Catalytic and Structural Studies on Complexes of a Binaphthyl−Phosphino−Oxazoline Auxiliary: The Meta Dialkyl Effect on Enantioselectivity

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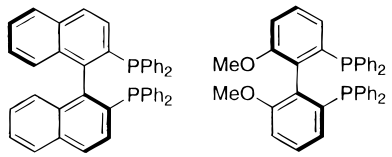
The chiral phosphino-oxazoline ligand (*S*,*R*)-2-[4-(isopropyl)oxazol-2-yl]-2′-bis(3,5-dimethylphenylphosphino)-1,1′-binaphthyl, **6b**, its Pd-dichloro complex, **9**, the *p*-cyanoaryl complex [PdBr(*p*-NC−C_6H_4](**6b**)], **10**, a model for the Heck reaction, the cationic 1,3-diphenylallyl derivative [Pd(η^3-PhCHCHCHPh)(**6b**)]OTf, **11**, a model for the allylic allylation, and the Rh- and Ir-1,5-COD compounds [M(1,5-COD)(**6b**)]BF_4, **12** and **13**, respectively, have been prepared. In enantioselective catalytic experiments, the presence of the 3,5-dimethylphenyl groups generally increases the observed ee. The solid-state structure of $PdCl_2$(**6b**), **9**, has been determined. 2-D and variable-temperature NMR experiments suggest that one of the two 3,5-dimethyl P-aryl rings interacts selectively with the remaining ligands. Consequently, the entire chiral pocket becomes slightly more rigid and the correlation with substrate improves.

Introduction

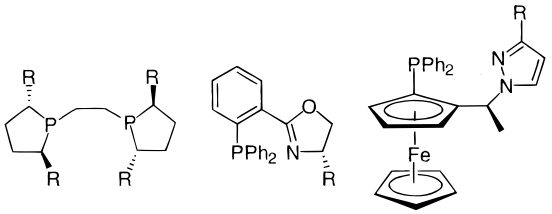
Enantioselective homogeneous catalysis represents a burgeoning area of chemical research. Apart from reduction with Rh and Ru complexes, increasing attention has been focused on the organometallic chemistry of palladium.[1] Amination and alkylation reactions of allyl derivatives[2] in addition to inter- and intramolecular carbon−carbon bond making processes (e.g., the Heck reaction[3]) are frequently reported to afford excellent enantiomeric excesses (ee's).[3d,e]

Much of the success in enantioselective homogeneous catalysis relies on the use of chiral auxiliaries containing tertiary phosphorus donors. Bidentate phosphine ligands such as Binap,[4] **1**, MeO−Biphep,[5] **2**, or Duphos,[6] **3**, and,



1 **2**

increasingly, P,N combinations, e.g., the Pfaltz/Helmchen phosphino-oxazoline,[7a] **4**, and derivatives thereof,[7] or the Togni pyrazole,[8] **5**, are now almost routinely employed with impressive success.



3, R = Me **4**, R = i-Pr **5** , R = Ph, naphthyl

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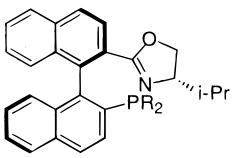
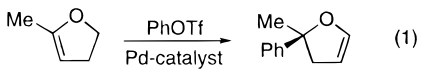
The P,N ligand **6a** has recently been reported by several groups.[9,10] We have prepared several of its Pd(0)



6a, R = Ph;
6b, R = 3,5-$Me_2C_6H_3$

complexes and found excellent enantioselectivity (up to 99% ee) in the allylic amination of a 1,3-diphenyl allyl precursor.[10] The solid-state structure of [Pd(η^3-PhCH-CHCHMe)(**6a**)]OTf, **7**, was determined[10] and showed two different diastereomeric cations within one unit cell; that is, both the *si* and *re* faces of the allyl crystallize together, the first example of this for a moderately large allyl ligand. The structures of both **7** and $PdCl_2$(**6a**), **8**, showed[10] that the oxazoline ring of **6a** is twisted relative to the P−Pd−N coordination plane, thus placing this ring substituent above and not below the coordination plane.

In connection with our studies correlating auxiliary structure and enantioselectivity, we have suggested that, in Ru, Pd, Rh, and Ir chemistry, 3,5-dialkylphenyl groups as P-substituents increase the rigidity of the chiral pocket, with increased ee's as a result.[11] An extreme case, the Heck phenylation of 5-methyl-2,3-dihydrofuran with phenyltriflate, shown in eq 1, re-



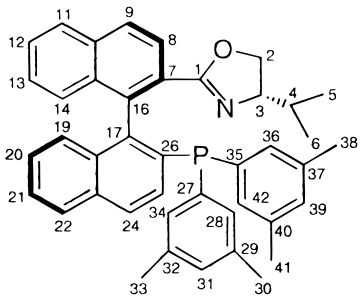
(1)

sulted in an ee increase of 78% (from 20 to 98% ee).[12] Apart from comparing ee's, we also showed that the bisphosphine MeO−Biphep ligand **2**, with 3,5-di-*tert*-butyl groups instead of phenyl, revealed relatively high barriers to rotation around the P−C(ipso) bonds in both Ru and Pd complexes.[11] We take this as one reflection of the crowding associated with the space proximate to where one expects to find complexed substrate. To further explore this 3,5-dialkyl effect on enantioselectivity, we have prepared the 3,5-dimethylphenyl P,N ligand **6b** and report here on structural and catalytic aspects of its chemistry.

Results

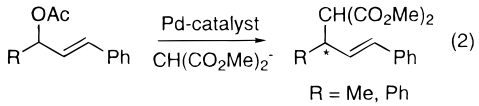
Ligand **6b** was prepared in analogy with **6a**.[10] The dichloro complex $PdCl_2$(**6b**), **9**, the *p*-cyanoaryl complex

Scheme 1



[PdBr(p-NC−C_6H_4](**6b**)], **10**, a model for the Heck reaction, the cationic 1,3-diphenylallyl derivative [Pd(η^3-PhCHCHCHPh)(**6b**)]OTf, **11**, a model for the allylic allylation, and the Rh and Ir compounds [M(1,5-COD)(**6b**)]BF_4, **12** and **13**, respectively, were prepared as described previously.[10−12] Scheme 1 shows the numbering scheme of the ligand.

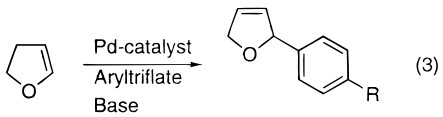
Catalytic Studies. The classical model reaction[3a] for the allylic alkylation is shown in eq 2. With ligands **6a,b**



(2)
R = Me, Ph

as auxiliaries, we find excellent chemical yields and, for R = Ph, ee's of 91%[13] and 97%, respectively, that is, the ee is better with the meta methyl substituents. A similar difference was observed for this same reaction using the chiral MeO−Biphep pair **2**, with a 3,5-di-*tert*-butyl analogue instead of the 3,5-dimethyl compound. The reaction of the unsymmetrical allyl, R = Me, afforded preferential attack at the smaller methyl terminus and poor ee's.

The Heck phenylation suggested by Hayashi,[14] shown in eq 3, was carried out using **6a,b**. Once again, for all



(3)
R = H, OMe, CO_2Me

three triflates, R = H, OMe, CO_2Me, the ee at ca. 86−90% is about 10−12% better with **6b** than with **6a**. No attempt was made to optimize the ee by varying solvent, temperature, or anion, since excellent results for this reaction are already known, e.g., ee >98%.[11,15,16] Table 1 shows ee's for both the allylation and Heck reactions. It would seem that it can be advantageous to use a 3,5-dialkyl variant of a P,N as well as a P,P chiral auxiliary.

X-ray Structure of 9. As the potential crowding in complexes of **6b** is not obvious, we have determined the solid-state structure of the dichloro compound $PdCl_2$(**6b**), **9**, by X-ray diffraction methods, and two views of

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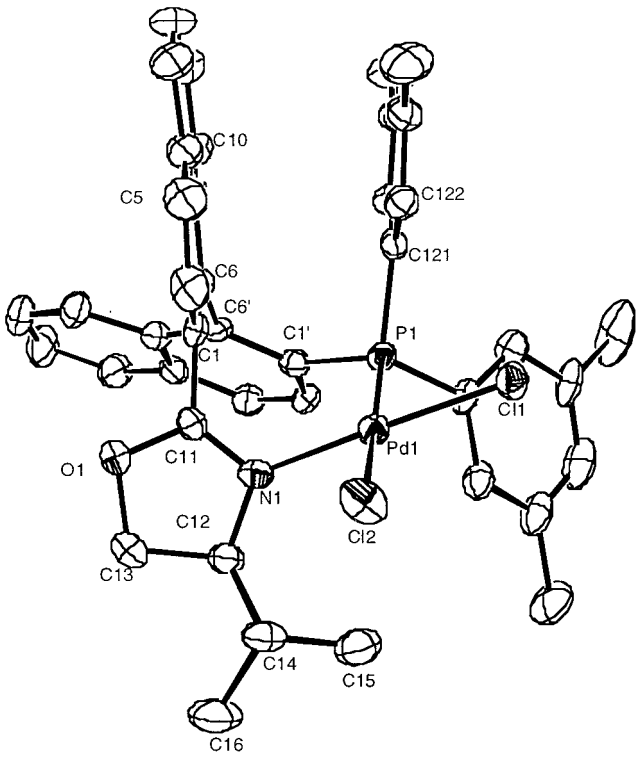

Figure 1. ORTEP view of **9** showing the coordination sphere, the stacking of the 3,5-dimethylphenyl P-aryl with one naphthyl moiety.

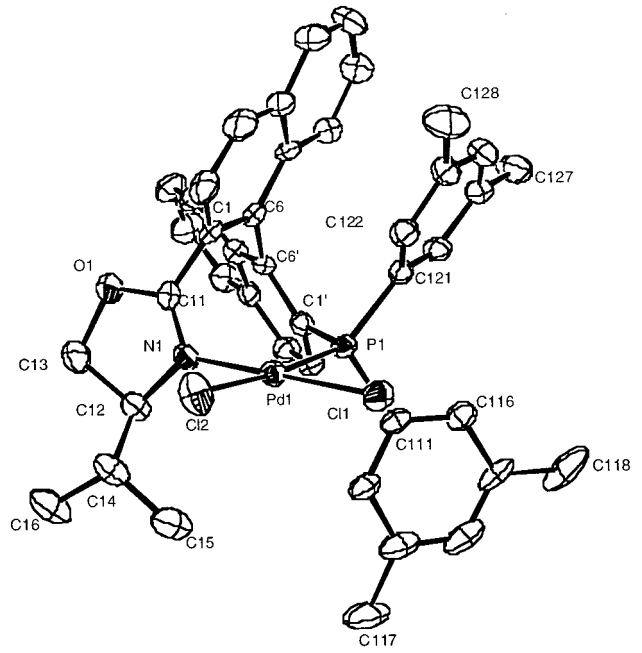

Figure 2. ORTEP view of **9** showing the oxazoline twisted away from the coordination plane.

the molecule are given in Figures 1 and 2. Details of the structure determination as well as a list of selected bond lengths and bond angles are given in Tables 2 and 3. The local coordination geometry is distorted square planar, with the four donor atoms deviating <0.1 Å from the plane defined by the Pd, P, N, and two Cl atoms.

The Pd−P(1), Pd−N(1), and two Pd−Cl separations are in good agreement with those found for the structure of $PdCl_2$(**6a**). The Pd−P(1), 2.2485(11) Å, and Pd−N(1), 2.030(3) Å, distances are relatively short.[17] Pd−Cl(2), trans to P(1), at 2.3671(11) Å, is longer than Pd(1)−Cl(1), 2.2887(11) Å. As expected (and noted earlier[9,10]), the oxazoline ring is twisted markedly out of the coordination plane, as indicated by the torsion angles P(1)−Pd(1)−N(1)−C(11), −71.9(3)°, and Cl(1)−Pd(1)−N(1)−C(11), −127(2)°. One 3,5-dimethylphenyl ring is "stacked"[18,19] with a binaphthyl moiety (see Figure 2) and lies on one side of the coordination plane, with

Table 1. Enantioselective Allylic Alkylation and Heck Reaction Results[a]

ligand	R	time (h)	yield (%)	ee (%)
		Heck Phenylation		
6a	H	72	85	73.8 (S)
6b	H	72	84	85.8 (S)
6a	OMe	48	81	74.8
6b	OMe	48	82	87.4
6a	COOMe	120	69	80.0
6b	COOMe	120	74	90.0
		Allylic Alkylation		
6a	Ph	2	99	91.0 (R)
6a	Me	1	98	21.0[b]
6b	Ph	2	99	97.0 (R)
6b	Me	0.5	95	17.0[c]

[a] The ee was determined by NMR methods using $Eu(hfc)_3$ as chiral shift reagent. In addition HPLC using ChiraGrom-2 (Heck chemistry) and OD-H (allylation) columns were employed to confirm the NMR results. Dimethyl malonate is used as nucleophile. [b]There are two regioisomers arising from attack at the methyl terminus (ee 21%) and at the phenyl terminus (ee not determined). The ratio of the isomers is 86:14, favoring attack at the methyl terminus. [c]The ratio of the isomers in this experiment is 90:10 in favor of attack at the methyl terminus.

Table 2. Crystal and Structure Refinement Data for $9\cdot C_5H_{14}$

formula	$C_{47}H_{52}Cl_2NOPPd$
mol wt	855.17
data coll T, K	200(2)
diffractometer	Bruker SMART CCD
cryst syst	monoclinic
space group	$P2_1$
a, Å	10.9585(4)
b, Å	16.5893(6)
c, Å	11.9765(4)
β, deg	105.57(1)
V, Å^3	2097.3(1)
Z	2
$\rho_{(calcd)}$, g cm^{-3}	1.354
μ, mm^{-1}	0.644
radiation	Mo Kα (graphite monochrom $\lambda = 0.71079$ Å)
measd reflns	$\pm h, \pm k, \pm l$
θ range, deg	$1.7 < \theta < 25.6$
no. data coll	15 741
no. ind data	7011
no. obsd data (n_o)	6047 [$\lvert I_o\rvert > 4.0\,\sigma(\lvert I\rvert)$]
transmission coeff	0.96226−0.90286
no. of params refined (n_v)	510
R_{av}[a]	0.035
R, R_w[2 b] (obsd reflns)	0.0343, 0.0653
R, R_w^2 (all data)	0.0478, 0.0706
GOF[c]	0.981

[a] $R_{av} = \sum\lvert F_o^2 - F_o^2{}_{,av}\rvert/\sum_i \lvert F_o^2\rvert$; $R = \sum(\lvert F_o - (1/k)F_c\rvert)/\sum\lvert F_o\rvert$. [b] $R_w^2 = [\sum w(F_o^2 - (1/k)F_c^2)^2/\sum w\lvert F_o^2\rvert^2]$ where $w = [\sigma^2(F_o^2) + (0.033P)^2 + 0.5838P]^{-1}$ and $P = \{[F_o^2 + 2.0(F_o^2)]/3.0\}$. [c] GOF $= [\sum_w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.

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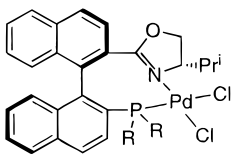
Table 3. Bond Lengths (Å) and Angles (deg) for 9

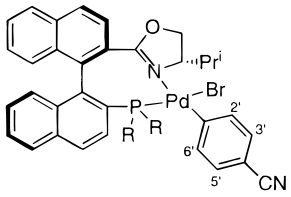
Bond Lengths			
Pd(1)−N(1)	2.030(3)	P(1)−C(1′)	1.841(4)
Pd(1)−P(1)	2.2485(11)	N(1)−C(11)	1.267(5)
Pd(1)−Cl(1)	2.2887(11)	N(1)−C(12)	1.499(5)
Pd(1)−Cl(2)	2.3671(11)	O(1)−C(11)	1.335(5)
P(1)−C(121)	1.821(4)	O(1)−C(13)	1.477(5)
P(1)−C(111)	1.818(4)		
Bond Angles			
N(1)−Pd(1)−P(1)	93.16(9)	C(111)−P(1)−C(1′)	103.76(17)
N(1)−Pd(1)−Cl(1)	177.79(10)	C(121)−P(1)−C(1′)	101.71(18)
P(1)−Pd(1)−Cl(1)	85.60(4)	C(111)−P(1)−C(121)	108.87(19)
N(1)−Pd(1)−Cl(2)	88.52(9)	C(111)−P(1)−Pd(1)	109.56(14)
P(1)−Pd(1)−Cl(2)	174.88(5)	C(121)−P(1)−Pd(1)	115.23(14)
Cl(1)−Pd(1)−Cl(2)	92.87(4)	C(1′)−P(1)−Pd(1)	116.81(13)
Torsion Angles			
P(1)−Pd(1)−N(1)−C(11)	−71.9(3)	P(1)−Pd(1)−N(1)−C(12)	106.0(3)
Cl(1)−Pd(1)−N(1)−C(11)	−127(2)	Cl(1)−Pd(1)−N(1)−C(12)	50(3)
Cl(2)−Pd(1)−N(1)−C(11)	103.2(3)	Cl(2)−Pd(1)−N(1)−C(12)	−78.8(3)

C(121) ca. 1.55 Å above this plane. The second 3,5-dimethylphenyl group appears remote from the binaphthyl, with C(111) ca. 1.40 Å below the coordination plane. The estimated ring−ring separations between the stacked aromatic groups are ca. 3.2−3.6 Å. The closest contacts to an ortho P-aryl carbon from the cis chloride, Cl-1, are H−C122 to Cl1, 2.84 Å and H−C112 to Cl1, 3.64 Å; all others are >4.0 Å.

NMR Spectroscopic Studies. With the structures of both dichloro compounds in hand we extended the comparisons of complexes **6a,b** via their variable-temperature and 2-D NMR spectra. Specifically, these studies should identify steric crowding and/or changes in the electronic characteristics of comparable complexes.

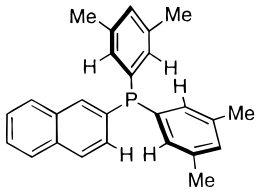


9, R = 3,5-$Me_2C_6H_3$



10, R = 3,5-$Me_2C_6H_3$

Figure 3 shows $^{31}P,^{1}H$ correlations for **9** in the aromatic region. The ambient-temperature spectrum (top) reveals three correlations: two from the phosphine ortho aryl protons (integral =2) and one from the single ortho naphthyl proton. It can be seen that one of the correlations stems from a very broad, two-proton signal. Cooling to 193 K affords the five nonequivalent ortho protons indicated in **14**, due to restricted rotation



14, non-equivalent aryl protons of compound **9**

around the P−C bonds. At 223 K, two of the four phosphine ortho aryl protons from one ring are well resolved and quite sharp (ca. δ 6.9 and ca. δ 7.9), whereas the remaining two are resolved but difficult to detect due to their >40 Hz line widths. Figure 4 shows the methyl region at ambient temperature and 193 K. Clearly, at ambient temperature one of the two methyl groups is already quite broad. The analogous dichloro complex with **6a** at room temperature does not show

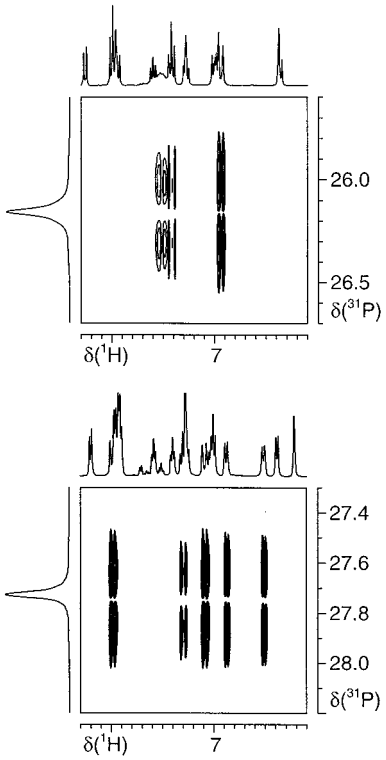


Figure 3. $^{31}P,^{1}H$ correlation for **9** at (top) ambient temperature with three correlations (the highest frequency of which is quite broad) and (bottom) at 193 K showing five strong correlations (400 MHz, CD_2Cl_2).

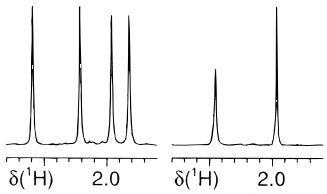
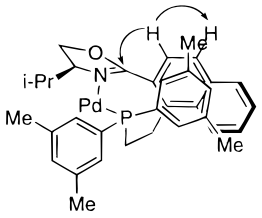


Figure 4. Methyl region of **9** at ambient temperature, showing two aryl-methyl signals, one of which is broad (right) and at 193 K, showing four nonequivalent aryl-methyl resonances (left) (400 MHz, CD_2Cl_2).

the very broad resonance in the aromatic region. We assign the more freely rotating P-aryl group to that 3,5-dimethylphenyl ring, which is stacked. This is surprising in that the X-ray data suggest just the opposite assignment based on the contacts, noted above, between an ortho P-aryl carbon and the cis chloride, Cl-1. The distinction between the two 3,5-dimethylphenyl groups was made as follows: (i) a three-bond $^{13}C,^{1}H$ correlation, from the imine oxazoline carbon, assigns the adjacent ortho naphthyl proton; (ii) a proton COSY reveals its proximate coupling partner (see **15**); and (iii) ambient-



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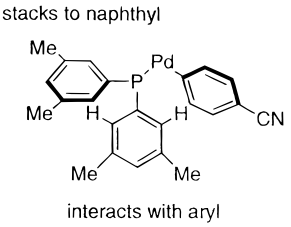
temperature NOEs from these two protons to the methyls and aryl protons of the stacked ring identify this 3,5-dimethylphenyl ring. The restricted rotation occurs only at the phosphine aryl ring, which does *not* stack with the naphthyl.[20]

Given the ee changes in our Heck reactions, we looked at the ^{1}H spectra for the (admittedly poor) model[21] bromoaryl compound **10**. The $^{31}P,^{1}H$ correlations in the aromatic region for this *p*-cyanophenyl derivative at room temperature and at 193 K are given in Figure 5. Again, the ambient-temperature spectrum (bottom) reveals the expected three correlations: two from the phosphine ortho aryl protons and the single ortho naphthyl proton. At the lower temperature (top) there are now four correlations: one appears as a doublet at δ ca. 6.5, with integral = 2, from *equivalent* ortho protons of one ring. Two further correlations of integral = 1 (one at δ ca. 5.6, the other at ca. δ ca. 6.5, so that this latter correlation appears to overlap with that of integral = 2), plus the naphthyl proton, δ ca. 7.7, complete the set. Again, NOE spectroscopy proves that the P−C(ipso) restricted rotation occurs only at the phosphine aryl ring which does not stack with the naphthyl moiety (see **16** and Figure 1).



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The two-proton doublet and the two methyl groups in meta position from the ring that stacks are always sharp from ambient temperature down to 183 K. Consequently, although these aromatic groups stack,

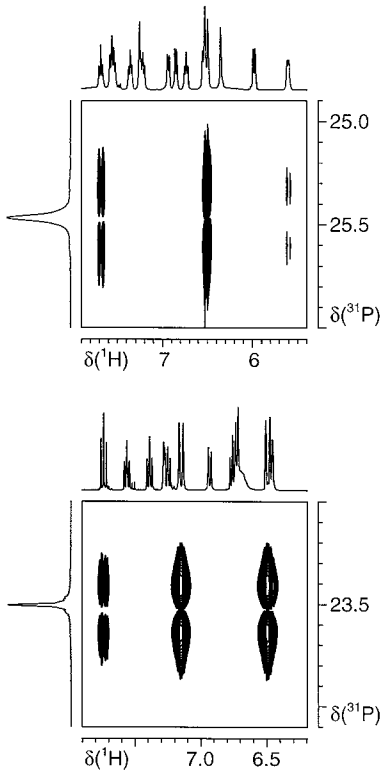
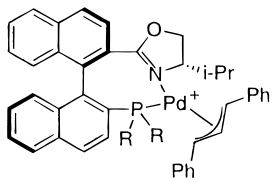


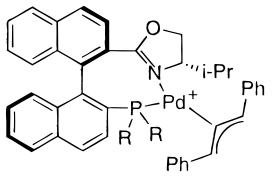
Figure 5. $^{31}P,^{1}H$ correlation for **10** at (bottom) ambient temperature with three clear correlations and (top) at 193 K showing four correlations, two of which overlap. The sharp doublet of integral = 2 overlaps with the broad doublet of integral = 1 in the region 6.5−6.6 ppm.

there is a very low barrier to rotation around the P−C(ipso) bond. These NMR results for both **9** and **10** suggest that one of the two P-aryl rings interacts with the remaining ligands more than the other. The lower trace of Figure 5 reveals a broad resonance at ca. 6.6 ppm, due to the four protons from the σ-bonded *p*-cyanoaryl ligand in **10**. We have prepared the analogous *p*-cyanoaryl complex with **6a,** and this broad resonance is absent.

The model cationic 1,3-diphenylallyl complex **11** exists in CD_2Cl_2 solution as a mixture of syn/syn endo and exo isomers, with the former the most abundant (**11a**/**11b** = ca. 3:1). The descriptors exo and endo refer to the



11a (endo), R = 3,5-dimethylphenyl



11b (exo), R = 3,5-dimethylphenyl

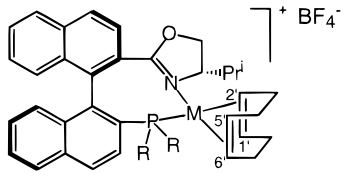
position of the central allyl proton relative to the i-Pr group (remember that the i-Pr group is not "below" the

(20) Since one P-aryl ring rotates freely, despite the stacking interaction, its ortho protons come close enough to the proximate naphthyl moiety to afford modest NOEs

(21) From a steric point of view, an olefin aryl complex would be a much better model.

coordination plane, as the dotted line might indicate (see X-ray structure above). Using our standard approach[22] for allyl species, NMR assignments for both diastereomers were made, and these are given in the Experimental Section. Interestingly, in contrast to **9** and **10**, none of the ^{1}H resonances suggest dynamic character. Further, 2-D exchange spectroscopy shows that (on the NMR time scale) **11a**,**b** are not in equilibrium. Selective NOEs between the allyl protons and the proximate i-Pr spins readily allow the distinction between **11a** and **11b**. With this assignment, a ^{13}C,^{1}H correlation then pinpoints the four allyl termini: $\delta = 102.4$ (trans to P) and $\delta = 67.4$ (trans to N) for **11a** and $\delta = 89.2$ (trans to P) and $\delta = 82.0$ (trans to N) for **11b**. The ^{13}C chemical shifts for the analogous 1,3-diphenylallyl cation with **6a** are as follows: endo, $\delta = 102.9$, $\delta = 67.6$, and exo, $\delta = 89.7$, $\delta = 82.6$, so that (at least in the ground state) there is no compelling evidence for bonding differences due to the meta methyl groups. If we continue to assume[23,24] that (i) the allyl pseudo-trans to the P-donor will be attacked preferentially and (ii) the carbon nucleophile attacks the highest frequency (most olefin-like) terminus, then one would predict the product from **11** to develop from attack at the $\delta = 102.4$ center and thus have the (*R*) configuration, in agreement with the observed result. The observed ee does not reflect the measured diastereomer populations.[25]

Using 2-D exchange spectroscopy, we noted earlier[26] that Rh-1,5-COD complexes of a variety of chelating ligands show a specific olefin-exchange process in which H-1′ and H-2′ exchange selectively with H-5′ and H-6′, respectively, i.e., the diolefin appears to rotate. Although rotation is not necessarily the correct mechanism,[26] this exchange was also observed for the Rh- and Ir-1,5-COD complexes of **6a**. To further our comparison of **6b** with **6a**, we measured the corresponding 2-D exchange spectra for **12** and **13** and show a section of the spectrum



12, M = Rh; **13**, M = Ir. R = 3,5-$Me_2C_6H_3$

for **13** in Figure 6. As can be seen, the selective exchange is present in **13** (and also in **12**) as well. Table 4 shows ^{13}C chemical shift data for the diene carbons in [M(1,5-COD)(**6a** or **6b**)]BF_4, M = Rh, Ir. These ^{13}C chemical

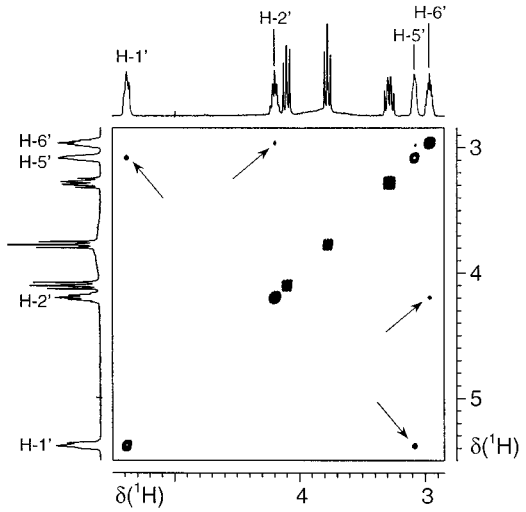


Figure 6. 2-D exchange spectrum for **13** showing the selective exchange between the four olefinic protons of the complexed 1,5-COD ligand, i.e., 1′ with 5′ and 2′ with 6′ (400 MHz, CD_2Cl_2).

Table 4. ^{13}C Data for 12, 13 and the 6a Analogues

	[Rh(1,5-COD)(P,N)]$^+$		[Ir(1,5-COD)(P,N)]$^+$	
	6a	**6b**	**6a**	**6b**
C1′	99.1	100.6	89.7	90.8
C2′	97.6	95.9	82.4	80.2
C5′	82.5	85.1	72.8	74.9
C6′	77.4	76.9	62.4	62.1

shift data are quite similar for both ligands, suggesting (as do the exchange data) only small differences in the donor characteristics of these P,N ligands. Interestingly, these ^{13}C data do support asymmetry in the mode of 1,5-COD bonding for all four complexes, in that one observes substantial differences in chemical shift for the two carbons of one double bond, especially for C5′ and C6′.

Discussion and Conclusions

The palladium catalytic results confirm that the 1,3-dialkyl effect on enantioselectivity exists in our phosphino-oxazoline system and that it is not limited to auxiliaries with two P-donors.[11,12]

In the recent literature one finds a number of cases in which the use of 3,5-dialkyl substituents improves enantioselectivity. There are examples from hydrogenation catalysts of Rh,[27,28] Ru,[29] and Ir[30] plus examples from Pd-allyl[31] and boron Lewis acid[32] chemistry. Although the ee enhancement can be quite large,[27,28,31] no explanation for the effect is offerred.

Turning to our comparisons, there seems to be little difference in the donor strengths between **6a** and **6b** on the basis of both the X-ray structure and the NMR allyl and olefin chemical shift data. However, for **9** and

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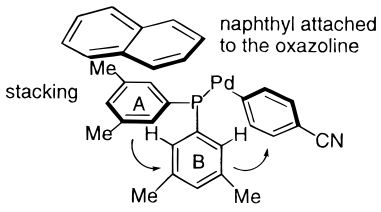
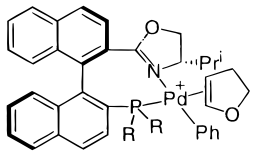
10 the NOESY and variable-temperature NMR studies suggest that *one* of the two P-aryl rings, that in pseudoequatorial position, moves closer to the space to be occupied by substrate, thus slightly restricting the chiral pocket. The biaryl backbone is an important structural feature in that it contributes to a buttressing effect. The P-aryl ring A, in **17**, cannot move toward the



17

naphthyl (the stacking results in separations of ca. 3.2−3.6 Å), with the result that the (ipso)C−P−C(ipso) angle can only open toward the space occupied by substrate. The entire chiral pocket becomes slightly more rigid, and the correlation with substrate improves. Consequently, we conclude that the effect on enantioselectivity arises due to a subtle change in steric interactions.

The cis chloride and cis aryl ligands of **9** and **10** are not sterically demanding (especially when the remaining ligand is a halogen). Although we do observe differences between complexed **6a** and **6b**, as reflected by the NMR line widths, the observation of selective restricted rotation about the P−C(ipso) bonds requires low temperatures. In the Heck chemistry of eq 3, a transition state with both complexed aryl *and* (in-plane) olefin ligands will be generated,[33,34] e.g., **18**. As complexed



18 R = 3,5-dimethylphenyl

dihydrofuran is larger than, for example, Cl or Br, the steric interaction should be more pronounced. The Pd-1,3-diphenylallyl and Rh- and Ir-(1,5-COD) complexes do not show broad NMR lines at room temperature because the "bite angle" of these organometallic chelating ligands is rather small. This is another way of stating that the observed effect on ee will be substrate dependent. The P-donor of complexed **6b** is not very intrusive, and the buttressing is minimal. Clearly, 3,5-di-$SiMe_3$ or 3,5-di-*tert*-butyl analogues might be more interesting, and preparative efforts in this direction are in progress.

Experimental Section

THF and ether were distilled from sodium benzophenone ketyl; dichloromethane and DMSO, from CaH_2. Acetonitrile was distilled from P_2O_5. Diarylphosphine oxides were prepared from dibutyl phosphite by a Grignard reaction. 5-Bromo-*m*-xylene was purchased from Lancaster. (*R*)-1,1′-Binaphthalene-2,2′-diylbis(triflurometh anesulfonate) was purchased from Fluxa. Ligand **6a** was prepared by our earlier published method.[10] The chloro-bridged dimer (η^3-PhCHCHCHPh)$_2$Pd$_2$-Cl_2 was prepared by the standard methods. (TMEDA)Pd(Br)-(4-C_6H_4CN) was prepared by literature methods.[35] Routine ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker DPX-250, 300, and 400 MHz spectrometers. Chemical shifts are given in ppm, and coupling constants (*J*) are given in Hz. The two-dimensional ^{1}H NOESY and ^{31}P,^{1}H-correlation experiments were carried out at 400 MHz. Elemental analyses and mass spectroscopic studies were performed at ETHZ.

Crystallography Colorless crystals of **9**, suitable for X-ray diffraction, were obtained by crystallization from CH_2Cl_2−ether and are air stable. A prismatic single crystal was mounted, for the data collection, on a glass fiber at a random orientation on a Bruker SMART CCD diffractometer and cooled by a nitrogen gas stream device to 200(2) K. The space group was unambiguously determined from the systematic absences, whereas the cell constants were refined, at the end of the data collection, using 7718 reflections ($2\theta_{max} \leq 25°$).

Data were collected by using an ω scans, in steps of 0.3 deg, up to $2\theta_{max} \leq 51.2°$; for each of the resulting 2142 "frames", the counting time was 20 s. The collected intensities were corrected for Lorentz and polarization factors by using the data reduction software SAINT.[36] An empirical absorption correction (based on the intensities of symmetry-related reflections)[37] was also applied. Selected crystallographic and other relevant data are listed in Table 2 and in Table S1. The standard deviations on intensities were calculated in terms of statistics alone, while those on F_o^2 were calculated as shown in Table S1.

The structure was solved by direct and Fourier methods and refined by full-matrix least-squares,[38] minimizing the function $[\sum w(F_o^2 - (1/k)F_c^2)^2]$. During the refinement the Fourier difference maps revealed a chlathrated molecule of solvent (*n*-pentane) that was refined without constraint. Anisotropic displacement parameters were used for all atoms. The contribution of the hydrogen atoms, in their calculated position, was included in the refinement using a riding model (U(H) = $1.5U_{(\text{bonded atom})}$ (Å^2)). The handedness of the structure was tested by refining the Flack parameter.[39] No extinction correction was deemed necessary. Upon convergence, the final Fourier difference map showed no significant peaks. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature[40] All calculations were carried out by using the PC version of the SHELX-97 programs.[38]

Synthesis of 6b. (*R*)-(+)-2-Cyano-2′-(3,5-dimethylphenylphosphinyl)-1,1′-binaphthyl was synthesized from (*R*)-1,1′-binaphthalene-2,2′-diylbis(triflurometh anesulfonate) and bis-(3,5-dimethylphenyl)phosphineoxide using a method similar to that used for synthesis of ligand **6a**. A mixture of (*R*)-(+)-2-cyano-2′-(3,5-dimethylphenylphosphinyl-1,1′-binaphthyl (535 mg, 1 mmol), (*S*)-valinol (140 mg, 1.35 mmol), and fused zinc chloride (327 mg, 2.4 mmol) in chlorobenzene (20 mL) was refluxed for 48 h under Ar. The reaction mixture was cooled

(33) We have not been able to detect such an intermediate. Brown et al.[34] have suggested that the olefin insertion is rapid.

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to room temperature, quenched with saturated NH_4Cl (10 mL), and extracted with dichloromethane (3 × 20 mL). The dichloromethane solution was washed with water and brine and dried with $MgSO_4$. The solvent was distilled, and the residue was dried under vacuum. The crude residue was then suspended in xylene (15 mL). Triethylamine (2.8 mL, 20.1 mmol) was added, followed by trichlorosilane (500 μL, 5 mmol) at 0 °C. The reaction mixture was heated slowly to 120 °C and maintained at this temperature for 5 h with stirring. After cooling to room temperature, the solution was diluted with ether and quenched with a few drops of $NaHCO_3$. The resulting suspension was filtered through Celite and the Celite washed with copious amount of ether. The combined organic layer was dried over $MgSO_4$ and the solvent distilled under reduced pressure. The residue was purified via column chromatography using a silica gel column (elution with 10% ethyl acetate in hexane, $R_f = 0.3$) to afford the product, **6b**, as a white solid. After crystallization from CH_2Cl_2−ether one obtains 525 mg, (87%) of product: mp = 95 °C. Anal. Calcd for $C_{42}H_{40}NOP$: C, 83.28; H, 6.66; N, 2.31. Found: C, 83.31; H, 6.78; N, 2.36. MS (EI): 605 (M+, 55), 535 (65), 408 (100). ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 3.84 (dd, $^2J_{HH} = 8.1$, $^3J_{HH} = 9.5$, *H*-2), 3.59 (m, *H*-3), 3.45 (t, $^2J_{HH} = 8.1$, $^3J_{HH} = 8.1$, *H*-2), 2.28 (s, C*H*$_3$), 2.14 (s, C*H*$_3$), 1.35 (m, H-4), 0.63 (d, $^3J_{HH} = 6.7$, *H*-6 or *H*-5), 0.60 (d, $^3J_{HH} = 6.7$, *H*-5 or *H*-6). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): −14.1 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 72.8 (s, *C*-3), 70.6 (s, *C*-2), 33.2 (s, *C*-4), 21.5 (s, *C*H$_3$), 21.3 (s, *C*H$_3$), 18.8 (s, *C*-6 or *C*-5), 18.4 (s, *C*-5 or *C*-6).

$PdCl_2$(6b), 9. A solution of $PdCl_2(PhCN)_2$ (38.4 mg, 0.1 mmol) and **6b** (61 mg, 0.1 mmol) in dichloromethane (5 mL) was strried for 3 h. The solvent was removed under reduced pressure. The crude complex was recrystallized from dichloromethane−ether and obtained as yellow plates. Yield = 71 mg, 91%. Anal. Calcd for $C_{42}H_{40}NOPCl_2Pd$ (783.1): C, 64.42, H, 5.15; N. 1.79. Found: C, 64.38; H, 5.28; N, 1.89. MS (FAB): 748 (M^+ − Cl, 70), 364 (100). ^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): 8.26 (d, $^3J_{HH} = 8.3$, *H*-9), 8.01 (d, $^3J_{HH} = 8.3$, *H*-8), 7.96 (m, *H*-11, *H*-19 and *H*-20), 7.60 (m, *H*-21), 7.52 (br, *H*-28 and *H*-34), 7.42 (m, *H*-25 and *H*-12), 7.28 (m, *H*-22 and *H*-31), 6.99 (m, *H*-13 and *H*-24), 6.94 (d, $^3J_{PH} = 12.2$, *H*-36 and *H*-42), 6.37 (s, *H*-39), 6.36 (d, $^3J_{HH} = 8.5$, *H*-14), 4.12 (t, $^2J_{HH} = 8.7$, $^3J_{HH} = 8.7$, trans *H*-2), 3.61 (m, *H*-3), 3.44 (dd, $^2J_{HH} = 8.7$, $^3J_{HH} = 9.4$, cis *H*-2), 3.00 (m, *H*-4), 2.45 (s, *H*-30 and *H*-33), 1.97 (s, *H*-38 and *H*-41), 1.35 (d, $^3J_{HH} = 6.6$, *H*-5 or *H*-6), 0.93 (d, $^3J_{HH} = 6.6$, *H*-6 or *H*-5). ^{31}P NMR (CD_2Cl_2, 298 K, 300 MHz): 26.2 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 300 MHz): 170.6 (d, $^3J_{PC} = 3.3$, *C*-1), 73.4 (s, *C*-3), 72.6 (s, *C*-2), 29.3 (s, *C*-4), 21.7 (s, *C*-30 and *C*-33), 21.5 (s, *C*-5 or *C*-6), 21.1 (s, *C*-38 and *C*-41), 16.6 (s, *C*-6 or *C*-5).

Synthesis of PdBr(*p*-CNC_6H_4)(6b), 10. A solution of PdBr(*p*-CNC_6H_4)(TMEDA) (40.5 mg, 0.1 mmol) and ligand **6b** (60.6 mg, 0.1 mmol) in THF (4 mL) was heated at 60 °C for 10 h. The solution was cooled to room temperature, and the THF was removed under reduced pressure. The residue was washed with ether (3 × 2 mL). The yellow complex thus obtained was recrystallized from dichloromethane−ether. Yield = 70. 5 mg, 79.0%. Anal. Calcd for $C_{49}H_{44}N_2OPBrPd$ (894.23): C, 65.82; H, 4.96; N, 3.13. Found: C, 65.09; H, 5.14; N, 3.28. MS (FAB): 813 (M^+ − Br, 15), 711 (21), 364 (100). ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 8.36 (d, $^3J_{HH} = 8.0$, *H*-9), 8.10 (d, $^3J_{HH} = 8.3$, *H*-8), 8.00 (m, *H*-11, *H*-22 and *H*-24), 7.74 (t, $^3J_{PH} = 8.5$, $^3J_{HH} = 8.4$, *H*-25), 7.56 (m, *H*-21), 7.39 (m, *H*-12), 7.28 (s, *H*-31), 7.26 (m, *H*-20), 7.15 (d, $^3J_{PH} = 12.1$, *H*-28 and *H*-34), 6.93 (d, $^3J_{HH} = 8.4$, *H*-19), 6.77 (m, *H*-13), 6.73 (br, *H*-1′, *H*-2′, *H*-3′ and *H*-4′), 6.49 (d, $^3J_{PH} = 12.3$, *H*-36 and *H*-42), 6.46 (s, *H*-39), 6.1 (d, $^3J_{HH} = 8.6$, *H*-14), 4.10 (dd, $^2J_{HH} = 9.6$, $^3J_{HH} = 8.8$, trans *H*-2), 3.72 (dd, $^2J_{HH} = 9.6$, $^3J_{HH} = 8.8$, cis *H*-2), 3.51 (m, *H*-3), 2.77 (m, *H*-4), 2.42 (s, *H*-30 and *H*-33), 1.84 (s, *H*-38 and *H*-41), 1.42 (d, $^3J_{HH} = 6.6$, *H*-5 or *H*-6), 0.91 (d, $^3J_{HH} = 6.6$, *H*-6 or *H*-5). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 23.5 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 168.7 (s, *C*-1), 156.3 (s, *C*-1′), 133.8 (d, $^2J_{PC} = 12.3$, *C*-36, *C*-42), 132.1 (d, $^2J_{PC} = 11.4$, *C*-28, *C*-34), 127.8 (d, $^2J_{PC} = 5.6$, *C*-25), 120. 3 (s, *C*N), 73.3 (s, *C*-3), 72.9 (s, *C*-2), 30.2 (s, *C*-4), 21.7 (s, *C*-30 and *C*-33), 20.9 (s, *C*-38 and *C*-41), 22.4 (s, *C*-5 or *C*-6), 17.5 (s, *C*-6 or *C*-5).

Synthesis of PdBr(*p*-CNC_6H_4)(6a). The procedures were similar to those for **10**. Yield = 69 mg, 82%. Anal. Calcd for $C_{45}H_{36}N_2OPBrPd$ (838.09): C, 64.49; H, 4.33; N, 3.34. Found: C, 63.82; H, 4.99; N, 3.58. MS (FAB): 757 (M^+ − Br, 26), 657 (36), 550 (29), 364 (100). ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 4.12 (m, *H*-2), 3.64 (m, *H*-2 and *H*-3), 2.78 (m, *H*-4), 1.34 (d, $^3J_{HH} = 6.7$, *H*-5 or *H*-6), 0.93 (d, $^3J_{HH} = 6.7$, *H*-6 or *H*-5). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 22.3 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 72.9 (s, *C*-3), 72.8 (*C*-2), 30.2 (s, *C*-4), 21.9 (s, *C*-5 or *C*-6), 17.14 (s, *C*-6 or *C*-5).

[Pd(η^3-PhCHCHCHPh)(6b)]$^+CF_3SO_3^-$, 11. A solution of [PdCl(η^3-PhCHCHCHPh)]$_2$ (33.5 mg, 0.05 mmol) and CF_3SO_3-Ag (25.7 mg, 0.1 mmol) in acetone (2 mL) was stirred for 1 h in the dark at room temperature. The AgCl formed was removed by filtration through Celite and the Celite washed with acetone. Ligand **6b** (61 mg, 0.1 mmol) in dichloromethane (1 mL) was added to the filtrate with stirring. Stirring was continued for 1 h, and then the solvent was evaporated under reduced pressure. The crude product formed was recrystallized from dichloromethane−hexane. Yield = 82 mg, 78%. Anal. Calcd for $C_{58}H_{53}NO_4F_3PSPd$ (1054.52): C, 66.06; H, 5.07; N, 1.33. Found: C, 65.86; H, 5.15; N, 1.28. MS (FAB): 904 (M^+ − CF_3SO_3) (100). Major isomer (endo) ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 6.33 (dd, $^3J_{HH} = 13.7$, $^3J_{HH} = 10.6$, *H*-2′), 5.91 (dd, $^3J_{HH} = 13.7$, $^3J_{PH} = 9.1$, *H*-1′), 4.49 (d, $^3J_{HH} = 10.6$, *H*-3′), 3.87 (m, cis *H*-2), 3.61 (dd, $^3J_{HH} = 9.3$, $^2J_{HH} = 12.3$, trans *H*-2), 3.10 (m, *H*-3), 2.22 (s, *H*-30 and *H*-33), 2.02 (s, *H*-38 and *H*-41), 1.18 (d, $^3J_{HH} = 6.6$, *H*-5 or *H*-6), 0.39 (d, $^3J_{HH} = 6.6$, *H*-6 or *H*-5), 0. 09 (m, *H*-4). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 30.4 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 108.7 (d, $^2J_{PC} = 5.4$, *C*-2′), 102.4 (d, $^2J_{PC} = 22.1$, *C*-1′), 74.4 (s, *C*-2), 73.7 (s, *C*-3), 67.4 (s, *C*-3′), 30.8 (s, *C*-4), 22.9 (s, *C*-5 or *C*-6), 21.3 (s, *C*-30 and *C*-33), 21.2 (s, *C*-38 and *C*-41), 18.2 (s, *C*-6 or *C*-5). Minor isomer (exo) ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 6.51 (m, *H*-2′), 5.54 (t, $^3J_{HH} = 11.6$, $^3J_{PH} = 11.6$, *H*-1′), 4.55 (d, $^3J_{HH} = 13.0$, *H*-3′), 4.07 (m, *H*-3), 3.87 (m, trans *H*-2), 3.10 (m, cis *H*-2), 2.49 (s, *H*-30 and *H*-33), 1.91 (s, *H*-38 and *H*-41), 1.00 (d, $^3J_{HH} = 6.9$, *H*-5 or *H*-6), 0.12 (d, $^3J_{HH} = 6.9$, *H*-6 or *H*-5). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 30.1 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 110.1 (d, $^2J_{PC} = 7.0$, *C*-2′), 89.2 (d, $^2J_{PC} = 26.5$, *C*-1′), 82.0 (s, *C*-3′), 72.6 (s, *C*-3), 71.2 (s, *C*-2), 29.6 (s, *C*-4), 21.6 (s, *C*-30 and *C*-33), 21.1 (s, *C*-38 and *C*-41), 19.8 (s, *C*-5 or *C*-6), 13.8 (s, *C*-6 or *C*-5).

Synthesis of [Rh(1,5-COD)(6b)]BF_4, 12. A solution of $[Rh(COD)_2]^+BF_4^-$ (20 mg, 0.05 mmol) and ligand **2** (30 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 2 h. The solvent was evaporated under reduced pressure, and the residue was washed with hexane. The complex obtained was recrystallized from CH_2Cl_2−ether. Yield = 40 mg, 89%. Anal. Calcd for $C_{50}H_{52}BNOF_4PRh$ (903.7): C, 66.46; H, 5.8; N, 1.55. Found: C, 66.4; H, 5.75; N, 1.51. MS (FAB): 816 (M^+ − BF_4) (100), 708.2 (29). ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 8.40 (d, $^3J_{HH} = 8.4$, *H*-9), 8.11 (d, $^3J_{HH} = 8.3$, *H*-11), 8.06 (d, $^3J_{HH} = 8.7$, *H*-24), 7.99 (d, $^3J_{HH} = 8.2$, *H*-22), 7.91 (d, $^3J_{HH} = 8.4$, *H*-8), 7.67 (dd, $^3J_{HH} = 8.7$, $^3J_{PH} = 7.7$, *H*-25), 7.58 (m, *H*-12 and *H*-21), 7.26 (m, *H*-20, *H*-28, *H*-31 and *H*-34), 7.10 (m, *H*-13), 6.76 (m, *H*-19, *H*-36 and *H*-42), 6.66 (s, *H*-39), 6.39 (d, $^3J_{HH} = 8.3$, *H*-14), 5.31 (br, *H*-1′), 4.88 (br, *H*-2′), 4.08 (t, $^2J_{HH} = 9.4$, $^3J_{HH} = 9.4$, trans *H*-2), 3.69 (t, $^2J_{HH} = 9.4$, $^3J_{HH} = 9.4$, cis *H*-2), 3.17 (br, *H*-5′ and *H*-6′), 3.08 (m, *H*-3), 2.43 (s, *H*-30 and *H*-33), 2.03 (m, *H*-4), 2.03 (s, *H*-38 and *H*-41), 1.41 (d, $^3J_{HH} = 6.8$, *H*-6 or *H*-5), 0.87 (d, $^3J_{HH} = 6.8$, *H*-5 or *H*-6). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 23.49 (d, $^1J_{RhP} = 148.1$). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 170.1 (s, *C*-1), 100.6 (t, $^1J_{RhC} = 9.4$, $^2J_{PC} = 9.4$, *C*-1′), 95.9 (dd, $^1J_{RhC} = 12.2$, $^2J_{PC} = 7.9$, *C*-2′), 85.1 (d, $^1J_{RhC} = 12.5$, *C*-6′ or *C*-5′), 76.9 (d, $^1J_{RhC} = 12.2$, *C*-5′

or *C*-6′), 73.5 (s, *C*-3), 71.9 (s, *C*-2), 21.9 (s, *C*-6 or *C*-5), 21.7 (s, *C*-30 and *C*-33), 21.2 (s, *C*-38 and *C*-41), 16.5 (s, *C*-5 or *C*-6).

Synthesis of [Ir(1,5-COD)(6b)]BF_4, 13. This was prepared as with **12** using $[Ir(COD)_2]BF_4^-$ (25 mg, 0.05 mmol). Yield: 43 mg, 88%. Anal. Calcd for $C_{50}H_{52}BNOF_4PIr$ (992.97): C, 60.48; H, 5.28; N, 1.41. Found: C, 60.13; H, 5.65; N, 1.73. MS (FAB): 906.3 ($M^+ - BF_4$) (53.5), 712.0 (100). ^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): 8.29 (d, $^3J_{HH}$ = 8.5, *H*-9), 8.11 (d, $^3J_{HH}$ = 8.5, *H*-24), 8.00 (d, $^3J_{HH}$ = 8.52, *H*-11 and *H*-22), 7.83 (d, $^3J_{HH}$ = 8.52, *H*-8), 7.74 (t, $^3J_{PH}$ = 8.5, $^3J_{HH}$ = 8.5, *H*-25), 7.58 (m, *H*-21), 7.50 (m, *H*-12), 7.24 (m, *H*-20 and *H*-31), 7.12 (d, $^3J_{PH}$ = 11.3, *H*-28 and *H*-34), 6.97 (m, *H*-13), 6.79 (d, $^3J_{PH}$ = 11.3, *H*-36 and *H*-42), 6.76 (d, $^3J_{HH}$ = 8.3, *H*-19), 6.50 (s, *H*-39), 6.21 (d, $^3J_{HH}$ = 8.5, *H*-14), 5.38 (br, *H*-1′), 4.21 (m, *H*-2′), 4.10 (dd, $^2J_{HH}$ = 9.4, $^3J_{HH}$ = 11.2, trans *H*-2), 3.76 (t, $^2J_{HH}$ = 9.4, $^3J_{HH}$ = 9.4, cis *H*-2), 3.28 (m, *H*-3), 3.08 (br, *H*-5′), 2.97 (m, *H*-6′), 2.40 (s, *H*-30 and *H*-33), 2.25 (m, *H*-4), 1.97 (s, *H*-38 and *H*-41), 1.41 (d, $^3J_{HH}$ = 6.6, *H*-5 or *H*-6), 0.91 (d, $^3J_{HH}$ = 6.6, *H*-6 or *H*-5). ^{31}P NMR (CD_2Cl_2, 298 K, 300 MHz): 19.76 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 300 MHz): 170.9 (s, *C*-1), 90.8 (d, $^2J_{PC}$ = 9.1, *C*-1′), 80.2 (d, $^2J_{PC}$ = 16.8, *C*-2′), 76.0 (s, *C*-3), 74.9 (s, *C*-5′), 72.5 (s, *C*-2), 62.1 (s, *C*-6′), 30.6 (s, *C*-4), 23.7 (s, *C*-5 or *C*-6), 21.7 (s, *C*-30 and *C*-33), 21.0 (s, *C*-38 and *C*-41), 17.4 (s, *C*-6 or *C*-5).

Heck Reaction. A solution of palladium acetate (3.4 mg, 0.015 mol, 3 mol %) and ligand **6b** (18 mg, 0.030 mmol) in benzene (3 mL) was stirred for 20 min. Phenyltriflate (81 μL, 0.5 mmol, 1 equiv), *N*,*N*-diisopropylethylamine (261 μL, 1.5 mmol, 3 equiv), and 2,3-dihydrofuran (189 μL, 2.5 mmol, 5 equiv) were added. The solution was stirred at 40 °C for 3 days under argon. The reaction mixture was cooled, diluted with pentane (200 mL), and filtered to remove the solid material. The solution was then washed with 0.1 N HCl and saturated $NaHCO_3$ and dried with $MgSO_4$. The solvent was removed under reduced pressure, and the residue purified via column chromatography using silica gel. The products were eluted with 5% ethyl acetate in hexane and gave 2-phenyl-2,5-dihydrofuran (61 mg, 84%). Enantiomeric excesses were determined by either NMR using $Eu(hfc)_3$ as chiral shift reagent or HPLC using ChiraGrom-2 as chiral column. The yields, reaction times, and the ee's are summarized in Table 1.

Allylic Alkylation. Dinuclear $Pd_2(PhCHCHCHPh)_2Cl_2$ (1.34 mg, 0.002 mmol) and the ligand **6b** (3.0 mg, 0.005 mmol) in CH_2Cl_2 (2 mL) were stirred for 20 min. 1,3-Diphenyl-2-propenyl acetate (50.4 mg, 0.2 mmol), dimethyl malonate (68 μL, 0.6 mmol), BSA (148 μL, 0.6 mmol), and KOAc (1 mg) were added and stirred at room temperature for 2 h. The reaction mixture was diluted with ether, washed with water and brine, and dried ($MgSO_4$). The solvent was evaporated, and the oily residue was purified by column chromatography (20% ethyl acetate in hexane) (64 mg, 99%, ee = 97%). The results are given in Table 1.

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Supporting Information Available: Tables of bond lengths and angles, complete atomic coordinates, anisotropic displacement coefficients, and isotropic displacement coefficients for hydrogen atoms, and an ORTEP plot with a full numbering scheme. This material is available free of charge via the Internet at http://pubs.acs.org.

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