93, 129.64, 134.43, 137.58, 138.11. Anal. Calcd for $C_{32}H_{30}Cl_2Pd_2$: C, 55.04; H, 4.33. Found: C, 54.96; H, 4.33.

Bis(μ-chloro)bis(1-(4-chlorophenyl)-3-(4-nitrophenyl)-η³-allyl)dipalladium, 7f. This compound was obtained in 60% yield: mp 295−297 °C (lit.[17] mp 298−300 °C); IR (KBr) 1595, 1511, 1342 cm^{-1}; ^1H NMR (250 MHz, C_2D_6SO) δ 5.22 (d, J = 12.1 Hz, 1H), 5.36 (d, J = 12.1 Hz, 1H), 7.13 (t, J = 12.1 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 8.00 (d, J = 8.0 Hz, 2H), 8.19 (d, J = 8.0 Hz, 2H); ^{13}C NMR (62.9 MHz, C_2D_6SO) δ 79.97, 83.96, 109.35, 123.91, 129.03, 129.64, 130.56, 133.14, 136.16, 145.54, 146.50.

Bis(μ-chloro)bis(1-(4-methoxyphenyl-3-phenyl-η³-allyl-)dipalladium, 7e. A degassed solution of 3-(4-methoxyphenyl)-1-phenyl-2-propen-1-ol, **6** (0.600 g, 2.52 mmol), in THF (3.5 mL) was added to a degassed mixture of $Pd(dba)_n$ ($1.5 < n < 2$) (0.483 g, 0.84−1.05 mmol), lithium chloride (0.183 g, 4.32 mmol), water (1 mL), THF (1.6 mL), and ethanol (2 mL). Then 12 N HCl (0.357 mL) was added to the dark suspension so formed. The color immediately changed to greenish. The mixture was magnetically stirred at room temperature for 3.5 h. The precipitate (0.314 g) was filtered out, washed with benzene, and dried under phosphorus pentoxide: Mp 211−214 °C; IR (KBr) 1606, 1510, 1491, 1253, 1174 cm^{-1}; ^1H NMR (250 MHz, C_2D_6SO) δ 3.77 (s, 3H), 5.13 (d, J = 11.7 Hz, 1H), 5.30 (d, J = 12.1, 1H), 6.85 (t, J ca 12 Hz, 1H), 6.92 (m, 2H), 7.35 (m, 3H), 7.70 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 7.3 Hz, 2H); ^{13}C NMR (62.9 MHz, C_2D_6SO) δ 55.37, 82.34, 86.02, 106.06, 114.50, 128.20, 128.62, 128.88, 129.37, 130.22, 137.72, 159.67. No satisfactory elemental analysis could be obtained.

(1,2-Bis(diphenylphosphino)ethane)(η³-1-(4-nitrophenyl)-3-phenylallyl)palladium Tetrafluoroborate, 8a. General Method. A degassed solution of **7a** (0.111 g, 0.15 mmol) in acetone (6 mL) was added under inert atmosphere to a magnetically stirred and degassed solution of silver tetrafluoroborate (0.057 g, 0.29 mmol) in acetone (10 mL). The mixture was magnetically stirred at room temperature for 1.75 h, and the formed precipitate was filtered off. To the yellow transparent filtrate was added a solution of 1,2-bis(diphenylphosphino)ethane (0.116 g, 0.29 mmol) in degassed acetone (6 mL). The mixture turned brown, and it was magnetically stirred for 24 h. The solvent was evaporated, and the residue was treated with diethyl ether to afford an insoluble crop of **8a** (0.188 g, 78% yield) which was further purified by digesting again in diethyl ether. Data for compound **8a**: Mp 117−119 °C; IR (KBr) 1594, 1514, 1436, 1337, 1055, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.05−2.70 (m, 4H), 5.53 (m, 1H), 5.64 (m, 1H), 6.70 (d, J = 7.3 Hz, 2H), 6.77 (t, J ca. 12.7 Hz, 1H), 6.85 (dd, J = 8.3 and 1.6 Hz, 2H), 6.90 (m, 2H), 6.98−7.05 (m, 3H), 7.08 (t, J = 7.3 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 7.23 (t, J = 7.3 Hz, 2H), 7.24 (m, 1H), 7.36−7.53 (m, 6H), 7.55−7.65 (m, 6H), 7.68 (dd, J = 7.3 and 1.6 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 27.80 (dd, J = 31.4 and 14.8 Hz), 28.88 (dd, J = 32.4 and 14.8 Hz), 84.70 (dd, J = 25.9 and 6.5 Hz), 93.95 (dd, J = 24.1 and 6.5), 113.11 (t, J = 7.4 Hz), 123.97, 125.50−134.50,

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135.46 (dd, J = 25.7 and 11.0 Hz), 144.26 (dd, J = 25.7 and 11.0 Hz), 145.61 (t, J = 11.0 Hz); ^{31}P NMR (162.0 MHz, $CDCl_3$) δ 47.74 (d, J_{PP} = 50.4 Hz), 50.26 (d, J_{PP} = 50.4 Hz). Anal. Calcd for $C_{41}H_{36}BF_4NO_2P_2Pd$: C, 59.34; H, 4.37; N, 1.69. Found: C, 59.98; H, 4.67; N, 2.02.

(1,2-Bis(diphenylphosphino)ethane)(η^3-1-(4-chlorophenyl)-3-phenylallyl)palladium Tetrafluoroborate, 8b. This compound was obtained in 95% yield: mp 212 °C (d); IR (KBr) 1436, 1055, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05−2.62 (m, 4H), 5.50 (t, J ca. 12.1 Hz, 2H), 6.58 (t, J ca. 12.6, 1H), 6.73 (dd, J = 8.1 and 1.0 Hz, 2H), 6.79 (d, J = 7.2 Hz, 2H), 6.83 (d, J = 8.1 Hz, 2H), 6.92−6.98 (m, 4H), 7.02−7.07 (m, 3H), 7.15−7.22 (m, 4H), 7.36−7.41 (m, 4H), 7.50−7.60 (m, 7H), 7.60 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 27.96−28.72 (m, 2C), 88.17 (dd, J = 26.8 and 6.5 Hz), 91.14 (dd, J = 24.1 and 6.5 Hz), 111.78 (t, J = 7.4 Hz), 126.60−133.84; ^{31}P NMR (162.0 MHz, $CDCl_3$) δ 46.17 (d, J_{PP} = 48.6 Hz), 47.70 (dd, J_{PP} = 48.6 Hz). Anal. Calcd for $C_{41}H_{36}BClF_4P_2Pd$: C, 60.10; H, 4.43. Found: C, 59.88; H, 4.46.

(1,2-Bis(diphenylphosphino)ethane)(η^3-1,3-diphenylallyl)palladium Tetrafluoroborate, 8c. This compound was obtained in 71% yield: Mp 203−205 °C; IR (KBr) 1489, 1052, 690 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.43 (m, 4H), 5.49 (dt, J ca. 13.5 and 6.6 Hz, 2H), 6.63 (t, J ca. 12.8 Hz, 1H), 6.70−7.60 (m, 30H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 27.96 (t, J = 23.1 Hz, 2C), 90.10 (t, J = 15.7 Hz, 2C), 111.60 (t, J = 7.40 Hz, 1C), 126.33, 126.67−126.85, 126.99, 127.36 (t, J = 2.8 Hz), 127.64, 127.96, 128.30, 128.69 (t, J = 1.9 Hz), 129.24 (t, J = 4.6 Hz), 129.76 (t, J = 5.6 Hz), 131.08, 131.61, 133.30, (t, J = 6.5 Hz), 136.32 (t, J = 4.6 Hz); ^{31}P NMR (162.0 MHz, $CDCl_3$) δ 47.09 (s, 2P). Anal. Calcd for $C_{41}H_{37}BF_4P_2Pd$: C, 62.74; H, 4.75. Found: C, 62.44; H, 4.84.

(1,2-Bis(diphenylphosphino)ethane)(η^3-1-(4-methylphenyl)-3-phenylallyl)palladium Tetrafluoroborate, 8d. This compound was obtained in 92% yield: mp 213−215 °C; IR (KBr) 1559, 1053, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 3H), 2.21−2.84 (m, 4H), 5.40 (m, 1H), 5.49 (m, 1H), 6.53 (t, J = 12.8 Hz, 1H), 6.69−6.78 (m, 6H), 6.90 (d, J = 7.9 Hz, 2H), 6.92 (d, J = 7.9 Hz, 2H), 6.77−7.05 (m, 3H), 7.11 (t, J = 7.9 Hz, 2H), 7.15 (t, J = 7.9 Hz, 2H), 7.29−7.40 (m, 4H), 7.42−7.56 (m, 8H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 21.20, 27.89 (dt, J = 23.1 and 2.8 Hz, 2C), 89.54 (t, J = 15.7 Hz), 90.72 (t, J = 15.7 Hz), 111.04 (t, J = 7.4 Hz), 126.55−126.87, 127.33, 128.69, 129.00−129.45, 129.66 (q, J = 5.6 Hz), 132.02 (d, J = 12.0 Hz), 131.45−131.80, 131.94, (d, J = 10.2 Hz), 133.08−133.52, 136.45 (t, J = 4.0 Hz), 137.58 (t, J = 2.8 Hz); ^{31}P NMR (162.0 MHz, $CDCl_3$) δ 46.21 (s, 2P). Anal. Calcd for $C_{42}H_{39}BF_4P_2Pd$: C, 63.14; H, 4.92. Found: C, 63.06; H, 4.92.

(1,2-Bis(diphenylphosphino)ethane)(η^3-1-(4-methoxyphenyl)-3-phenylallyl)palladium Tetrafluoroborate, 8e. It was obtained in 85% yield: Mp 192 °C (d); IR (KBr) 1513, 1436, 1055, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12−2.53 (m, 4H), 3.66 (s, 3H), 5.32 (m, 1H), 5.51 (m, 1H), 6.44 (d, J = 8.1 Hz, 2H), 6.50 (t, J = 12.8 Hz, 1H), 6.76 (m, 4H), 6.86−7.05 (m, 7H), 7.14 (m, 4H), 7.26−7.40 (m, 4H), 7.45−7.60 (m, 8H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 27.90 (dd, J = 26.8 and 16.7 Hz, 2C), 55.22, 88.90 (dd, J = 23.1 and 9.2 Hz), 91.45 (dd, J = 22.2 and 8.3), 110.32 (t, J = 7.4 Hz), 114.07, 126.76 (t, J = 3.7 Hz), 127.24, 128.10 (t, J = 3.7 Hz), 128.68, 129.13−129.77, 131.02 (dd, J = 7.4 and 1.9 Hz), 131.50−132.40, 133.31 (dd, J = 16.7 and 13.0), 136.46−136.61; ^{31}P NMR (162.0 MHz, $CDCl_3$) δ 45.49 (d, J_{PP} = 48.3 Hz), 46.08 (d, J_{PP} = 48.3 Hz). Anal. Calcd for $C_{42}H_{39}BF_4OP_2Pd$: C, 61.90; H, 4.82. Found: C, 61.69; H, 4.93.

(1,2-Bis(diphenylphosphino)ethane)(η^3-1-(4-chlorophenyl)-3-(4-nitrophenyl)allyl)palladium Tetrafluoroborate, 8f. This compound was obtained in 56% yield: mp 134−135 °C (lit.[17] mp 140 °C); IR (KBr) 1594, 1514, 1436, 1340, 1055, 691 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.20−2.72 (m, 4H), 5.43 (ddd, J = 12.8, 7.9 and 2.6 Hz, 1H), 5.55 (ddd. J = 12.8, 9.9 and 3.3 Hz, 1H), 6.82 (1H), 6.72−7.64 (m, 28H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 28.38 (dd, J = 31.4 and 14.8 Hz), 28.90 (dd, J = 31.4 and 14.8 Hz), 85.41 (dd, J = 25.0 and 7.4 Hz), 91.84 (dd, J = 23.1 and 7.4), 113.75 (t, J = 6.5 Hz), 124.06−134.45, 144.23 (dd, J = 5.6 and 2.8 Hz), 145.77 (t, J = 3.0 Hz); ^{31}P NMR (162.0 MHz, $CDCl_3$) δ 47.62 (d, J = 50.6 Hz), 48.82 (d, J = 50.6 Hz).

Pd-Catalyzed Reaction of Pentane-2,4-dione with Acetates 9. Pentane-2,4-dione (0.354 g, 3.54 mmol) and sodium hydride (0.259 g of 40% suspension, 4.25 mmol), washed with anhydrous THF, were mixed in anhydrous THF (25 mL) under inert atmosphere. To the above mixture were sequentially added a solution of $Pd(dba)_n$ (n = 1.5−2.0) (0.102 g, 0.177−0.223 mmol) and 1,2-bis(diphenylphosphino)ethane (0.141 g, 0.354 mmol) in THF (15 mL) and then a solution of a mixture of 3-(4-methoxyphenyl)-1-phenyl-2-propen-1-ol acetate and 1-(4-methoxyphenyl)-3-phenyl-2-propen-1-ol acetate, **9** (1.00 g, 3.54 mmol), in THF (15 mL). The mixture was refluxed for 10 h and evaporated to dryness. The residue was taken in diethyl ether and the ethereal solution was washed with aqueous ammonium chloride and with aqueous sodium chloride, dried, and evaporated. The residue was chromatographed through a silica gel column with hexanes−ethyl acetate (9:1) as eluent to afford first 0.172 g (15.1%) of a mixture of 3-(1-(4-methoxyphenyl)-3-phenyl-1-propenyl)-4-hydroxy-3-penten-2-one, **11a**, and 3-(3-(4-methoxyphenyl)-1-phenyl-1-propenyl)-4-hydroxy-3-penten-2-one, **11b**, in a ratio 71:29: Bp 250 °C/0.5 mmHg; IR (film) 1605, 1510, 1259, 1178, 1092, 1080, 1033, 827, 800, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) for **11a** δ 1.92 (s, 6H), 3.43 (d, J = 7.3 Hz, 2H), 3.79 (s, 3H), 6.37 (t, J = 7.3 Hz, 1H), 6.84 (dd, J = 8.8 and 1.9 Hz, 2H), 7.1−7.4 (m, 7H), 16.65 (s, 1H), for **11b** δ 1.93 (s, 6H), 3.39 (d, J = 7.3 Hz, 2H), 3.78 (s, 3H), 6.45 (t, J = 7.3 Hz, 1H), 6.84 (dd, J = 8.8 and 1.9 Hz, 2H), 7.1−7.4 (m, 7H), 16.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for **11a** and **11b** δ 23.4 and 23.4 (CCH_3), 36.0 and 35.2 (CH_2), 55.29 (for both, OCH_3), 110.5 and 110.3 (C-3), 114.0 and 114.1 (CH_3OCCH), 125.8, 126.2, 127.0, 127.5, 128.0, 128.3 (CH_2CCH for **11a**), 128.6, 129.2 ($CH_3OCCHCH$ for **11b**), 129.4 and 131.8 (olefinic CCH), 132.9 ($CH_3OCCHCHC$ for **11a**), 135.5 and 135.7 (CH_2C aromatic), 140.1 and 140.4 (olefinic CCH), 159.2 (CH_3OC for **11a**), 191.5 (for both, C-2). Anal. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found (for the mixture): C, 78.31; H, 6.98. On further elution a mixture (0.690 g, 60.4%) of 3-(1-(4-methoxyphenyl)-3-phenyl-2-propenyl)pentane-2,4-dione, **10a**, and 3-(3-(4-methoxyphenyl)-1-phenyl-2-propenyl)pentane-2,4-dione, **10b**, in a ratio 69:31, was obtained: IR (film) 1718, 1694, 1610, 1513, 1497, 1358, 1251, 1178, 1153, 1031, 966, 830, 822, 742, 699, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) for **10a** δ 1.95 (s, 3H), 2.25 (s, 3H), 3.75 (s, 3H), 4.22−4.30 (m, 2H), 6.17 (dd, J = 15.7 and 4.8, 1H), 6.39 (d, J = 15.7 Hz, 1H), 6.85 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.30−7.45 (m, 5H), for **10b** δ 1.93 (s, 3H), 2.25 (s, 3H), 3.80 (s, 3H), 4.22−4.30 (m, 2H), 6.04 (ddd, J = 15.7, 6.2, and 1.5, 1H), 6.36 (d, J = 15.7 Hz, 1H), 6.80 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.30−7.45 (m, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) for the mixture δ 29.6 and 29.8, 48.2 and 49.1, 55.0 and 55.1, 74.4 and 74.5, 113.8 and 114.2, 126.1, 126.9, 127.0, 127.5, 127.7, 128.3, 128.8, 129.4, 130.9, 131.2, 131.9, 136.5, 140.2, 158.5 and 159.1, 202.7 and 202.8. Anal. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found (for the mixture): C, 78.24; H, 6.94.

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Supporting Information Available: IR, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra of compounds **8** (20 pages). Ordering information is given on any current masthead page.

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