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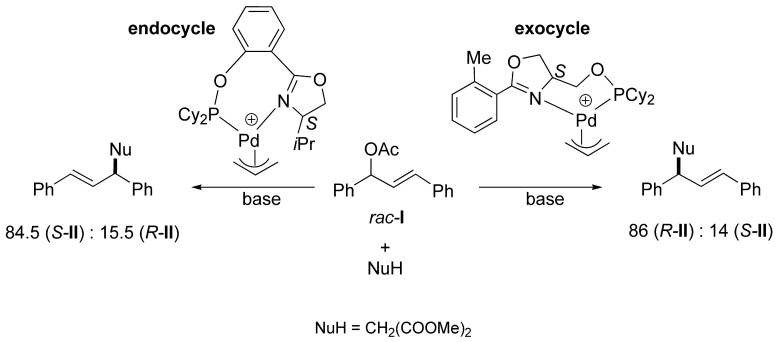

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Exo- and Endocyclic Oxazolinyl−Phosphane Palladium Complexes: Catalytic Behavior in Allylic Alkylation Processes

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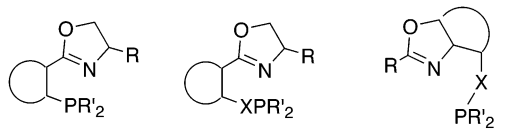
The new bidentate chiral N,P-donor oxazolinyl−phosphane ligands **7**−**15** are described. Upon coordination to the palladium metal, ligands **7**−**12** gave endocyclic oxazolinyl−phosphane complexes having seven-membered rings, while ligands **13**−**15** afforded exocyclic oxazolinyl−phosphinite complexes with six-membered rings, depending on the relative C═N oxazoline bond and metal ring position. Ionic palladium(II) complexes containing N,P-bidentate ligands and allyl groups (η^3-C_3H_5 for **16**−**22** and η^3-1,3-Ph_2-C_3H_3 for **23**−**26**) were prepared and fully characterized. X-ray structures were determined for complexes **18** and **19**. Pd catalytic systems containing ligands **7**−**15** were tested in the asymmetric allylic alkylation of the racemic substrates *rac*-3-acetoxy-1,3-diphenyl-1-propene (**I**) and *rac*-3-acetoxy-1-cyclohexene (**III**). The endocyclic systems show better activites and selectivites (ee values up to 82%) than the exocyclic ones (ee values up to 72%) for substrate **I**. In particular, palladium endocyclic oxazoline−phosphinite systems containing the PCy_2 group (**20**, **21**) give the highest activities, but the best enantioselectivities were observed for those containing PPh_2 (**18**, **19**).

Introduction

In the last two decades, optically pure oxazoline ligands have been largely applied in enantioselective catalytic processes.[1] In particular, chiral N,P-bidentate ligands have been used as chiral auxiliaries, inducing excellent selectivities, especially in Pd-catalyzed allylic substitution processes.[2a,b] Depending on the relative position of the two functional groups, phosphane and oxazoline, three types of ligands could be considered (Chart 1).

Type A phosphino−oxazolines (2-aryl, 2-ferrocenyl, or 2-alkyl substituent, Chart 1) have been tested in several metal-catalyzed organic processes, giving excellent results, mainly in enantioselectivity.[2a,b] From the point of view of their coordination chemistry, these compounds usually act as bidentate ligands, giving six-membered chelates.[2c,d] However, structurally related phosphito,[3] phosphinito,[4] and aromatic phosphane[5] derivatives (B), which can lead to the formation of seven-membered metallic rings, have been less applied in catalysis. In contrast, there are many recent works in the literature where type C phosphino−[6] and phosphinito−oxazolines are used with an open[7] or cyclic backbone.[8] This arrangement leads to the formation of a six-membered

Chart 1



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† Universitat de Barcelona.
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Publication on Web 05/20/2004

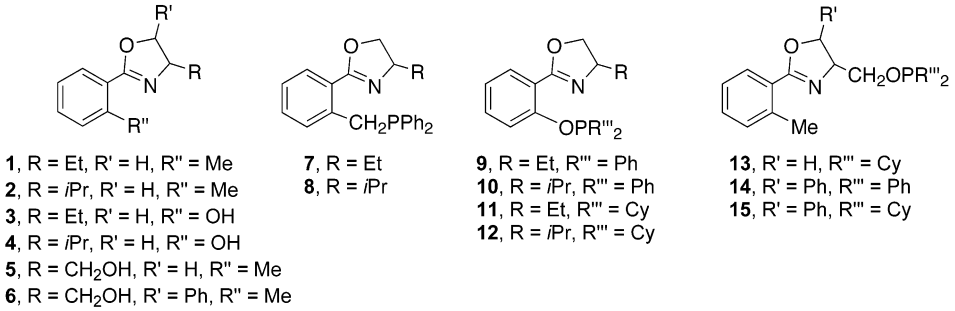
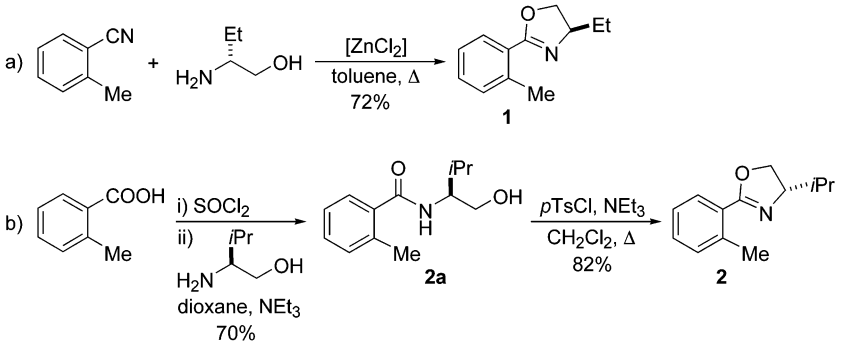


Figure 1. Free phosphane−oxazolines (**1**−**6**), oxazolinyl−phosphines (**7** and **8**), and oxazolinyl−phosphinites (**9**−**15**).

Scheme 1



chelate ring upon coordination to the metal, analogously to A ligands. However, now the imine double bond is arranged in an exo way in relation to the position of the double bond in the metallic cycle, unlike A and B ligands, where the arrangement is endo. However, structural studies concerning exocyclic palladium complexes containing type C ligands are very scarce in the literature.[3]

The study of new modular N,P-donor ligands (phosphines **7** and **8** and phosphinites **9**−**15**) in the Pd-catalyzed allylic alkylation reactions follows our research in enantioselective catalysis with chiral ligands containing an oxazoline moiety.[9] We plan to evaluate the influence of the nature of the palladium κ^2N,P chelate: endocyclic (**7**−**12**) and exocyclic (**13**−**15**) in this organic reaction. Moreover, we also studied the nature of stereocenter substituents (iPr, Et) and phosphane group (PPh_2, PCy_2) (Figure 1). Concerning the organometallic chemistry, a structural work related to the palladium allyl precursors (**16**−**22**) and intermediates (**23**−**26**), both in solution (NMR studies) and the solid state (X-ray diffraction), was carried out. Theoretical modeling of Pd(II) intermediates (at the semiempirical PM3(tm) level) was also analyzed in order to justify the stereochemistry observed in the catalytic processes.

Synthesis of Ligands

Oxazolinyl−phosphane ligands **7**−**15** were synthesized from the corresponding oxazolines **1**−**6**, which were prepared by following previously described methodologies with some modifications.[10] Ligands **1** and **6** were prepared in a one-step synthesis by two different synthetic procedures. **1** was isolated in good yield by Zn-catalyzed condensation of 2-methylbenzonitrile and (*R*)-2-aminobutanol (Scheme 1a),[11] while **6** was efficiently obtained by basic condensation of 2-methylbenzonitrile and the appropriate amino alcohol.[12] Zn-catalyzed condensation gave less than 10% yield of **6**. **2** was easily prepared in good yield in a two-step synthesis, via amide formation from 2-methylbenzoic acid and L-valinol, followed by cyclization under basic conditions (Scheme 1b).[13]

For synthesis of the *o*-tolyloxazoline **5**, the chiral starting material is the amino acid (*S*)-serine, whose direct reduction leads to the achiral amino alcohol. The analogous phenyloxazoline was prepared from the corresponding protected amino alcohol with minimum racemization,[14] but this procedure failed for the analogous *o*-tolyl derivative. We followed the five-step synthesis shown in Scheme 2, based on the methodology described by Meyers.[15] We prepared the amide **5a** from the serine methyl ester hydrochloride[16] and the 2-methylbenzoic acid chloride. The alcohol group was protected with *tert*-butyldimethylsilyl chloride (TBDMSCl), giving **5b**. Its ester group was then reduced with $NaBH_4$ to lead to the formation of **5c**. This amide was cyclized by treatment with *p*-tosyl chloride under basic conditions, affording the oxazoline **5d**.[17] Ligand **5** was isolated by

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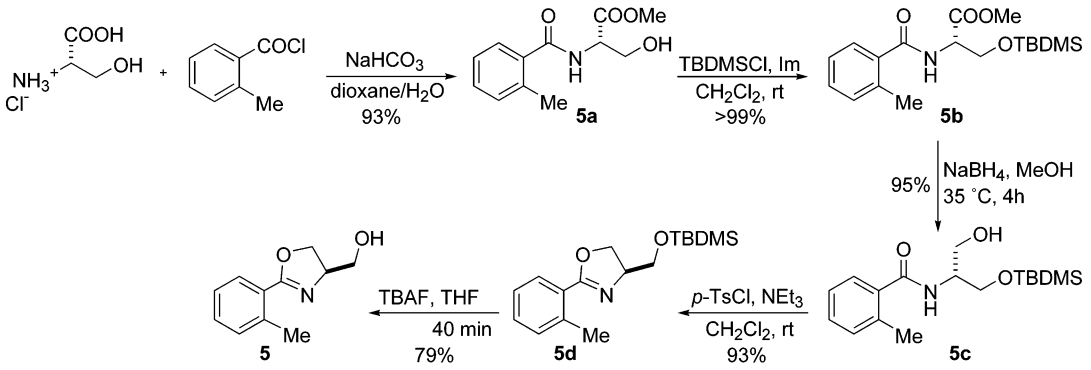
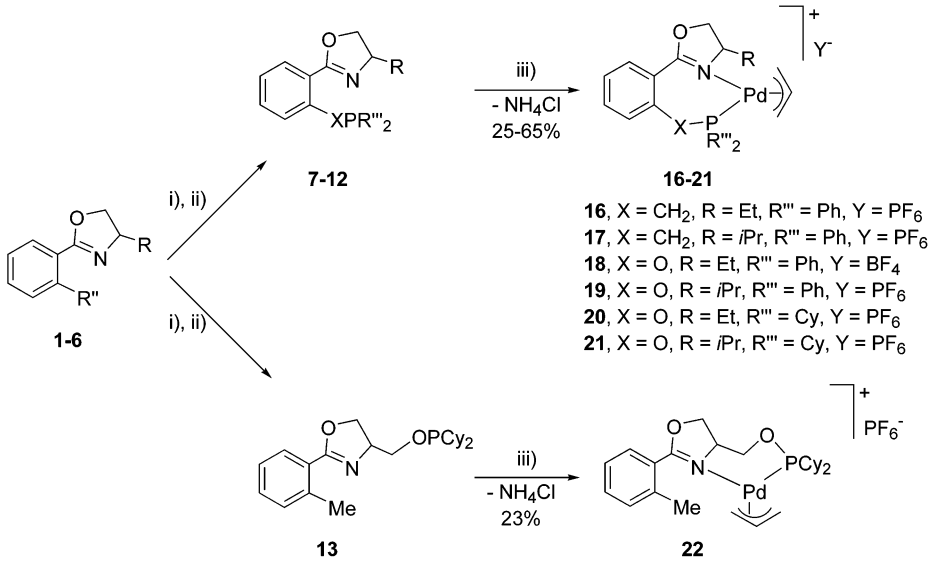
Scheme 2



Scheme 3[a]

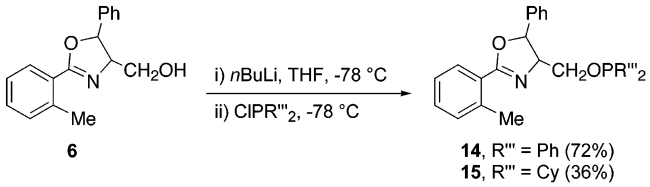


[a] Conditions: (i) *n*BuLi, THF, −78 °C to room temperature; (ii) ClPR‴$_2$, −78 °C to room temperature; (iii) [Pd(C_3H_5)Cl]$_2$ (for **18**, [Pd(C_3H_5)(cod)]BF_4), NH_4PF_6, CH_2Cl_2, room temperature.

desilylation using TBAF, in 64% overall yield. While our work was still in progress, Richards and co-workers reported a similar procedure for analogous ligands. In their case, however, the synthetic route leads to the (*S*)-oxazoline because the cyclization is carried out with the ester amide (second step in our sequence; see Scheme 2).[18] However, following the methodology here described from the (*S*)-serine, the oxazoline (*R*)-**5** is obtained because the configuration inversion occurred in the reduction of ester **5b**.

Phosphine (**7** and **8**) and phosphinite (**9**−**15**) derivatives were prepared by following the two-step procedure described previously (Scheme 3):[4,6b,c] (i) deprotonation of the methyl or hydroxy group by *n*BuLi at low temperature and (ii) addition of the appropriate chlorophosphine (ClPPh$_2$ or ClPCy$_2$). The reactions were monitored by ^{31}P NMR spectroscopy. The purification of these ligands was achieved by formation of their π-allyl complexes (**16**−**22**, Scheme 3),[19] although ligands **14** and **15** were isolated and purified by flash chromatography (Al_2O_3, using ethyl acetate/hexane (4/1) as eluent) (Scheme 4).

Scheme 4



Palladium Allyl Complexes

Ionic palladium complexes containing the allyl (**16**−**22**) and 1,3-diphenylallyl group (**23**−**26**) were prepared from the corresponding standard palladium dimer and the appropriate chiral ligand, in the presence of ammonium hexafluorophosphate (Schemes 3 and 5), using CH_2Cl_2 or toluene as solvent, following the methodology previously described.[20] These compounds were obtained as monometallic complexes of the general formula [Pd(η^3-allyl)(L)]PF_6 (allyl = C_3H_5, 1,3-Ph$_2$-C_3H_3), where L acts as a κ^2N,P bidentate ligand.

Upon complexation to the metal, ligands **7**−**12** give endocyclic complexes of a seven-membered chelate ring,

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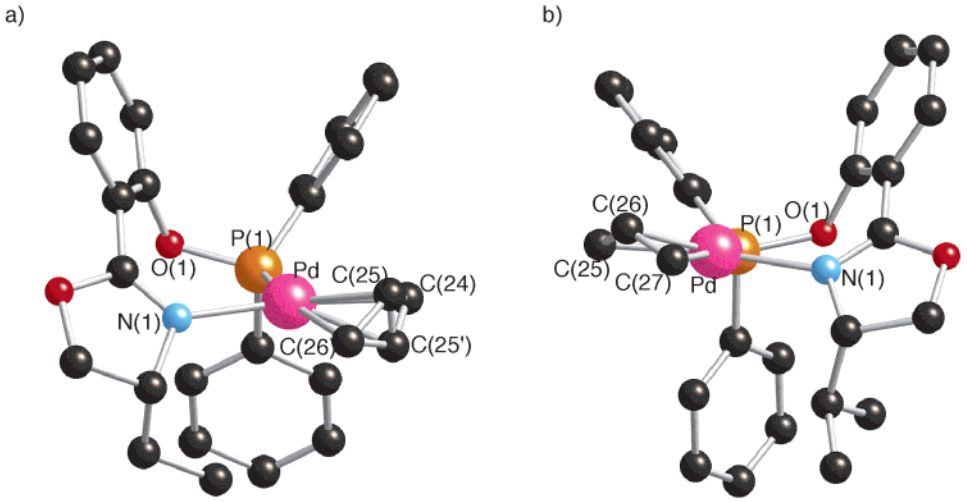
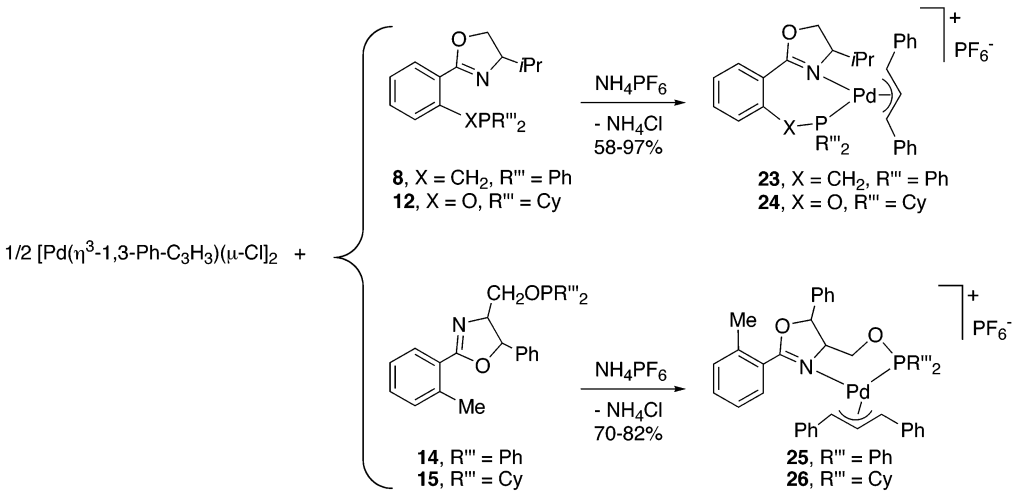


Figure 2. View of the molecular structures of (a) **18** and (b) **19**. Hydrogen atoms and tetrafluoroborate (for **18**) and hexafluorophosphate anions (for **19**) have been omitted for clarity.

Scheme 5



while **13**−**15** afford exocyclic complexes of a six-membered chelate, depending on the relative C═N oxazoline bond position and the metallacycle. Complexes **16**−**26** were fully characterized by the usual techniques. IR spectra showed strong signals at 1630−1640, 1080−1090, and 830−853 cm^{-1}, assigned to the C═N stretching of the oxazoline moiety, the P−O stretching of the phosphinite ligand, and P−F stretching of the PF_6 anion, respectively, all of them in similar positions to those observed for the free ligands. Positive FAB mass spectra exhibited, in all cases, the peak corresponding to the $[Pd(\eta^3\text{-allyl})(L)]^+$ fragment (allyl = C_3H_5, 1,3-Ph_2-C_3H_3).

X-ray Structures

Suitable monocrystals for X-ray diffraction measurements were obtained from dichloromethane solutions of **18** and **19** by slow diffusion of diethyl ether (Figure 2).

In both structures, the palladium atom shows a distorted-square-planar coordination (Table 1), bonded to one nitrogen, one phosphorus, and two terminal allylic carbon atoms, which are nearly coplanar (torsion angles N(1)−C(26)−C(24)−P(1) = 2.4° and N(1)−C(27)−C(25)−P(1) = 0.8° for **18** and **19**, respectively). The higher trans influence of the phosphinito moiety, as compared to that of the oxazoline group, is evidenced by the Pd−terminal allyl carbon distance being longer trans to the P than trans to the N atom (2.257 vs 2.099 Å and 2.269 vs 2.096 Å for **18** and **19**, respectively). For both complexes the metallacycle shows a pseudo-boat seven-membered arrangement, as observed previously for palladium complexes with phenyl-bridged bis(oxazoline) ligands.[21]

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 18 and 19 (with Esd's in Parentheses)

	18	**19**
Pd(1)−N(1)	2.099(2)	2.096(5)
Pd(1)−P(1)	2.2566(7)	2.2693(15)
Pd(1)−C(24)	2.105(3)	
Pd(1)−C(25)	2.180(4)	2.111(7)
Pd(1)−C(25′)	2.169(5)	
Pd(1)−C(26)	2.232(4)	2.132(7)
Pd(1)−C(27)		2.211(7)
N(1)−Pd(1)−P(1)	92.88(6)	92.03(13)
C(24)−Pd(1)−C(26)	66.96(15)	
C(25)−Pd(1)−C(27)		66.3(3)
N(1)−Pd(1)−C(26)	100.53(13)	
P(1)−Pd(1)−C(24)	99.40(10)	
N(1)−Pd(1)−C(27)		98.0(3)
P(1)−Pd(1)−C(25)		103.3(2)

Complex **18** crystallized as a mixture of exo and endo isomers, depending on the relative position of the central allylic carbon atom and the phenyl group of the backbone (carbon atom points in the same direction as the phenyl, or in the opposite direction, respectively), in the ratio 0.61/0.39, respectively. However, for **19** only the exo isomer crystallized.

NMR Studies

NMR spectroscopy allowed us to determine the structure of these complexes in solution. ^{31}P NMR spectra of most complexes show two signals, suggesting the presence of two isomers. Tables 2 and 3 collect NMR data for compounds **16**−**22** and **23**−**26**, respectively.

The phosphorus chemical shifts of complexes lie downfield as compared to those of the free ligand. The magnitude of the coordination shift, $\Delta\delta$ ($\Delta\delta = \delta$(complex) − δ(free ligand)), depends on the phosphapalladacycle size. For seven-membered rings (**16**−**21**, **23**, **24**), $\Delta\delta$ is in the range ca. 40−50 ppm, while for six-membered chelates (**22**, **25**, **26**) the range is ca. 5−20 ppm. The difference between ^{31}P chemical shifts of the two isomers of one complex is shorter for nonsubstituted allylic complexes (**16**−**22**) than for substituted allylic ones (**23**−**26**). For complexes **16**, **17**, **20**, and **22** only one signal was observed at room temperature, but at low temperature (273 K) two well-defined signals appeared. The ratio observed for the two isomers (major/minor) for nonsubstituted allyl complexes is around 60/40, without important changes in the temperature range studied (308−273 K). Substituted allylic complexes **23**−**26** are present in the ratios 70/30, 80/20, 55/45, and 75/25, respectively.

The best signal resolution observed for ^{1}H NMR experiments was at 273 K. Two sets of signals for each syn and anti proton are observed for each pair of isomers (major and minor) of **16**−**26**, due to the C_1 symmetry of the P−N ligands. From ^{1}H−^{13}C heterocorrelation experiments, we can unmistakably assign the chemical shifts of allylic protons. Therefore, the central allylic hydrogen appears at lower field than the terminal hydrogens, and allylic hydrogen atoms located on the carbon atom trans to phosphorus atom appear at lower fields than do those in the cis position (as also observed for similar compounds).[22] Chemical shifts of allylic protons for substituted allyl complexes (**23**, **24**) appear at lower field than for nonsubstituted related compounds (**17**, **21**), probably due to the presence of the allyl phenyl groups.

^{13}C chemical shifts for allylic carbon show that the central atom resonates at lower field than the terminal atoms and the carbon atom located in a position trans to phosphorus is more deshielded than the cis carbon, which is usually coupled to the phosphorus atom.

To elucidate the solution structure of these complexes and their dynamic behavior, 2D NOESY NMR experiments were carried out at 273 K. NOE contacts between allylic protons and the phosphinite−oxazoline ligand were not observed; therefore, a solution structure for major and minor isomers could not be proposed. However, interesting exchange signals between allylic protons were observed for the nonsubstituted allylic complexes (**16**−**18**, **20**, **22**). Exchange signals between syn and anti protons bonded to carbon in positions cis to the phosphorus were detected for major and minor isomers. In addition, exchange signals for allylic hydrogen trans to the phosphorus were observed between syn/syn and anti/anti protons for each isomer. In Scheme 6 one example of allyl exchange signals is shown for complex **22**. This behavior suggests the Pd−C bond opening in a position trans to the phosphorus atom, then rotation through a σ(Pd−C) bond cis to the P atom, and formation of the other π-allyl isomer. We note that this movement is observed for either seven-membered endocyclic (**16**−**18**, **20**) or six-membered exocyclic (**22**) complexes. For complexes **24**−**26**, containing a 1,3-diphenylallyl group, no exchange signals between allylic protons were observed at 273 K. Rotation through a σ-(Pd−C) bond cis to the phosphorus atom is hindered, presumably because of the bulky phenyl substituents in the allylic moiety.

Complexes containing substituted allyl groups can give rise to several isomers, depending on the position occupied by allyl phenyl groups (syn/syn, syn/anti, anti/anti); however, complexes **23**−**26** appear only as syn/syn isomers.

Pd-Catalyzed Allylic Alkylation

Asymmetric allylic alkylations of the racemic substrates *rac*-3-acetoxy-1,3-diphenyl-1-propene (**I**) and *rac*-3-acetoxy-1-cyclohexene (**III**) with dimethyl malonate under basic Trost conditions[23] were carried out using Pd catalytic systems containing ligands **7**−**15** (Scheme 7). The results are summarized in Tables 4 and 5.

We observe that catalytic systems containing the oxazolinyl−phosphines **7** and **8** are less selective than the analogous catalytic systems containing type A ligands (ee values up to 98.5% for model allylic alkylation),[24] which form six-membered palladium cycles, in contrast to the seven-membered chelates for complexes **16** and **17** (ee up to 78%; entry 2, Table 4). This loss of enantioselectivity can be associated with the more flexible cycle formed with ligands **7** and **8** and, consequently, less steric hindrance to enhance the electrodifferentiation between the two terminal allylic carbon atoms. For the related oxazolinyl−phosphinites, **9** and **10**, the selectivity is greater than for **7** and **8** (ee up to 82%; entry 4, Table 4). The π-acceptor nature of the phosphinito ligands (**9** and **10**) is higher than that for the related oxazolinyl−phosphines (**7** and **8**), which could explain the increase of the enantiomeric excess in the substitution product **II**. Concerning the phosphorus substituent effect, PPh_2 moiety containing ligands (**9** and **10**) are less active than the analogous ligands containing PCy_2 groups (**11** and **12**), although they are more selective (entries 3 and 4 vs 5 and 6, Table 4). This is probably due to the different basicities of the phosphines: more basic (−PCy_2) behavior leads to a minor electrodifferentiation between the terminal allylic carbons. Other effects, such as the capability of giving oxidative addition from the Pd(0) intermediate with the

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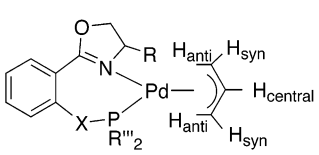
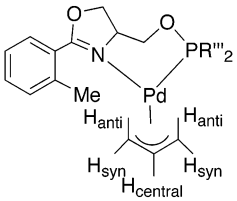
Table 2. Selected NMR Data[a] (δ in ppm, in $CDCl_3$) for Allylic Complexes 16−22





complex	central[b] [$C_{central}$]	syn [$C_{terminal}$]	anti	P[c]
16[d]				[−7.9]
major	5.63 (m; 6.5) [121.2]	5.08 (t; 6.0) 3.52 (bs) [81.9; 55.4]	3.62 (bs) 2.65 (d; 12.5)	39.13
minor	5.69 (bs) [121.1]	5.02 (bs) 3.55 (d; 3) [81.4; 55.4]	3.84 (bt; 9.5) 2.45 (d; 11.5)	38.62
17				[−8.5]
major	5.66 (m) [121.6]	5.15 (m) 4−3.4 [82.8; 55.7]	4−3.4 2.68 (d; 11.5)	38.14
minor	5.55 (m) [121.6]	5.04 (m) 4−3.4 [82.3; 53.9]	4−3.4 2.41 (d; 11.5)	37.97
18[d]				[113.5]
major	5.82 (m) [122.7]	5.22 (m) 3.65 (d,5) [82.6 (d; 30); 55.4]	3.81 (t; 12.5) 2.83 (d; 12)	152.49
minor	5.82 (m) [120.1]	5.17 (m) 3.72 (bs) [85.4; 53.4]	4.08 (t; 12.5) 2.74 (d; 12)	150.31
19				[110.4]
major	5.83 (m) [123.0]	5.19 (m) 3.59 (pd; 4.5) [83.1 (d; 32); 55.4]	3.74 (m) 2.84 (d; 12)	151.72
minor	5.83 (m) [120.4]	5.07 (m) 3.74 (m) [86.2 (d; 32); 53.2]	4.10 (m) 2.68 (d; 12)	149.96 (s)
20[e]				[143.1]
major	5.52 (bs) [121.7]	4.98 (bs) 3.43 (bs) [82; 50]	3.72 (bt) 2.62 (d; 5.2)	187.5[f]
minor	5.67 (bs) [118.8]	4.98 (bs) 3.62 (bs) [85; 48]	3.85 (bt) 2.42 (bd; 5.2)	*f*
21[e]				[142.4]
major	5.64 (bs) [124.7]	5.01 (bd; 15) 3.54 (bs) [82.6 (d; 32); 47.6]	3.78 (bs) 2.60 (bs)	190.0
minor	5.64(bs) [123.1]	5.01 (bd; 15) 3.58 (bs) [85.5 (d; 30); 46.4]	4.03(bs) 2.50(bs)	186.62
22				[147.5]
major	5.09 (m) [137.9]	3.42 (d; 6) 3.05 (pt; 5.5) [84 (d; 28); 47.77]	3.30 (m) 2.30 (t; 11)	153.35
minor	5.28 (m) [137.5]	3.50 (pt) 3.32 (d, 4.5) [83.25 (d; 27.8); 47.14]	2.70 (pq) 2.30 (t; 6)	153.25

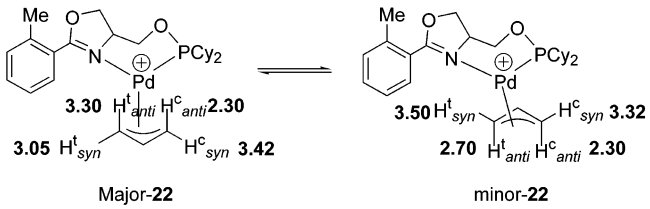
[a] ^1H NMR: 273 K, 500 MHz. ^{13}C NMR: 298 K, 100.56 MHz. $^{31}P\{^1H\}$ NMR: 273 K, 101.2 MHz. Multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad signal. Coupling constants are given in Hz and are shown in parentheses after the multiplicity. ^{13}C chemical shifts are given in brackets unless otherwise stated. [b] See the figure below the table title for atom labels. [c] ^{31}P chemical shifts for the free ligand are given in brackets. [d] Spectrum registered at 298 K. [e] The spectrum presents broad signals even at low temperature. [f] Unique signal at 298 K.

Table 3. Selected NMR Data (δ in ppm, in $CDCl_3$) for Allylic Complexes 23−26[a]

complex[b]	central[c] [$C_{central}$]	anti [$C_{terminal}$]	P[d]
23			[−8.5]
major (70)	6.7[e] [109.3]	5.63 (dd; 13.9) 4.23 (d; 11) [99.5 (d; 12.6); 71.7]	36.63
minor (30)	6.2[e] [110.4]	5.46 (t; 11.5) 5.37 (d; 12.5) [92.8; 77.8]	42.10
24			[142.4]
major (80)	6.59 (dd; 14,11) [112.6 (d; 7.0)]	5.74 (dd; 29,10) 4.47 (d; 11) [104.4 (d; 23); 62.2]	186.9
minor (20)	6.37 (t; 12.5) [112.1 (d; 5)]	5.58 (t; 11.5) 5.23 (d; 12) [95.7 (d; 25); 79.9]	189.37
25			[115.2]
major (55)	6.28−6.12 (m) [109.8]	6.39 (t; 11) 4.66 (d; 10) [103.4; 71.9]	132.26
minor (45)	6.28−6.12 (m) [11.3]	5.25 (d; 10) 4.71 (t; 12.5) [95.6; 72.21]	124.9
26			[149.32]
major (75)	6.36 (t; 12.5) [111.41 (d; 6.1)]	5.03 (d; 12) 4.77 (t; 12.5) [96.46 (d; 26.7); 73.67]	151.5
minor (25)	f	4.47 (d; 10)[g] [85.7; 104.5]	151.07

[a] ^1H NMR: 273 K, 500 MHz. ^{13}C NMR: 298 K, 100.56 MHz. $^{31}P\{^1H\}$ NMR: 273 K, 101.2 MHz. Multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad signal. Coupling constants are given in Hz and are shown in parentheses after the multiplicity. ^{13}C chemical shifts are given in brackets unless otherwise stated. [b] The ratio of isomers is given in parentheses. [c] See Table 2 for labeling. [d] ^{31}P chemical shifts for the free ligand are given in brackets. [e] Signal overlapped with aromatic protons. [f] Not observed. [g] Only one proton observed.

Scheme 6



Exchange signals observed:

3.42 ⟷ 2.30
2.30 ⟷ 3.32
3.30 ⟷ 2.70
3.05 ⟷ 3.50

substrate coordinated toward Pd(II) allyl species, can explain this different behavior. The product configuration is related to the stereochemistry at the oxazoline 4-position.

The catalytic systems containing type C palladium species (ligands **13**−**15**) are less active than the analogous type B ones (total conversion of substrate in 2.5−3 h vs 0.5−1.5 h; entries 7−9 versus entries 3−6); however, in both cases, good enantioselectivities are obtained (72 and 78%, entries 9 and 3, respectively). For the exocyclic palladium species, we observe the positive effect of the substituent on the 3-position of the oxazoline group (entry 7 versus entry 9). This is similar to what was previously observed with bis(oxazoline) palladium systems.[19] However, the exocyclic palladium

Scheme 7

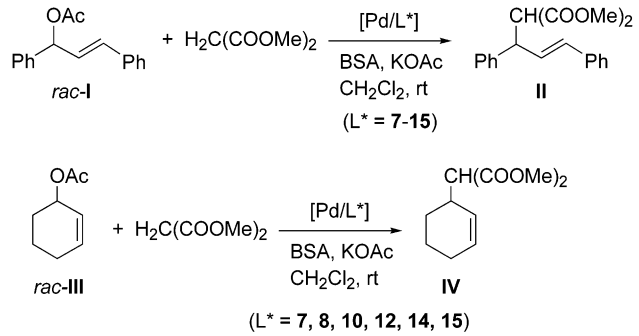


Table 4. Results of Asymmetric Allylic Alkylation of *rac*-3-Acetoxy-1,3-diphenyl-1-propene with Dimethyl Malonate[a]

entry	catalyst	time (h)	ee (%)[b]
1[c]	**16** (**7**)	1	59 (*R*)
2[c]	**17** (**8**)	1	78 (*S*)
3[c]	**18** (**9**)	1	78 (*R*)
4[c]	**19** (**10**)	1.5	82 (*S*)
5[c]	**20** (**11**)	0.5	44 (*R*)
6[c]	**21** (**12**)	0.5	69 (*S*)
7[c]	**22** (**13**)	3	58 (*R*)
8[d]	**14**	2.5	28 (*R*)
9[d]	**15**	2.5	72 (*R*)

[a] Results determined from duplicate experiments. [b] Determined by HPLC on a Chiralcel-OD column. The absolute configuration of II is given in parentheses, determined by optical rotation: Leutenegger, U.; Umbricht, G.; Fahrni, C.; Matt, P. V.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143. [c] Using complexes **16**−**22** as catalytic precursors. The corresponding ligand of the complex is given in the next column in parentheses. [d] Catalytic precursor generated in situ from $[PdCl(C_3H_5)]_2$ and the appropriate ligand (ratio Pd/L = 1/1.25, L = **14**, **15**).

Table 5. Results of Asymmetric Allylic Alkylation of *rac*-3-Acetoxy-1-cyclohexene with Dimethyl Malonate[a]

entry	L*	time (h)	ee (%)[b]
1[c]	**16** (**7**)	16	10 (*R*)
2[c]	**17** (**8**)	10	20 (*S*)
3[c]	**19** (**10**)	10	24 (*S*)
4[d]	**14**	3	0
5[d]	**15**	5	9 (*R*)

[a] Results determined from duplicate experiments. [b] Determined by GC. [c] Using complexes **16**, **17**, and **19** as catalytic precursors. The corresponding ligand of the complex is given in parentheses in the next column. [d] Catalytic precursor generated in situ from $[PdCl(C_3H_5)]_2$ and the appropriate ligand (ratio Pd/L = 1/1.25, L = **14**, **15**).

catalytic species containing a PPh_2 group ligand (ligand **14**) is less selective than **13** and **15**, which contain a PCy_2 moiety (entry 8 vs entries 7 and 9), probably due to the different steric hindrance. The product configuration is now related to the stereochemistry of the metallacycle, favoring in all cases the formation of (*R*)-**II** product.

We also analyzed the allylic alkylation for the cyclic substrate *rac*-3-acetoxy-1-cyclohexene (**III**), under the same conditions described above for the open acetate *rac*-**I**. The results are shown in Table 5. The catalytic systems are less active and selective in this process than the reaction with *rac*-**I**, achieving only 24% ee for **IV** when **19** is used as the catalytic precursor (entry 3, Table 5). This system also afforded the best enantiomeric excess for the alkylation of **II** (entry 4, Table 4). For type C catalytic species, only the catalytic system Pd/**15** induces a very low enantioselectivity (entries 5 and 6, Table 5). The absolute configuration of the substitution product, **IV**, follows the trend observed for **II** (see above). For both substrates, *rac*-**I** and *rac*-**III**, used in the studied allylic alkylation reactions, the absolute configuration of the substitution product is not related to the nature of the phosphane group (PCy_2 or PPh_2).

In conclusion, no good matching was produced between the experimental ratio of isomers for endocyclic and exocyclic **23**, **24**, **25**, or **26** with the enantiomeric excesses of the organic process, although the trend corresponds to the diastereomeric excess.

Modeling of Allyl Palladium Intermediates

We observed that, for ligands which afford endocyclic complexes (**7**−**12**), the stereochemistry of the Pd-catalyzed allylic alkylation depends on the stereochemistry of the oxazoline substituent. On the other hand, for ligands **13**−**15**, which upon coordination lead to the formation of exocyclic complexes, the substitution product always shows the *R* absolute configuration. Accepting that for soft nucleophiles the selectivity of the allylic substitution processes is governed by the external nucleophilic attack on the palladium(II) allyl intermediate species, we planned to carry out a theoretical study of the intermediate palladium complexes containing the 1,3-diphenylallyl group (by means of semiempirical PM3(tm) calculations), to justify the nature of the major species and the preference for nucleophilic attack to favor the formation of one of the two enantiomers (*R* or *S*) of the alkylated product, **II**.

For endocyclic compounds (ligands **7**−**12**), we detected, both in solution and in the solid state, two isomers for both nonsubstituted (**16**−**21**) and substituted (**23** and **24**) complexes (see above). From the X-ray data for **18** and **19**, a pseudo-boat conformation of the metallacycle is observed. In addition, for oxazolinyl−phosphines giving six-membered metallacycles, a mixture of two isomers is also observed with a boat conformation.[22] Thus, we propose that the isomers are due to the relative positions of the central allylic carbon and the bridge phenyl group of the ligand: exo, if both groups point in the same direction, and endo, if they point to opposite sides. We carried out theoretical calculations at the PM3(tm) level, of the structures of complexes with the 1,3-diphenylallyl-containing **8** and **12** (with an isopropyl as substituent group of the oxazoline moiety and the *S* absolute configuration on this stereocenter). These calculated structures and the relative values of the formation enthalpy are shown in Figure 3, the boat-endo structures being the most stable. We propose that this arrangement corresponds to that of the major species observed in solution (by means of NMR spectroscopy). If the nucleophilic attack occurs on the terminal allylic carbon trans to the phosphorus atom, the major species leads to the formation of the *S* alkylated product, as was observed experimentally.

Exocyclic complexes containing oxazolinyl−phosphinite ligands (**13**−**15**) can show two different six-membered cycle conformations: chair and boat. The X-ray structure of the related oxazolinyl−phosphine complex, reported by Burgess and co-workers,[6a,b] shows a chair conformation in the solid state with an exo disposition

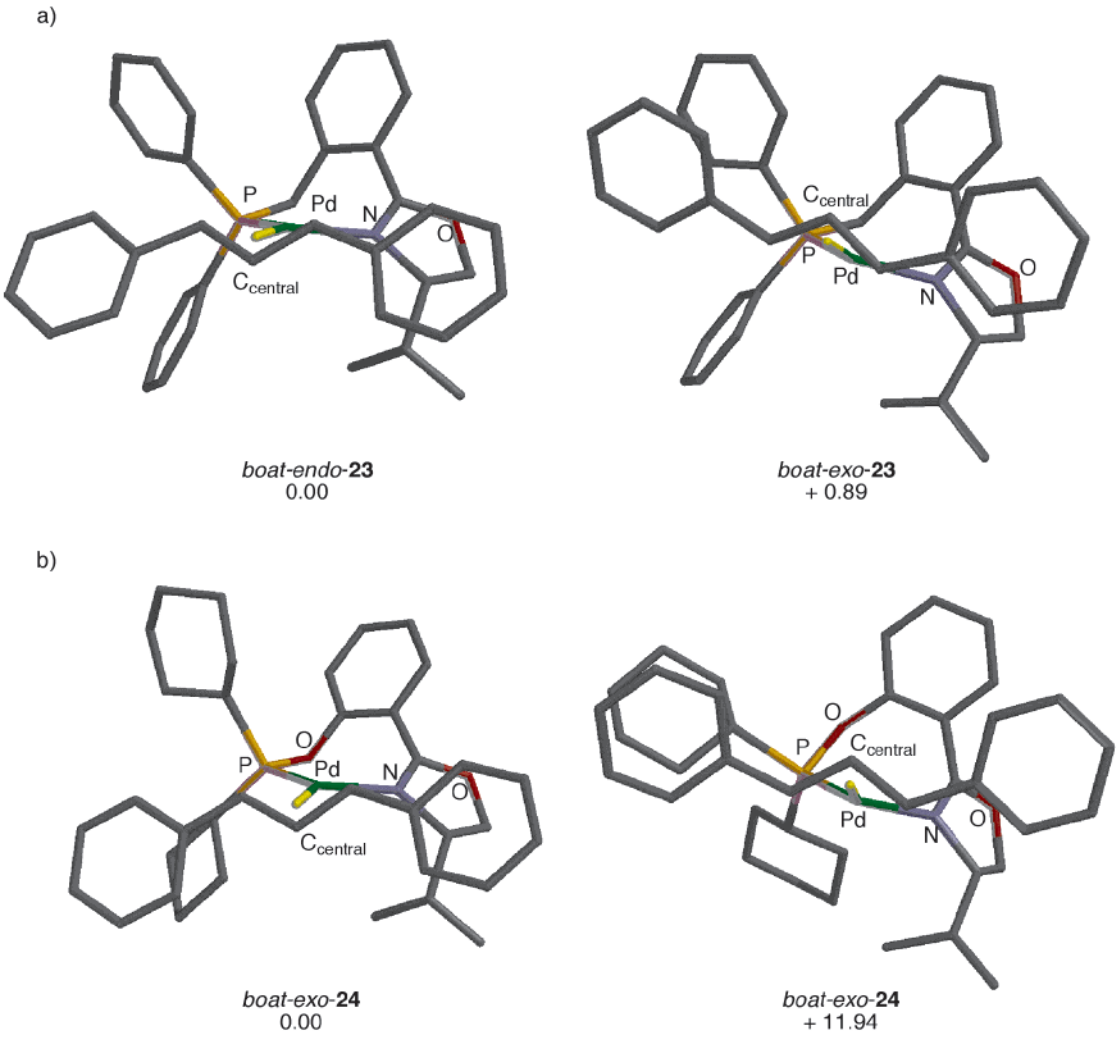


Figure 3. Calculated structures (PM3(tm)) for cationic species of complexes (a) **23** and (b) **24** and their relative formation enthalpies (kcal/mol).

concerning the relative position of the central allylic carbon and the methylenic group close to the oxazoline moiety; however, in solution, two isomers were detected in a ca. 4:1 ratio. This is due to the exo/endo relative allylic arrangement: chair-exo and chair-endo. For our exocyclic compounds, two isomers were also observed in solution for both nonsubstituted (**22**) and substituted (**25** and **26**) complexes, as stated above. Unfortunately, however, we could not obtain suitable monocrystals for X-ray diffraction studies. To propose an assignment for both isomers, chair-exo and chair-endo, we analyzed theoretically, as analogously described above for endocyclic compounds, complexes **25** and **26**. These calculated structures and their relative values of formation enthalpy are shown in Figure 4, where a major stability is indicated for the chair-exo isomers. Therefore, we suggest this type of isomer for the major species.

Concerning the absolute configuration of the organic product **II** (Scheme 7), the chair-exo isomers may explain the formation of (*R*)-**II** if the nucleophilic attack occurs on the terminal allylic carbon trans to the phosphorus atom.

Conclusions

New bidentate oxazolinyl−phosphane ligands **7**−**15** have been synthesized. Upon complexation to palladium, ligands **7**−**12** give endocyclic complexes of the seven-membered chelate ring, while **13**−**15** afford exocyclic complexes of the six-membered chelate ring, depending on the C═N oxazoline bond position in the metallacycle.

Endocyclic (**23** and **24**) and exocyclic (**25** and **26**) compounds containing the 1,3-diphenyl-η^3-allyl group have been prepared. NMR spectroscopic data show the presence of two isomers in solution with a diastereomeric ratio of ca. 75/25 for **23**, **24**, and **26**, but for ligand **25** the ratio is lower (55/45).

Palladium catalytic systems with ligands **7**−**15** have been tested in allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene and *rac*-3-acetoxy-1-cyclohexene, using dimethyl malonate as the nucleophile. For the model substrate, phosphinito−oxazoline ligands forming endocyclic complexes show better activities and selectivities than phosphine−oxazoline ligands. In addition, for the analogous structural environment, phosphinito ligands are more effective catalysts than the analogous phosphines, due to the increased π-acceptor ability of the phosphinite fragment. For PCy_2-phosphinito oxazoline ligands, the activity is higher but the selectivity is lower than for analogous PPh_2 derivatives. The absolute configuration obtained for the major alkylated product depends on the chiral stereocenter for those ligands,

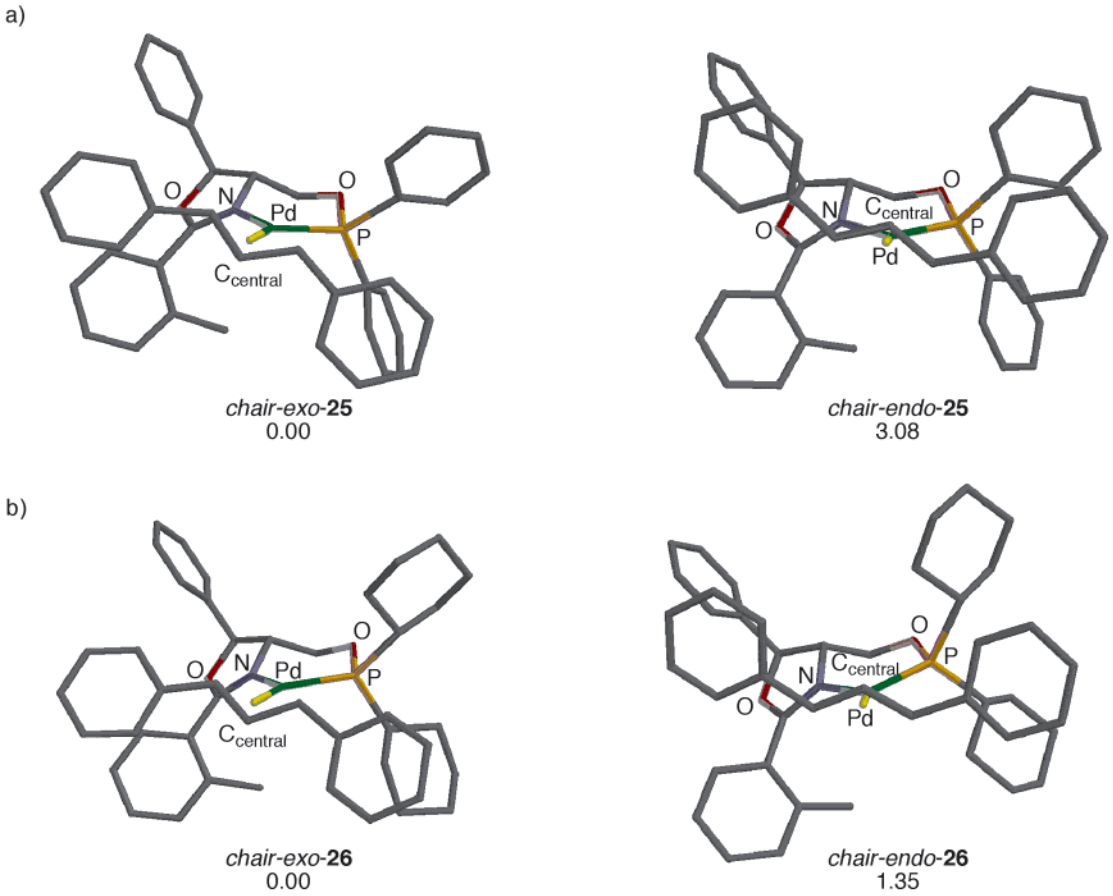


Figure 4. Calculated structures (PM3(tm)) for cationic species of complexes (a) **25** and (b) **26** and their relative formation enthalpies (kcal/mol).

forming seven-membered exocyclic complexes (**7**−**12**). However, for those ligands giving six-membered exocyclic compounds (**13**−**15**), the absolute configuration depends on the metallacycle arrangement. We have observed a good trend between the diastereomeric ratio of intermediate palladium allyl complexes and the enantiomeric excesses of the alkylated product. Modeling of these structures allows us to justify the selectivity observed on the catalytic process.

Experimental Section

General Data. All compounds were prepared under a purified nitrogen atmosphere using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen. $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$,[25] $[Pd(\eta^3\text{-}1,3\text{-}Ph_2{-}C_3H_3)(\mu\text{-}Cl)]_2$,[20] and ligand **10**[4] were prepared as previously described. NMR spectra were recorded on Varian XL-500 (^{1}H, standard $SiMe_4$), Bruker DRX 500 (^{1}H, standard $SiMe_4$), Varian Gemini (^{13}C, 50 MHz, standard $SiMe_4$), and Bruker DRX 250 spectrometers in $CDCl_3$ unless otherwise cited. Chemical shifts were reported downfield from standards. IR spectra were recorded on Nicolet 520 FT-IR, Nicolet 510 FT-IR, and FTIR Nicolet Impact 400 spectrometers. FAB mass chromatograms were obtained on a Fisons V6-Quattro instrument. The GC analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph (50 m Ultra 2 capillary column, 5% phenylmethylsilicone and 95% dimethylsilicone) with an FID detector. The GC/MS analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph (50 m Ultra 2 capillary column) interfaced to a Hewlett-Packard 5971 mass selective detector. Optical rotations were measured on a Perkin-Elmer 241MC spectropolarimeter. Enantiomeric excesses were determined by HPLC on a Hewlettt-Packard 1050 Series chromatograph (Chiralcel-OD chiral column) with a UV detector and by GC on a Hewlett-Packard 5890 Series II gas chromatograph (25 m FS-cyclodex-*β*-I/P column: heptakis(2,3,6-tri-*O*-methyl)-*β*-cyclodextrin/polysiloxane) with an FID detector. Elemental analyses were carried out by the Serveis Cientifico-Tècnics de la Universitat de Barcelona on an Eager 1108 microanalyzer.

1-[(4′*R*)-4′-Ethyl-3′,4′-dihydrooxazol-2′-yl]-2-methylbenzene (1). A 5.65 g (48.3 mmol) amount of 2-methylbenzonitrile, 4.71 g (53.1 mmol) of (*R*)-2-aminobutanol, and 0.16 g (1.20 mmol) of zinc chloride were dissolved in 20 cm^3 of toluene. The mixture was heated at reflux temperature for 48 h. The solvent was then removed under reduced pressure, and the residue was dissolved in 20 cm^3 of dichloromethane and washed with water (5 × 10 cm^3). The organic phase was then dried over anhydrous sodium sulfate and filtered off and the solvent removed under reduced pressure. The residue was purified by column chromatography (SiO_2; ethyl acetate/NEt_3, 50/1). The oxazoline was obtained as a yellow oil. Yield: 6.50 g (72%). IR (NaCl): 1650 cm^{-1} (C═N). MS (EI): *m*/*z* 189 ([M]$^+$). ^{1}H NMR (250 MHz): *δ* 7.77 (d, 7.5 Hz, 1H), 7.30 (m, 1H), 7.20 (m, 2H), 4.41 (dd, 9.4 Hz, 7.6 Hz, 1H), 4.25 (m, 1H), 4.00 (pt, 7.6 Hz, 1H), 2.57 (s, 3H), 1.75 (m, 1H), 1.62 (m, 1H), 1.00 (t, 7.5 Hz, 3H) ppm.

1-[(4′*S*)-4′-Isopropyl-3′,4′-dihydrooxazol-2′-yl]-2-methylbenzene (2). (a) Synthesis of 2a. A 2.5 g amount (18.4 mmol) of 2-methylbenzoic acid was treated with 7 cm^3 of $SOCl_2$. The mixture was heated at reflux temperature for 20 h. The solvent was then removed under reduced pressure, and the residue was washed with diethyl ether (3 × 15 cm^3), affording

(25) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 342.

the corresponding acid chloride as a colorless oil. Yield: 2.30 g (80%). IR (NaCl): 1772 cm^{-1} (C═O). A 0.41 g amount (4 mmol) of L-valinol was dissolved in 6 cm^3 of dioxane in the presence of 0.80 g (8 mmol) of NEt_3. The mixture was cooled to 0 °C< and a solution of the acid chloride (0.59 g, 3.8 mmol in 5 cm^3 of dioxane) was then added dropwise. The mixture was then stirred for 1 h at 0 °C and warmed to room temperature. The mixture was filtered off, the solvent was removed, and the residue was dissolved in dichloromethane and this solution then washed with a 10% aqueous solution of ammonium chloride (3 × 5 cm^3) and water (5 × 10 cm^3). The organic phase was then dried over anhydrous sodium sulfate, and **2a** was obtained as a white solid after removing the solvent under reduced pressure. Yield: 0.60 g (70%). Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.32; H, 8.85; N, 6.38. IR (KBr): 1638 cm^{-1} (C═O). ^{1}H NMR (500 MHz): δ 7.36 (dd, 7.5 Hz, 1.0 Hz, 1H), 7.30 (td, 7.5 Hz, 1.5 Hz, 1H), 7.20 (m, 2H), 5.90 (bs, 1H), 3.95 (m, 1H), 3.80 (m, 1H), 3.70 (m, 1H), 2.47 (bs, 1H), 2.44 (s, 3H), 1.96 (m, 1H), 1.01 (t, 7.5 Hz, 6H) ppm; ^{13}C NMR (50 MHz): δ 170.9 (C), 136.5 (C), 135.8 (C), 130.9 (CH), 129.8 (CH), 126.5 (CH), 125.6 (CH), 63.9 (CH2), 57.3 (CH), 29.1 (CH), 19.8 (CH_3), 19.6 (CH_3), 18.9 (CH_3) ppm.

(b) Synthesis of 2. A 0.5 g amount (2.26 mmol) of **2a** and 1.14 g (11.3 mmol) of NEt_3 were dissolved in 7 cm^3 of dichloromethane. A 0.47 g amount (2.44 mmol) of *p*-tosyl chloride was then added, and the mixture was refluxed for 24 h. The mixture was washed with water (5 × 10 cm^3), and the organic phase was then dried over anhydrous sodium sulfate. After the solvent was removed, the residue was purified by column chromatography (SiO_2; ethyl acetate). The oxazoline **2** was obtained as a yellow oil. Yield: 0.38 g (82%). IR (NaCl): 1653 cm^{-1} (C═N). MS (EI): *m*/*z* 203 ($[M]^+$). ^{1}H NMR (500 MHz): δ 7.74 (dd, 8.0 Hz, 1.5 Hz, 1H), 7.27 (td, 7.5 Hz, 1.5 Hz, 1H), 7.20 (m, 2H), 4.34 (dd, 9.5 Hz, 8.0 Hz, 1H), 4.12 (m, 1H), 4.08 (dd, 15.8 Hz, 7.5 Hz, 1H), 2.56 (s, 3H), 1.85 (m, 2H), 1.02 (d, 7.0 Hz, 3H), 0.94 (d, 7.0 Hz, 3H) ppm. ^{13}C NMR (50 MHz): δ 164.3 (C), 139.0 (C), 131.5 (CH), 130.7 (CH), 130.2 (CH), 126.3 (C), 125.9 (CH), 73.4 (CH), 69.8 (CH_2), 33.3 (CH), 21.9 (CH_3), 19.3 (CH_3), 18.6 (CH_3) ppm.

1-[(4′*S*)-4′-Isopropyl-3′,4′-dihydrooxazol-2′-yl]-2-hydroxybenzene (4). A 1 g amount (5.23 mmol) of 2-hydroxybenzonitrile, 0.653 g (6.3 mmol) of L-valinol, and 0.018 g (0.13 mmol) of zinc chloride were dissolved in 8 cm^3 of toluene. The mixture was heated at reflux temperature for 1 day. The solvent was then removed under reduced pressure, and the residue was extracted in 20 cm^3 of diethyl ether and washed with water (5 × 10 cm^3). The organic phase was then dried over anhydrous sodium sulfate and filtered off, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2; hexane/diethyl ether, 2/3). The oxazoline was obtained as a yellow oil. Yield: 1.07 g (99%). IR (NaCl): 1619 (C═N) cm^{-1}. ^{1}H NMR (200 MHz): δ 13.0 (1H, OH), 7.63 (1H, dd, 7.7 Hz, 1.7 Hz), 7.36 (1H, dd, 8.4 Hz, 1.8 Hz), 7.00 (1H, dd, 8.4 Hz, 1.2 Hz), 6.86 (1H, ptd, 7.9 Hz, 1.0), 4.41 (1H, m), 4.11 (1H, pt, 5.5 Hz), 4.09 (1H, m), 1.78 (1H, m), 1.01 (3H, 7 Hz), 0.94 (3H, d, 6.8 Hz,) ppm. ^{13}C NMR (50 MHz): δ 163.5 (C═N), 158.7 (C, Ph), 132.1 (C, Ph), 126.8 (CH), 125.5 (CH), 117.4 (CH), 115.5 (CH), 70.3 (CH), 68.7 (CH), 31.9 (CH_2), 17.6 (CH_3) ppm. $[\alpha]^{23}_D = -28.5°$ (c = 1 in $CHCl_3$).

1-[(4′*R*)-4′-Hydroxymethyl-3′,4′-dihydrooxazol-2′-yl]-2-methylbenzene (5). (a) Synthesis of 5a. A 0.62 g amount (4.0 mmol) of (*S*)-serine methyl ester hydrochloride and 0.66 g (7.8 mmol) of sodium hydrogencarbonate were dissolved in 6 cm^3 of water and cooled to 0 °C. A 0.59 g amount (3.8 mmol) of 2-methylbenzoic acid chloride dissolved in 5 cm^3 of dioxane was then added dropwise. The mixture was stirred at room temperature overnight. Ethyl acetate was then added, the mixture was filtered off, and the solvent was evaporated under reduced pressure. The yellow oil obtained was purified by column chromatography (SiO_2; ethyl acetate/hexane, 1/1). The prodcut was obtained as a colorless oil. Yield: 0.61 g (67%). IR (NaCl): 1743 (C═O ester), 1645 (C═O amide), 1526 (N−C═O st) cm^{-1}. MS (EI): *m*/*z* 238 ($[M]^+$). ^{1}H NMR (200 MHz): δ 7.4−7.1 (m, 4H), 6.89 (d, 7.8 Hz, 1H), 4.76 (dt, 7.8 Hz, 3.8 Hz, 1H), 4.03 (dd, 11.2 Hz, 3.8 Hz, 1H), 3.92 (dd, 11.2 Hz, 3.6 Hz, 1H), 3.77 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (50 MHz): δ 170.8 (C), 170.3 (C), 136.2 (C), 135.2 (C), 130.9 (CH), 130.2 (CH), 126.9 (CH), 125.6 (CH), 63.0 (CH_2), 54.8 (CH), 52.7 (CH_3), 19.7 (CH_3) ppm.

(b) Synthesis of 5b. A 0.51 g amount (2.1 mmol) of **5a** and 0.67 g (4.4 mmol) of *tert*-butyldimethylsilyl chloride (TBDMSCl) were dissolved in 5 cm^3 of dichloromethane and cooled to 0 °C. A 0.30 g amount (4.4 mmol) of imidazole was added portionwise over 5 min. The mixture was warmed to room temperature and stirred for 24 h. The mixture was then treated successively with an aqueous solution of HCl (2 M, 3 × 10 cm^3) and water (5 × 10 cm^3). The organic phase was dried over anhydrous sodium sulfate. After the solvent was removed, a colorless oil was obtained. Yield: 0.75 g (>99%). IR (NaCl): 1749 (C═O ester), 1660 (C═O amide), 1653 (C═O st) cm^{-1}. MS (EI): *m*/*z* 295 ($[M - t\mathrm{Bu}]^+$). ^{1}H NMR (200 MHz): δ 7.5−7.2 (m, 4H), 6.62 (d, 8.0 Hz, 1H), 4.85 (pdt, 8.4 Hz, 3.0 Hz, 1H), 4.15 (dd, 10.0 Hz, 3.0 Hz, 1H), 3.96 (dd, 10.0 Hz, 3.0 Hz, 1H), 3.77 (s, 3H), 2.47 (s, 3H), 0.84 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H) ppm. ^{13}C NMR (50 MHz): δ 170.7 (C), 169.5 (C), 136.1 (C), 135.6 (C), 130.9 (CH), 125.7 (CH), 63.5 (CH_2), 54.6 (CH), 52.4 (CH_3), 25.7 (CH_3), 19.8 (CH_3), 8.0 (C), −5.5 (CH_3), −5.7 (CH_3) ppm.

(c) Synthesis of 5c. A 0.20 g amount (0.6 mmol) of **5b** was dissolved in 4 cm^3 of methanol, and 0.084 g (2.24 mmol) of sodium tetrahydroborate was added at once. The mixture was warmed to 35 °C for 3 h (reaction monitored by TLC: hexane/ethyl acetate, 9/1). At completion, 10 cm^3 of water was added and extractions with chloroform were carried out (3 × 10 cm^3). The organic phase was dried over anhydrous sodium sulfate and the solvent evaporated. The residue was purified by column chromatography (SiO_2; dichloromethane/ethyl acetate, 9/1). The product was obtained as a colorless oil. Yield: 0.17 g (95%). IR (NaCl): 1652 (C═O), 1646 (C═O), 1632 (C═O) cm^{-1}. ^{1}H NMR (200 MHz): δ 7.4−7.2 (m, 4H), 6.50 (d, 7.4 Hz, 1H), 4.16 (m, 1H), 3.9−3.7 (m, 4H), 3.25 (s, 1H), 2.46 (s, 3H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H) ppm. ^{13}C NMR (50 MHz): δ 170.2 (C), 135.9 (C), 130.9 (CH), 129.9 (CH), 126.8 (CH), 125.7 (CH), 63.3 (CH_2), 54.5 (CH), 52.5 (CH_2), 25.8 (CH_3), 19.8 (CH_3), 18.1 (C), −5.5 (CH_3) ppm.

(d) Synthesis of 5d. A 0.25 g amount (0.77 mmol) of **5c** and 0.39 g (3.85 mmol) of triethylamine were dissolved in 8 cm^3 of dichloromethane, and 0.16 g (0.83 mmol) was then added. The mixture was refluxed for 24 h (reaction monitored by TLC: dichloromethane/ethyl acetate, 9/1). The mixture was cooled to room temperature and washed with water (5 × 10 cm^3). The organic phase was dried over anhydrous sodium sulfate and the solvent evaporated. The residue was purified by column chromatography (SiO_2; hexane/ethyl acetate, 9/1). The product was obtained as a colorless oil. Yield: 0.21 g (93%). IR (NaCl): 1643 (C═N) cm^{-1}. MS (EI): *m*/*z* 305 ($[M - 1]^+$). ^{1}H NMR (200 MHz): δ 7.77 (d, 7.6 Hz, 1H), 7.4−7.1 (m, 3H), 4.3−4.2 (m, 3H), 3.89 (dd, 10.4 Hz, 3.2 Hz, 1H), 3.66 (dd, 10.7 Hz, 5.0 Hz, 1H), 2.57 (s, 3H), 0.88 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H) ppm; ^{13}C NMR (50 MHz): δ 165.3 (C), 138.6 (C), 131.0 (CH), 130.4 (CH), 129.7 (CH), 127.3 (C), 125.4 (CH), 69.5 (CH_2), 68.6 (CH), 65.0 (CH_2), 25.9 (CH_3), 21.7 (CH_3), 18.3 (C), −5.2 (CH_3), −5.3 (CH_3) ppm.

(e) Synthesis of 5. A 0.50 g amount (1.63 mmol) of **5d** was dissolved in 15 cm^3 of THF, and 3.0 cm^3 of a 1.0 M solution of TBAF (in THF (3.0 mmol)) was added. The reaction mixture was stirred for 40 min (reaction monitored by TLC: dichloromethane/ethyl acetate, 9/1). The solvent was then removed under reduced pressure, and the obtained oil was purified by column chromatography (SiO_2; dichloromethane/ethyl acetate, 4/1). The product was obtained as a white paste. Yield: 0.25

g (79%). IR (KBr): 1642 (C═N) cm^{-1}. MS (EI): *m*/*z* 191 ($[M]^+$). ^1H NMR (200 MHz): δ 7.75 (d, 7.6 Hz, 1H), 7.4−7.1 (m, 3H), 4.5−4.4 (m, 3H), 4.25 (m, 1H), 3.90 (dd, 11.6 Hz, 3.0 Hz, 1H), 3.64 (dd, 11.2 Hz, 4.0 Hz, 1H), 2.87 (bs, 1H), 2.53 (s, 3H) ppm. ^{13}C NMR (50 MHz): δ 166.1 (C), 138.6 (C), 131.1 (CH), 130.7 (CH), 129.8 (CH), 126.7 (C), 125.5 (CH), 68.7 (CH_2), 68.2 (CH), 64.3 (CH_2), 21.7 (CH_3) ppm.

1-[(3′*S*,4′*S*)-3′-Phenyl-4′-(hydroxymethyl)-3′,4′-dihydrooxazol-2′-yl]-2-methylbenzene (6). A 1.21 g amount (7.25 mmol) of (1*S*,2*S*)-(+)-2-amino-1-phenyl-1,3-propanediol, 0.50 g (4.27 mmol) of 2-methylbenzonitrile, and 118 mg of potassium carbonate were treated with a solution of 1 cm^3 of glycerol in 1.8 cm^3 of dry ethylene glycol. The resulting mixture was heated to 105 °C for 72 h. The mixture was then cooled to room temperature and poured over a mixture of 20 cm^3 of water and dichloromethane. The mixture was washed with water (7 × 10 cm^3), and the organic phase was then dried over anhydrous sodium sulfate. After the solvent was removed, the residue was purified by column chromatography (SiO_2; ethyl acetate/hexane, 1/1). The oxazoline was obtained as a white solid. Yield: 0.50 g (44%). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 75.0; H, 6.4; N, 5.39. IR (KBr): 1638 cm^{-1} (C═N). MS (CI): *m*/*z* 268 ($[M + 1]^+$). ^1H NMR (500 MHz): δ 7.86 (dd, 7.5, 1.5, 1H), 7.40−7.30 (m, 6H), 7.24 (m, 2H); 5.44 (d, 7.5 Hz, 1H), 4.28 (ddd, 7.5 Hz, 4.5 Hz, 4.0 Hz, 1H), 4.02 (dd, 11 Hz, 4 Hz, 1H), 3.76 (dd, 11.5 Hz, 4.5 Hz, 1H), 2.59 (s, 3H) ppm. ^{13}C NMR (50 MHz): δ 165.5 (C), 140.5 (C), 138.8 (C), 131.2 (CH), 130.8 (CH), 130.0 (CH), 128.8 (CH), 128.2 (CH), 126.7 (C), 125.6 (CH), 82.3 (CH), 76.9 (CH), 64.0 (CH_2), 21.9 (CH_3) ppm. $[\alpha]^{23}_D = +48.0°$ (c = 1 in $CHCl_3$).

1-[(3′*S*,4′*S*)-3′-Phenyl-4′-((diphenylphosphinito)methyl)-3′,4′-dihydrooxazol-2′-yl]-2-methylbenzene (14). A 0.187 g amount (0.70 mmol) of **6** was dissolved in 13 cm^3 of freshly distilled THF. The mixture was then cooled to −78 °C and 0.43 cm^3 of *n*-BuLi (ca. 1.6 M, 0.70 mmol) was added. The mixture was stirred for 15 min and then warmed to room temperature for $^1/_2$ h. A 0.168 g amount (0.77 mmol) of $ClPPh_2$ was then added dropwise at −78 °C and warmed to room temperature. After 1 h, the reaction was complete (monitored by ^{31}P NMR spectroscopy). The solvent was then removed under reduced pressure, and the resulting oil was purified by flash column chromatography (Al_2O_3; ethyl acetate/hexane, 4/1). The compound was obtained as a yellow oil. Yield: 0.86 g (72%). MS (CI): *m*/*z* 452 ($[M]^+$). ^1H NMR (250 MHz): δ 7.90 (d, 2.5 Hz, 1H), 7.35−7.28 (m, 18H), 5.52 (d, 7.5 Hz, 1H), 4.44 (m, 1H), 4.17 (m, 2H), 2.59 (s, 3H) ppm. ^{13}C NMR (50 MHz): δ 164.4 (C═N), 141.0 (C, Ph), 139.1 (C, Ph), 132.5 (C, Ph), 131.2 (C, Ph), 130.6 (CH), 130.5 (C, Ph), 130.5 (CH), 130.2 (CH), 130.0 (CH), 129.3 (CH), 129.3 (CH), 128.7 (CH), 128.7 (CH), 128.3 (CH), 128.2 (CH), 128.2 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 125.7 (CH), 125.7 (CH), 125.6 (CH), 125.6 (CH), 125.5 (CH), 82.5 (CH), 77.2 (CH), 71.3 (CH_2, d, 18 Hz), 21.9 (CH_3) ppm. ^{31}P NMR (101 MHz): δ 115.2 ppm.

1-[(3′*S*,4′*S*)-3′-Phenyl-4′-((dicyclohexylphosphinito)-methyl)-3′,4′-dihydrooxazol-2′-yl]-2-methylbenzene (15). A 0.247 g amount (0.93 mmol) of **6** was dissolved in 15 cm^3 of freshly distilled THF. The mixture was then cooled at −78 °C and 0.58 cm^3 of *n*-BuLi (ca. 1.6 M, 0.93 mmol) was added. The mixture was stirred for 15 min and then warmed at room temperature for $^1/_2$ h. A 0.234 g amount (1.02 mmol) of $ClPCy_2$ was then added dropwise at −78 °C, and the mixture was warmed to room temperature. After 1 h, the reaction was complete (monitored by ^{31}P NMR spectroscopy). The solvent was then removed under reduced pressure, and the resulting oil was purified by flash column chromatography (Al_2O_3; ethyl acetate/hexane, 4/1). The compound was obtained as a yellow oil. Yield: 0.65 g (36%). MS (FAB positive): *m*/*z* 464 ($[M - H]^+$). ^1H NMR (250 MHz): δ 7.82 (d, 1.5, 1H), 7.30−7.13 (m, 8H), 5.43 (d, 6.3 Hz, 1H), 4.27 (m, 1H), 3.92 (m, 1H), 3.84 (m, 1H), 2.56 (s, 3H) ppm, 1.70 (m, 11H), 1.20 (m, 11H). ^{13}C NMR (50 MHz): δ 164.9 (C═N), 140.7 (C, Ph), 139.1 (C, Ph), 131.3 (C, Ph), 131.2 (CH), 130.7 (CH), 128.7 (CH), 128.6 (CH), 128.3 (CH), 128.2 (CH), 125.7 (CH), 125.6 (CH), 125.5 (CH), 82.5 (CH), 75.7 (CH), 73.8 (CH_2OP, d, 19 Hz), 36.8 (CH, d, 23 Hz), 35.5 (CH, d, 25 Hz), 26.9 (CH_2), 26.6 (CH_2), 26.4 (CH_2), 26.1 (CH_2), 26.0 (CH_2), 25.9 (CH_2), 25.7 (CH_2), 25.5 (CH_2), 25.3 (CH_2), 25.0 (CH_2), 19.8 (CH_3) ppm. ^{31}P NMR (101 MHz): δ 149.3 ppm.

(η^3-Allyl){1-[(4′*R*)-4′-ethyl-3′,4′-dihydrooxazol-2′-yl]-2-((diphenylphosphinyl)methyl)phenyl-*N*,*P*}palladium(II) Hexafluorophosphate (16). (a) Synthesis of 7. A 0.470 g amount (2.48 mmol) of **1** was dissolved in 25 cm^3 of freshly distilled diethyl ether. The solution was cooled to −78 °C, and 1.7 cm^3 (2.73 mmol) of *n*-BuLi solution (1.6 M in hexane) was added. The red solution was warmed to 0 °C for 15 min. A 0.6 g amount (2.73 mmol) of $ClPPh_2$ in 10 cm^3 of ether was added at −78 °C, and after addition the temperature was raised to 0 °C. The solution became cream-colored. The phosphine formation was monitored by ^{31}P NMR spectroscopy. The mixture was washed with deoxygenated water (3 × 10 cm^3), dried over anhydrous Na_2SO_4, and concentrated to dryness under vacuum. The ligand was used without further purification. ^{31}P NMR (acetone-d_6, 101.3 MHz): δ −7.9 ppm.

(b) Synthesis of 16. A 0.457 g amount (1.22 mmol) of **7** was dissolved in 10 cm^3 of freshly distilled CH_2Cl_2, and 0.22 g (0.61 mmol) of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in 5 cm^3 of CH_2Cl_2 was added at room temperature. The orange solution was stirred at room temperature for 1 h. A 0.198 g amount (1.22 mmol) of NH_4PF_6 dissolved in 5 cm^3 of absolute ethanol was then added. CH_2Cl_2 was removed under vacuum, and after 3 h at low temperature, a red precipitate was obtained. Yield: 80 mg (10%). Anal. Calcd for $C_{27}H_{29}F_6NOP_2Pd$: C, 48.70; H, 4.39; N, 2.10. Found: C, 47.75; H, 4.49; N, 2.11. IR (KBr): 1638 (st, C═N), 838 (st, P−F) cm^{-1}. MS (FAB positive): *m*/*z* 520 ($[M - PF_6]^+$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): at 220 K, δ 39.1 ppm (major), 38.6 ppm (minor); at 330 K, δ 38.56 ppm.

(η^3-Allyl){1-[(4′*S*)-4′-isopropyl-3′,4′-dihydrooxazol-2′-yl]-2-((diphenylphosphinyl)methyl)phenyl-*N*,*P*}-palladium(II) Hexafluorophosphate (17). Compound **17** was synthesized in a way similar to that used for the preparation of **16**.

Starting materials for **8**: 0.150 g (0.74 mmol) of **2** dissolved in 8 cm^3 of freshly distilled diethyl ether, 0.51 cm^3 (0.81 mmol) of 1.6 M *n*-BuLi solution in hexane, 0.179 g (0.81 mmol) of $ClPPh_2$. ^{31}P NMR (acetone-d_6, 101.3 MHz): δ −8.5 ppm.

Starting materials for **17**: 0.132 g (0.34 mmol) of **8** in 8 cm^3 of CH_2Cl_2, 0.060 g (0.17 mmol) of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in 3 cm^3 of CH_2Cl_2, 0.081 g (0.50 mmol) of NH_4PF_6 in 5 cm^3 of absolute ethanol. Yield: 0.145 g (63%). Anal. Calcd for $C_{28}H_{31}F_6NOP_2Pd$: C, 49.46; H, 4.60; N, 2.06. Found: C, 49.38; H, 4.56; N, 1.87. IR (KBr): 1637 (st, C═N), 857 (st, P−F) cm^{-1}. MS (FAB positive): *m*/*z* 534 ($[M - PF_6]^+$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): at 273 K, δ 38.1 ppm (major), 38.0 ppm (minor); at 298 K, δ 38.05 ppm.

(η^3-Allyl){1-[(4′*R*)-4′-ethyl-3′,4′-dihydrooxazol-2′-yl]-2-(diphenylphosphinito)phenyl-*N*,*P*}palladium(II) Tetrafluoroborate (18). (a) Synthesis of 9. 9 was prepared by following the methodology described in the literature.[4] A 1.984 g portion (10.4 mmol) of **3** and 1.05 g (10.4 mmol) of NEt_3 were dissolved in 25 cm^3 of freshly distilled toluene under a N_2 atmosphere. A 2.3 g portion (10.4 mmol) of $ClPPh_2$ dissolved in 10 cm^3 of toluene was added dropwise at −78 °C. The mixture was stirred for 3 h while the solution was warmed gradually to room temperature. The phosphinite−oxazoline formation was monitored by ^{31}P NMR. The white precipitate was filtered off and the solution concentrated under reduced pressure to yield an orange oil. The ligand was used without further purification. ^{31}P NMR (acetone-d_6, 101.3 MHz): δ 113.1 ppm.

(a) Synthesis of 18. A 0.32 g portion (0.85 mmol) of **9** in 10 cm^3 of CH_2Cl_2 was added to a solution of 0.286 g (0.85 mmol) of $[Pd(\eta^3\text{-}C_3H_5)(cod)]BF_4$ in 10 cm^3 of CH_2Cl_2 under N_2. The

orange solution was stirred for 1 h, the solvent was evaporated under reduced pressure, and the obtained oil was washed with freshly distilled ether (5 × 10 cm^3) to eliminate the COD, giving a cream-colored solid. Yield: 0.345 g (67%). Anal. Calcd for $C_{26}H_{27}NO_2PBF_4Pd$: C, 51.21; H, 2.80; N, 4.46. Found: C, 49.90; H, 2.33; N, 4.46. IR (KBr): 1639 (st, C═N), 1092, 1037 (st, P−O), 1377 (st, B−F) cm^{-1}. MS (FAB positive): *m*/*z* 522 ($[M - PF_6]^+$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): δ 152.4 ppm (major), 150.3 ppm (minor).

(η^3-Allyl){1-[(4′*S*)-4′-isopropyl-3′,4′-dihydrooxazol-2′-yl]-2-(diphenylphosphinito)phenyl-*N*,*P*}palladium(II) Hexafluorophosphate (19). (a) Synthesis of 10. A 0.250 g portion (1.23 mmol) of ligand **4** was dissolved in 5 cm^3 of freshly distilled THF. The solution was cooled to 0 °C, and 0.77 cm^3 (1.23 mmol) of *n*-BuLi solution (1.6 M in hexane) was added. The dark solution was warmed to room temperature for 30 min. A 0.27 g portion (1.23 mmol) of $ClPPh_2$ was added at 0 °C. The orange solution was stirred for 2 h. The formation of the phosphinite ligand was monitored by ^{31}P NMR spectroscopy. The solution reaction was concentrated under reduced pressure, and the ligand was used without further purification. ^{31}P NMR (acetone-d_6, 101.3 MHz): δ 110.4 ppm.

(b) Synthesis of 19. A 25 cm^3 portion of toluene was added to the residue of **10**. A 0.223 g portion (0.62 mmol) of [Pd(η^3-C_3H_5)Cl]$_2$ was added, and the mixture was stirred for 15 min before addition of 0.303 g (1.86 mmol) of NH_4PF_6. The solution was filtered off and concentrated under reduced pressure to yield an oil. Yield: 0.471 g (56%). Anal. Calcd for $C_{27}H_{29}NF_6O_2P_2Pd$: C, 47.56; H, 4.29; N, 2.05. Found: C, 46.68; H, 4.32; N, 2.06. IR (KBr): 1637 (st, C═N), 1092, 1040 (st, P−O), 857 (st, P−F) cm^{-1}. MS (FAB positive): *m*/*z* 536 ($[M]^+$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): δ 151.7 ppm (major), 150.0 ppm (minor).

(η^3-allyl){1-[(4′*R*)-4′-ethyl-3′,4′-dihydrooxazol-2′-yl]-2-(dicyclohexylphosphinito)phenyl-*N*,*P*}palladium(II) Hexafluorophosphate (20). Compound **20** is synthesized in a way similar to that used for the preparation of **19**. Starting materials for **11**: 0.250 g (1.31 mmol) of ligand **3** dissolved in 5 cm^3 of THF, 0.82 cm^3 (1.31 mmol) of 1.6 M *n*-BuLi solution in hexane, 0.305 g (1.31 mmol) of $ClPCy_2$. ^{31}P NMR (acetone-d_6, 101.3 MHz): δ 143.1 ppm.

Starting materials for **20**: 0.250 g (0.66 mmol) of **11** in 25 cm^3 of toluene, 0.148 g (0.33 mmol) of [Pd(η^3-C_3H_5)Br]$_2$, 0.161 g (0.99 mmol) of NH_4PF_6 in 5 cm^3 of absolute EtOH. Yield: 0.180 g (40%). Anal. Calcd for $C_{26}H_{39}NF_6O_2P_2Pd$: C, 45.93; H, 5.78; N, 2.06. Found: C, 43.17; H, 5.52; N, 1.99. IR (KBr): 1637 (st, C═N), 1079, (st, P−O), 859 (st, P−F) cm^{-1}. MS (FAB positive): *m*/*z* 534 ($[M - PF_6]^+$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): δ 187.5 (bs) ppm.

(η^3-Allyl){1-[(4′*S*)-4′-isopropyl-3′,4′-dihydrooxazol-2′-yl]-2-(dicyclohexylphosphinito)phenyl-*N*,*P*}palladium(II) Hexafluorophosphate (21). Compound **21** is synthesized in a way similar to that used for the preparation of **19**. Starting materials for **12**: 0.150 g (0.73 mmol) of ligand **4** dissolved in 4 cm^3 of THF, 0.46 cm^3 (0.73 mmol) of 1.6 M *n*-BuLi solution in hexane, 0.170 g (0.73 mmol) of $ClPCy_2$. ^{31}P NMR (acetone-d_6, 101.3 MHz): δ 142.4 ppm.

Starting materials for **21**: 0.164 g (0.365 mmol) of [Pd(η^3-C_3H_5)Br]$_2$ was added to the phosphinite−oxazoline solution reaction, and after 15 min of stirring, 0.178 g (1.045 mmol) of NH_4PF_6 in 5 cm^3 of absolute EtOH was added. The solution was concentrated to dryness, the residue was washed with deoxygenated water, and the solid was filtered off. Recrystallization from $CHCl_3$/pentane led to the complex. Yield: 0.140 g (28%). Anal. Calcd for $C_{27}H_{41}NF_6O_2P_2Pd$: C, 46.73; H, 5.96; N, 2.02. Found: C, 44.61; H, 5.72; N, 1.9. IR (KBr): 1632 (st, C═N), 1081 (st, P−O), 860 (st, P−F) cm^{-1}. MS (FAB positive): *m*/*z* 548 ($[M - PF_6]^+$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): δ 188.99 (major) 186.62 (minor) ppm.

(η^3-Allyl){1-[(4′*S*)-4′-((dicyclohexylphosphinito)methyl)-3′,4′-dihydrooxazol-2′-yl]-2-methylphenyl-*N*,*P*}palladium(II) Hexafluorophosphate (22). Compound **22** is synthesized in a was similar to that used for the preparation of **19**. Starting materials for **13**: 0.071 g (0.37 mmol) of ligand **6** in 4 cm of THF, 0.23 cm^3 (0.37 mmol) of 1.6 M *n*-BuLi solution in hexane, 0.086 g (0.37 mmol) of $ClPCy_2$. ^{31}P NMR (acetone-d_6, 101.3 MHz): δ 147.0 ppm.

Starting materials for **22**: 0.083 g (0.185 mmol) of [Pd(η^3-C_3H_5)Br]$_2$ was added to the phosphinite−oxazoline solution reaction, and after 15 min of stirring, 0.09 g (0.55 mmol) of NH_4PF_6 in 5 cm^3 of absolute EtOH was added. Yield: 0.057 g (23%). Anal. Calcd for $C_{26}H_{39}NF_6O_2P_2Pd$: C, 45.93; H, 5.78; N, 2.06. Found: C, 45.96; H, 6.07; N, 1.88. IR (KBr): 1636 (st, C═N), 841 (st, P−F) cm^{-1}. MS (FAB positive): *m*/*z* 534 ($[M - PF_6]^+$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): at 273 K, δ 153.35 ppm (minor), 153.23 ppm (major); at 298 K, δ 153.2 ppm.

(η^3-1,3-Diphenylallyl){1-[(4′*S*)-4′-isopropyl-3′,4′-dihydrooxazol-2′-yl]-2-((diphenylphosphinyl)methyl)phenyl-*N*,*P*}palladium(II) Hexafluorophosphate (23). A 0.372 g portion (0.98 mmol) of ligand **8** was dissolved in 30 cm^3 of absolute ethanol in a purged Schlenk, and 0.328 g of [Pd(η^3-1,3-Ph_2-C_3H_3)Cl]$_2$ (0.49 mmol) was added. After 1 h of stirring, 0.239 g (1.47 mmol) of NH_4PF_6 was added. The reaction mixture was stirred overnight at room temperature. The yellow precipitate was filtered off. Yield: 0.48 g (58%). Anal. Calcd for $C_{40}H_{39}NF_6O_2P_2Pd$: C, 57.74; H, 4.72; N, 1.68. Found: C, 57.75; H, 4.91; N, 1.70. IR (KBr): 1638 (st, C═N), 853 (st, P−F) cm^{-1}. MS (FAB positive): *m*/*z* 686 ($[M - PF_6]^+$). ^{31}P NMR ($CDCl_3$, 273 K, 101.3 MHz): δ 36.63 ppm (major), 42.04 ppm (minor).

(η^3-1,3-Diphenylallyl){1-[(4′*S*)-4′-isopropyl-3′,4′-dihydrooxazol-2′-yl]-2-(dicyclohexylphosphinito)phenyl-*N*,*P*}-palladium(II) Hexafluorophosphate (24). In a purged Schlenk containing 0.200 g (0.973 mmol) of **12**, 10 cm^3 of freshly distilled toluene was added. A 0.327 g portion (0.488 mmol) of [Pd(η^3-1,3-Ph_2-C_3H_3)Cl]$_2$ dissolved in 2 cm^3 of toluene was then added. The yellow solution was stirred for 1 h at room temperature, and 0.159 g of NH_4PF_6 (0.975 mmol) dissolved in 1 cm^3 of distilled THF was added to the mixture. After 1 h of stirring, the solution was placed in the refrigerator for 2 h. The yellow precipitate that formed was filtered off under nitrogen and dried under vacuum. Yield: 0.8 g (97%). Anal. Calcd for $C_{39}H_{49}NO_2F_6P_2Pd$: C, 55.35; H, 5.79; N, 1.65. Found: C, 58.4; H, 6.1; N, 1.5. IR (KBr): 1630 (st, C═N), 1082 (st, P−O), 842 (st, P−F). MS (FAB positive): *m*/*z* 700 ($[M - PF_6]^+$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): δ 188.35 ppm (major), 185.82 ppm (minor).

(η^3-1,3-Diphenylallyl){1-[(3′*S*,4′*S*)-3′-phenyl-4′-((diphenylphosphinito)methyl)-3′,4′-dihydrooxazol-2′-yl]-2-methylphenyl-*N*,*P*}palladium(II) Hexafluorophosphate (25). In a purged Schlenk containing 0.306 g (0.678 mmol) of **14** was added 15 cm^3 of freshly distilled toluene. A 0.227 g portion (0.359 mmol) of [Pd(η^3-1,3-Ph_2-C_3H_3)Cl]$_2$ dissolved in toluene was then added. The yellow solution was stirred for 1 h at room temperature, and 0.110 g of NH_4PF_6 (0.678 mmol) dissolved in 1 cm^3 of distilled THF was added to the mixture. After 1 h of stirring, the solution was placed in the refrigerator for 2 h. The precipitate that formed was filtered off under nitrogen. The solid was dissolved in toluene and the solution washed with degassed water (3 × 2 cm^3) and dried over degassed anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the orange precipitate was washed with 6 cm^3 of distilled hexane. The complex was recrystallized from THF/hexane. Yield: 0.5 g (82%). Anal. Calcd for $C_{44}H_{39}NO_2F_6P_2Pd$: C, 58.97; H, 4.39; N, 1.56. Found: C, 55.38; H, 4.40; N, 1.73. IR (KBr): 1612 (st, C═N), 1100 (st, P−O), 1050 (C−O), 841 (st, P−F). MS (FAB positive): *m*/*z* 750 ($[M - PF_6]^+$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): δ 124.93 ppm (minor), 132.26 ppm (major).

(η^3-1,3-Diphenylallyl)-{1-[(3′*S*,4′*S*)-3′-phenyl-4′-((dicyclohexylphosphinito)methyl)-3′,4′-dihydrooxazol-2′-yl]-2-methylphenyl-*N*,*P*}palladium(II) Hexafluorophosphate

Table 6. Crystal Data for Complexes 18 and 19

	18	**19**
empirical formula	$C_{26}H_{27}BF_4NO_2PPd$	$C_{27}H_{29}F_6NO_2P_2Pd$
formula wt	609.67	681.85
cryst dimens, mm^3	0.50 × 0.40 × 0.35	0.55 × 0.25 × 0.15
temp, K	298(2)	298(2)
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	11.757	9.8551(1)
b, Å	14.3783(2)	13.8146(1)
c, Å	15.4551(2)	21.6204(2)
V, Å^3	2612.62(5)	2943.49(7)
Z	4	4
calcd density, Mg m^{-3}	1.550	1.539
abs coeff, mm^{-1}	0.824	0.802
F(000)	1232	1376
transmissn factors (max; min)	1.0000; 0.8096	0.8892; 0.6667
scan type	ϕ and ω	ϕ and ω
θ range for data collecn, deg	1.93−28.29	1.75−28.28
no. of rflns collected	14 595	20 418
no. of indep rflns	6478 (R_{int} = 0.0267)	72538 (R_{int} = 0.0597)
completeness to θ_{max}, %	99.6	99.7
abs cor	semiempirical	semiempirical
no. of params refined, restraints	332, 0	381, 0
final R indices ($I > 2\sigma(I)$)	R1 = 0.0310	R1 = 0.0583
final wR2 indices (all data)[a]	wR2 = 0.0715	wR2 = 0.1165
weights[b] (*a*, *b*)	0.0366, 0.0540	0.0440, 1.9277
GOF on F^2	1.081	1.014
abs structure param[c]	0.02(2)	−0.02(4)
largest diff peak and hole, e Å^{-3}	0.289 and −0.712	0.631 and −0.566

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = \{\sum[w(F_o^2 - F_c^2)]/\sum[w(F_o^2)^2]\}^{1/2}$. [b] The weighting scheme employed was $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. [c] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876−881.

(26). In a purged Schlenk containing 0.131 mg (0.282 mmol) of **15** was added 5 cm^3 of freshly distilled toluene. A 0.094 mg portion (0.140 mmol) of $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)Cl]_2$ dissolved in toluene was then added. The yellow solution was stirred for 1 h at room temperature, and 0.046 g of NH_4PF_6 (0.282 mmol) dissolved in 1 cm^3 of distilled THF was added to the mixture. After 1 h of stirring, the solution was placed in the refrigerator for 2 h. The yellow precipitate that formed was filtered off under nitrogen. The solid was dissolved in toluene, washed with degassed water (3 × 2 cm^3), and dried over degassed anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the yellow precipitate was washed with 6 cm^3 of distilled hexane. The complex was recrystallized from THF/hexane. Yield: 0,14 g (70%). Anal. Calcd for $C_{44}H_{51}NO_2F_6P_2Pd$: C, 58.18; H, 5.62; N, 1.54. Found: C, 47.20; H, 4.87; N, 2.99. IR (KBr): 1607 (st, C═N), 1103 (st, P−O), 1079 (C−O), 831 (st, P−F). MS (FAB positive): *m*/*z* 762 ([M − PF_6]$^+$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): δ 151.50 ppm (major), 151.07 ppm (minor).

Crystallography. A prismatic yellow crystal of **18** and block colorless crystal of **19** were selected and mounted on a Bruker SMART CCD area detector single-crystal diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) operating at 50 kV and 30 mA. Crystal data are summarized in Table 6.

A total of 1271 frames of intensity data were collected over a hemisphere of the reciprocal space by a combination of three exposure sets. Each frame covered 0.3° in ω, and the first 50 frames were re-collected at the end of data collection to monitor crystal decay. The crystals used for the diffraction studies showed moderate decomposition during data collection, 2.2% in the case of **18** and 3.1% for **19**. Absorption corrections were applied using the SADABS program.[26] The structures were solved using the Bruker SHELXTL-PC software[27] by direct methods and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined in the riding mode.

General Procedure for Palladium-Catalyzed Allylic Alkylation. (a) Allylic Alkylation of *rac*-3-Acetoxy-1,3-diphenyl-1-propene (I). A 0.02 mmol portion of the appropriate complex (**16**−**22**) was dissolved in CH_2Cl_2 (2 cm^3). For catalytic systems containing ligands **14** and **15**, the catalytic precursor was generated in situ from $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and the appropriate ligand (0.02 mmol of Pd and 0.025 mmol of chiral ligand) dissolved in 2 cm^3 of CH_2Cl_2 for 30 min before adding the substrate. *rac*-3-Acetoxy-1,3-diphenyl-1-propene (252 mg, 1 mmol), dissolved in CH_2Cl_2 (2 cm^3), was added followed by dimethyl malonate (396 mg, 3 mmol), BSA (610 mg, 3 mmol), and a catalytic amount of KOAc. The mixture was stirred at room temperature until total conversion of substrate (monitored by TLC). Then, the solution was diluted with diethyl ether, filtered over Celite, and washed with saturated ammonium chloride solution (4 × 10 cm^3) and water (4 × 10 cm^3). The organic phase was dried over anhydrous Na_2SO_4 and filtered off, and the solvent was removed under reduced pressure. Purification of the product was done by column chromatography (SiO_2; ethyl acetate). The enantiomeric excesses were determined by HPLC on a Chiralcel OD column, using hexane/2-propanol (99/1) as eluent, in a flow of 0.3 cm^3/min.

(b) Allylic Alkylation of *rac*-3-Acetoxy-1-cyclohexene (III). The procedure was analogous to that described for *rac*-3-acetoxy-1,3-diphenyl-1-propene. Purification of the product was done by column chromatography (SiO_2; ethyl acetate). The enantiomeric excesses were determined by GC on a FS-cyclodex-β-I/P column.

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Supporting Information Available: NMR data for **16**−**26** (Tables S1 and S2) and X-ray data for **18** and **19** (Tables S3−S12 and Figures S1 and S2); X-ray data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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