Palladium−Duphos Structural and Enantioselective Hydroarylation Chemistry

Daniela Drago and Paul S. Pregosin*

Laboratory of Inorganic Chemistry, ETHZ, Hönggerberg, 8093 Zürich, Switzerland

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A series of Pd(II) complexes of 1,2-bis((2*R*,5*R*)-2,5-dimethylphospholano)benzene (MeDuphos; **1**) have been prepared, and the solid-state structures for five of these, PdBr(*p*-CN-C_6H_4)(**1**), PdX(C_6F_5)(**1**) (X = Br, I), Pd(OAc)$_2$(**1**), and [Pd(CH_3CN)$_2$(**1**)](PF_6), have been determined by X-ray diffraction. Several of these complexes are catalyst precursors for the enantioselective hydroarylation of norbornene with PhX (X = Br, I, OTf). The maximum ee, 75%, is higher than the corresponding values previously reported for bidentate phosphine auxiliaries. NOESY NMR results show how complexed **1** interacts with the aryl ligand in PdBr(*p*-CN-C_6H_4)(**1**).

Introduction

The amplification of chiral information by transition-metal catalysts represents a cornerstone of asymmetric synthesis on both a laboratory and industrial scale. The growing interest in asymmetric catalysis largely stems from the capacity to generate a relatively large amount of enantiomerically enriched material from a small amount of a chiral catalyst. This approach is by far the most efficient use of chirality transfer, and many useful transition-metal-based catalytic reactions are known.[1]

Metal complexes possessing chiral phosphine ligands are widely employed in a variety of enantioselective homogeneously catalyzed reactions.[2] Binap, introduced by Noyori,[3] and MeO-Biphep, from Roche,[4] are useful auxiliaries in this connection. Many successful chiral phosphine auxiliaries bear at least two aryl substituents on the phosphorus center (e.g. the Binap type), and the stereogenicity arises from the bridging backbone. The mechanism of chirality transfer has been associated with a manifestation of the backbone chirality via the proper orientation of the phenyl substituents on phosphorus.[5] Indeed, frequently, phenyl substituents on the P atom are an indispensable structural feature connected with observed high enantioselectivity.

MeDuphos ((*R*,*R*)-MeDuphos = 1,2-bis((2*R*,5*R*)-2,5-dimethylphospholano)benzene; **1**), developed by Burk and co-workers,[6] represents a new ancillary ligand which is relatively small and contains basic P-donors, in contrast to ligands with *P*-phenyl substituents. The use of "small" electron-rich chiral phosphines remains relatively unexplored and, although recent literature[6,7] describing the application of Rh and Ru complexes of **1** in asymmetric hydrogenation is available, little is known[8] on the application of this ligand in palladium chemistry.

We report here on the synthesis, structure, and catalytic properties of several new Pd(II) complexes of **1** and suggest that these molecules demonstrate useful potential: e.g., medium-high enantiomeric excesses in catalytic homogeneous hydroarylation reactions.

Results and Discussion

X-ray Crystallography for the Pd−MeDuphos Complexes. Our previous studies[9] on Pd(II) compounds of **1** suggested that this ligand was relatively small; nevertheless, its success as an auxiliary warrants further attention, so that we have begun to consider how **1** interacts with various ligands within a square-planar

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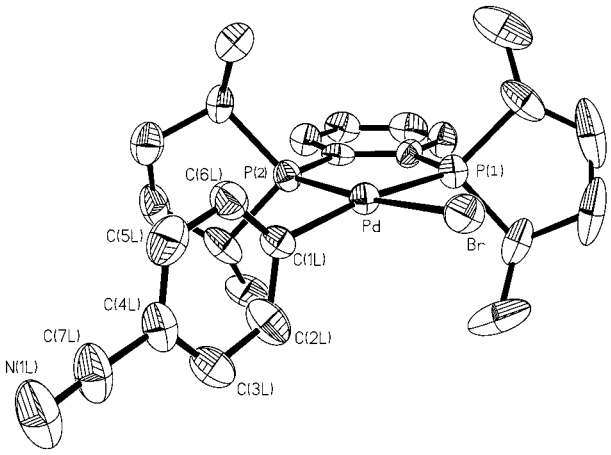
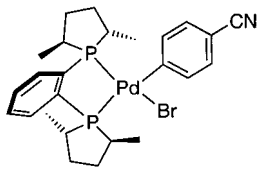


Figure 1. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

coordination sphere. We begin with a series of solid-state structures on model complexes, several of which are catalyst precursors.

The structure of the complex PdBr(*p*-CN-C_6H_4)(**1**) (**2**) is shown in Figure 1. Selected bond lengths and bond



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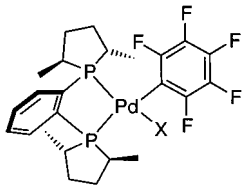
angles are given in Table 1, experimental parameters are given in Table 2, and a view of the molecule is shown in Figure 1. The local coordination geometry is slightly distorted square planar with the immediate coordination sphere consisting of the two P atoms, the bromide, and carbon C1L. The Pd−P bond lengths, Pd−P(2) = 2.215(2) Å and Pd−P(1) = 2.290(2) Å, are quite different, with the latter supporting a relatively large trans influence for the *p*-CN-C_6H_4 ligand. The Pd−C1L = 2.052(8) Å, and Pd−Br = 2.4693(12) Å separations fall within the normal range.[10] A similar value for the Pd−P(1) separation, 2.291(2) Å, has been reported by Tanaka and co-workers[11] in the structure of a 1-palladа-2-silacyclopentane−dmpe complex. In Pd(2,2′-biphenyl)-(depe), Jones et al.[12] found Pd−P distances of 2.3034(13) and 2.3196(13) Å, suggesting that the observed value for the Pd−P(1) separation in **2**, 2.290(2) Å, is as expected for **1** in this electronic environment. The P−Pd−P angle, ca. 86°, is normal for a five-membered ring; however, the two trans angles, C1L−Pd−P(1) = ca. 171° and P(2)−Pd−Br = ca. 175° are somewhat small, suggesting a slight tetrahedral distortion. Interestingly, the proximate methyl group, C(18), is found fairly close to the aryl ring: C18−C6L = 3.780 Å, and H18C−H6L = 2.247 Å.

With a view to a possible correlation between Pd−P bond length and trans influence of the aryl donor, the compounds PdX,(C_6F_5)(**1**) (X = Br, I) were prepared. Given the larger number of electron-withdrawing groups on the C_6F_5 ring, it seemed likely that this ligand would possess a smaller trans influence than that of the *p*-CN-C_6H_4 analogue. Crystals of **3** and **4** were obtained from



3, X= Br 4, X = I

CH_2Cl_2/Et_2O, and ORTEP views of these molecules are given in Figures 2 and 3, respectively. The local coordination geometry is again pseudo square planar in both cases, with the two P atoms, the halogens, and C1L comprising the immediate coordination spheres for both compounds. The two Pd−P bond lengths within **3**, Pd−P(2) = 2.229(4) Å and Pd−P(1) = 2.264(4) Å, and

Table 1. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for Complexes 2−6

	2	**3**	**4**	**5**	**6**
Pd(1)−C(1L)	2.052(8)	2.095(4)	2.089(12)		
Pd(1)−P(1)	2.290(2)	2.2620(11)	2.264(4)	2.2043(10)	2.225(2)
Pd(1)−P(2)	2.215(2)	2.2302(11)	2.229(4)	2.2132(11)	2.222(2)
Pd(1)−X	2.4693(12)	2.4681(7)	2.6174(17)		
Pd(1)−O(1)				2.104(3)	
Pd(1)−O(4)				2.113(3)	
Pd−N(1)					2.081(8)
Pd−N(2)					2.086(7)
P(2)−Pd(1)−P(1)	86.46(8)	86.17(4)	86.05(14)	86.47(4)	85.38(8)
C(1L)−Pd(1)−P(1)	171.1(2)	168.24(13)	168.9(3)		
C(1L)−Pd(1)−P(2)	92.3(2)	94.36(11)	95.5(3)		
C(1L)−Pd(1)−X	90.2(2)	90.11(11)	88.5(3)		
P(2)−Pd(1)−X	174.74(6)	173.48(3)	172.69(11)		
P(1)−Pd(1)−X	91.68(7)	90.41(3)	91.28(11)		
O(1)−Pd(1)−O(4)				92.80(13)	92.80(13)
O(1)−Pd(1)−P(1)				88.47(10)	88.47(10)
O(4)−Pd(1)−P(1)				174.26(11)	174.26(11)
O(1)−Pd(1)−P(2)				171.85(11)	171.85(11)
O(4)−Pd(1)−P(2)				92.86(10)	92.86(10)
N(1)−Pd−N(2)					89.6(3)
N(1)−Pd−P(2)					92.6(2)
N(2)−Pd−P(2)					176.7(2)
N(1)−Pd−P(1)					177.9(2)
N(2)−Pd−P(1)					92.5(2)

Table 2. Crystallographic Data for 2−6

	2	3	4	5	6
chem formula	$C_{25}H_{32}BrNP_2Pd$	$C_{24}H_{28}BrF_5P_2Pd$	$C_{24}H_{28}F_5IP_2Pd$	$C_{22}H_{34}O_4P_2Pd$	$C_{22}H_{34}F_{12}N_2P_4Pd$
fw	594.77	659.71	706.70	538.83	628.85
temp, K	293(2)	293(2)	293(2)	293(2)	293(2)
wavelength, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	orthorhombic	orthorhombic	orthorhombic	tetragonal	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P4_32_12$	$P2_12_12_1$
unit cell dimens					
a, Å	11.016(5)	10.7018(16)	10.691(8)	18.1468(8)	9.7601(2)
b, Å	13.790(7)	14.328(2)	14.332(10)	18.1468(8)	16.0392(4)
c, Å	16.821(7)	16.861(3)	17.296(9)	15.8612(11)	21.1154(5)
$\alpha = \beta = \gamma$ (deg)	90	90	90	90	90
V, Å^3	2555(2)	2585.4(7)	2650(3)	5223.2(5)	3305.49(13)
Z	4	4	4	8	4
calcd density, Mg/m^3	1.546	1.695	1.771	1.370	1.580
μ, mm^{-1}	2.427	2.434	2.032	0.858	0.839
F(000)	1200	1312	1384	2224	1578
final *R* indices (I > 2σ(*I*))					
R1	0.0238	0.0376	0.0299	0.0482	0.1032
wR2	0.0577	0.0706	0.0617	0.1351	0.1658
R indices (all data)					
R1	0.0263	0.0580	0.0446	0.1007	0.2080
wR2	0.0585	0.0777	0.0650	0.1587	0.2039

within **4**, Pd−P(2) = 2.2302(11) Å and Pd−P(1) = 2.2620(11) Å, are still different; however, the Pd−P(1) distances are now shorter than the corresponding separation in **2**; i.e., the C_6F_5 aryl is a weaker ligand.

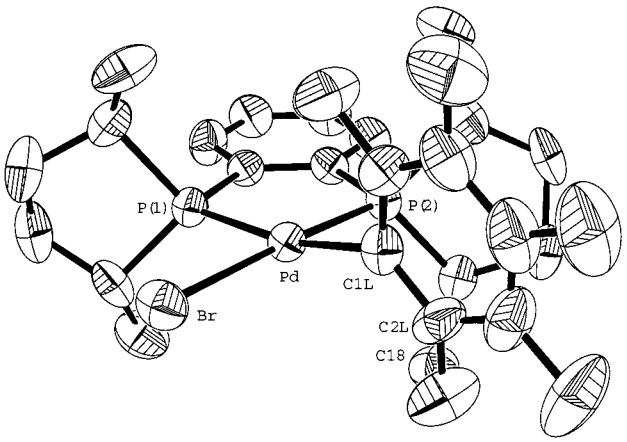


Figure 2. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

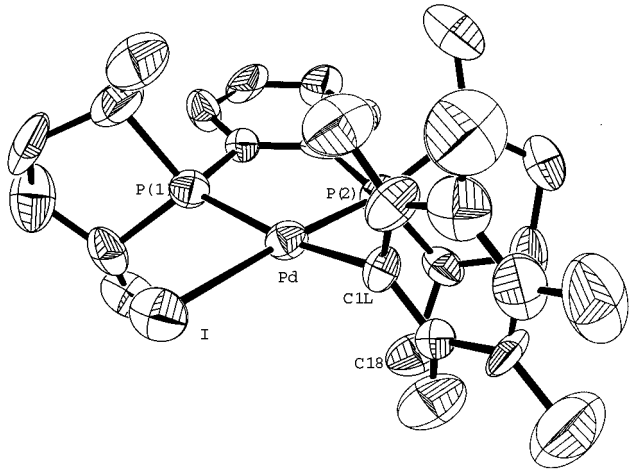


Figure 3. ORTEP drawing of **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

The Pd−C1L distances in **3** and **4**, 2.089(12) and 2.095(4) Å, respectively, are ca. 0.04 Å longer than in **2**, and the combination of these two correlated observations supports the idea that increasing the number of electron-withdrawing groups on the phenyl weakens the aryl σ-donor component and thus the trans influence.

Surprisingly, in **3** and **4** one finds a marked distortion from typical local square-planar geometry. Indeed, the aryl C1L and the halogen ligands deviate from the coordination plane defined by the two P donors and the metal, by +0.43 Å and −0.24 Å, respectively, for **3** and −0.40 and +0.31 Å, respectively, for **4**. In **2**, the observed deviations are smaller, −0.31 and +0.21 Å. Further, these distortions in **3** and **4** are partially reflected in the values of the trans angle P(1)−Pd−CL1 and the cis angle P(2)−Pd−CL1, in that the former are relatively small, ca. 169 and 168°, respectively, whereas the latter are somewhat large, ca. 94 and 96°, respectively (see Table 1). Again one finds a close contact from the aryl ligand to C18 due to the proximate atoms of the fluoroaryl moiety.

To gain further insight into the steric environment imposed by **1**, the molecular structure of $Pd(OAc)_2$(**1**) (**5**), a catalyst precursor in the asymmetric hydroarylation of norbornene, was determined. An ORTEP view of this molecule is given in Figure 4. This view originates behind the acetate donors and shows the two phospholane moieties extending horizontally. The local coordination geometry is pseudo square planar, with the two MeDuphos P atoms and the two oxygen atoms of the acetate ligands comprising the immediate coordination sphere. The Pd−P bond lengths, Pd−P(2) = 2.2132(11) Å and Pd−P(1) = 2.2043(10) Å, are relatively short and nearly identical. The Pd−O distances Pd−O(1) = 2.104(3) Å and Pd−O(4) = 2.113(4) Å are not significantly different. We find a series of short contacts from the auxiliary to the acetate: O2 to H2A, 2.497 Å; O4 to H18C, 2.570 Å; O3 to H14A, 2.448 Å. For all four structures **2**−**5**, the P−Pd−P bite angle is ca. 86°, in

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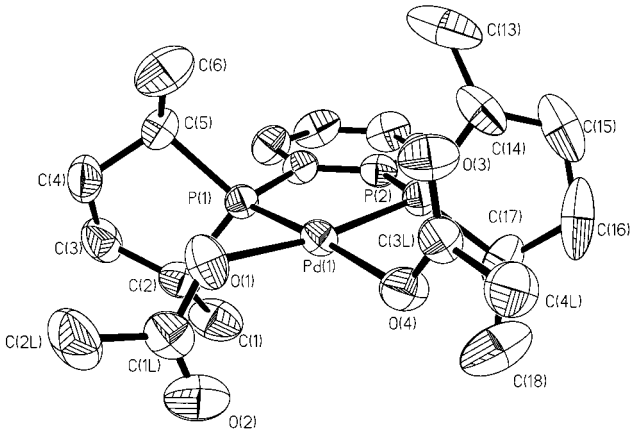


Figure 4. ORTEP drawing of **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

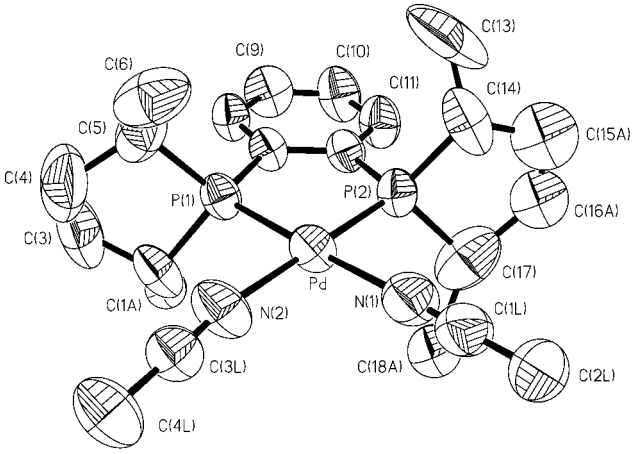
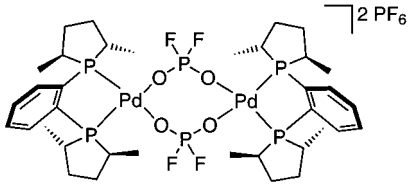


Figure 5. ORTEP plot showing the cation of complex **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

agreement with values observed in other bis(phosphino)-benzene complexes.[13]

Since nitrile complexes of Pd(II) are useful catalyst precursors, we attempted the synthesis of $[Pd(CH_3CN)_2$-(**1**)$](PF_6)_2$ (**6**). Although we were able to obtain a suitable crystal of this compound (see Figure 5), the mixture was often contaminated with another species. This complex, **7**, afforded a rather poor crystal whose structure could



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not be determined accurately (see Figure 6) but was sufficient to shed some light on the synthetic problem. Clearly the PF_6 hydrolyzes to form PF_2O_2, which uses the O atoms to bridge the two Pd atoms.[14] Returning

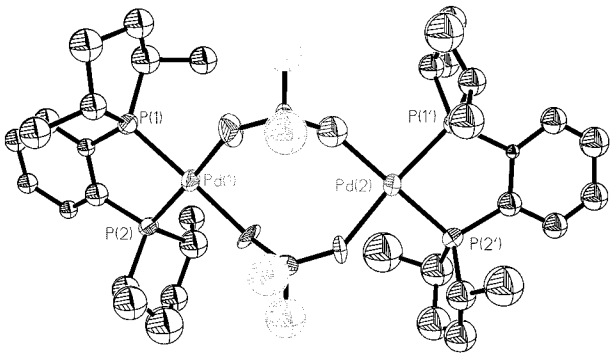
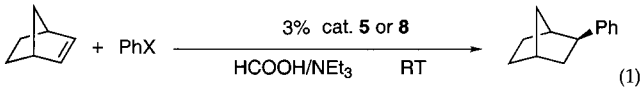


Figure 6. Structure of complex **7**.

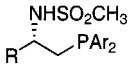
briefly to **6**, the bond angles and bond lengths are conventional and selected values of these, plus additional data, for **2**−**5** are summarized in Table 1.

Hydroarylation. To evaluate the effectiveness of these new complexes of **1**, we chose the enantioselective hydroarylation of norbornene as test reaction using the reductive conditions (NEt_3/HCOOH) described by Larock[15] and Brunner[16] (see eq 1). The choice of nor-



(1)

bornene as substrate allows a direct comparison with the literature and has the further advantage that some 2-phenyl-substituted norbornane derivatives show activity against Parkinson's disease.[17] Brunner[16] has reported ee's for this reaction in DMSO at 60 °C in the range 1.2−37.7%, using the bidentate phosphines Diop, Prophos, Chiraphos, and Norphos, among others. Achiwa[18] reports the same reaction in DMSO at 65 °C using Binap (ee = 10.8%), various Valphos derivatives (ee = 61.9−71.4%), and several other auxiliaries with the maximum observed ee = 71.9%.



Valphos compounds

The complexes $Pd(OAc)_2$(**1**) (**5**) and PdI(Ph)(**1**) (**8**) catalyze the hydrophenylation reaction shown. The reaction proceeds smoothly, at room temperature, and results are given in Table 3. The following points are worthy of note.

(a) MeDuphos **1** affords the best ee, 75%, of any bidentate phosphine employed to date (although a P,N ligand reported by Kaufmann, ee = 86.4%, is known to be better).

(b) Slightly higher ee's are observed with X = OTf as the leaving group in DMF.

(c) The reaction can be carried out without solvent and still afford good enantioselectivity.

(d) The aryl group occupies an exo position of the norbornane product; i.e., the reaction is regioselective.

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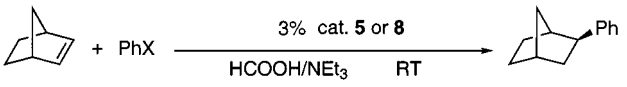
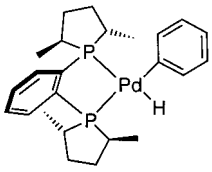
Table 3. Hydroarylation of Norbornene[a]



solvent	X	time (h)	conv (%)	yield[b] (%)	ee[c]	cat.
DMF	Br	24	100	80	68	**5**
DMSO	Br	24	100	78	60	**5**
DMF	OTf	24	76	70	75	**5**
no solvent	OTf	24	50	45	70	**5**
toluene	OTf	23	84	74	68	**5**
DMSO	OTf	23	85	76	68	**5**
DMF	I	24	80	62	64	**8**
DMF	OTf	24	70	60	74	**8**
no solvent	OTf	24	62	50	74	**8**

[a] The reaction was carried out at room temperature under an argon atmosphere using formic acid as the hydride source and triethylamine as the base. [b] The chemical yield refers to isolated products. [c] Optical yields determined by chiral HPLC (see Experimental Section).

(e) There is no indication of a diphenylation reaction. Small amounts of benzene were detected and it is known[16] that a competing reaction pathway can proceed under comparable conditions, i.e., reductive dehalogenation of Ar−X. Presumably, the reduction arises from an intermediate with structure **9**. In most cases the



9

conversion was > 80% and frequently, 100%. The reaction was complete in < 24h.

One can use this catalyst in a transfer hydrogenation reaction. Reaction of commercially available 3-methylcyclohexenone, with the standard catalyst, afforded a 40% yield of 3-methylcyclohexanone, with an ee of ca. 30% (the remaining material is unreacted 3-methylcyclohexenone, see Experimental Section).

No attempt was made to optimize this procedure.

NMR Studies. Clearly, **1** is not a very large ligand.[9] It has a moderate bite angle and thus might not be expected to strongly intrude into the remaining coordination spheres. Given the X-ray data for **2**−**6**, in which we clearly see selected contacts, we have measured its ^{1}H NOESY to determine how an organometallic ligand and the auxiliary **1** interact in solution. A section of this spectrum for one of these, **2**, is shown in Figure 7 and clearly reveals fairly strong cross-peaks from *both* the MeDuphos methine, H-2, and the methyl, Me-6, to the ortho protons of the *p*-NCC_6H_4 aryl ligand (see **10**). These ortho protons are found as a broad triplet,[20] one

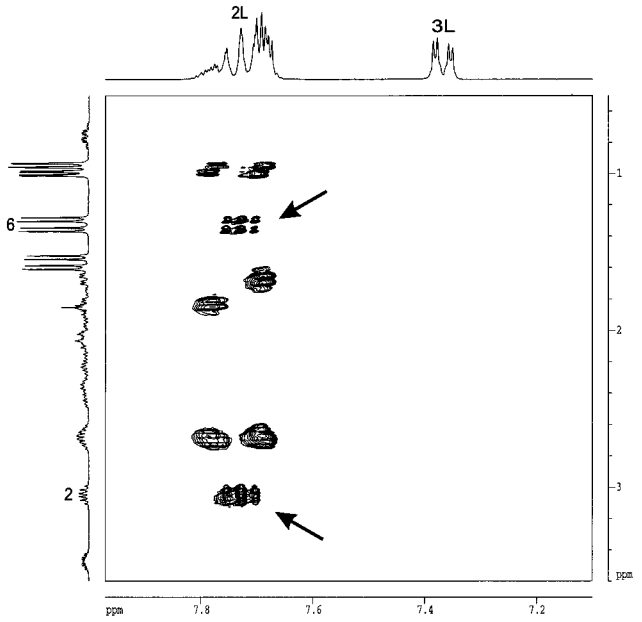
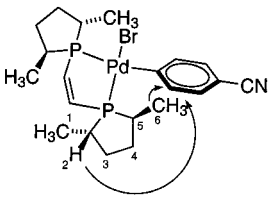


Figure 7. Section of the NOESY spectrum of **2**. The three sets of cross-peaks (see arrows) stem from the broad triplet due to the ortho protons of the aryl ligand and show contacts to the CH and CH_3 of **1** (CD_2Cl_2, 400 MHz). The signals 2L and 3L represent the ortho and the meta protons of the aryl ligand. The NMR numbering system corresponds to that used for X-ray results.

part of which is overlapped by other signals; nevertheless, the cross-peaks show the triplet-type structure. An identical picture emerges from the NOESY analysis of PdI(Ph)(**1**), and this spectrum is given as Supporting Information. Although **1** may be slim, it is clearly sufficiently intrusive to influence a cis-positioned organometallic ligand.



10, fragment of **2** showing inter-ligand NOE's

The assignment of the *p*-NCC_6H_4 aryl ligand ortho and meta protons follows from both the ^{1}H COSY and long-range ^{13}C,^{1}H correlations. The latter allows the assignment of the σ-bound aryl resonance: δ 174.0, $^2J(P,C)_{trans}$ = 138 Hz, $^2J(P,C)_{cis}$ = 2 Hz. This high-frequency position is reasonable.[21]

On previous occasions[22] we have found that oxidative addition of PhX to Pd(0) proceeds relatively rapidly when the zerovalent oxidation state is produced by reaction of $PdCl_2$(PP) with excess $NaBH_4$. When $PdCl_2$-(**1**) (**11**) is treated with 2 equiv of $NaBH_4$ and then with

(19) Hydrodehalogenation of aryl halides: Cortese, N. A.; Heck, R. F. *J. Org. Chem.* **1977**, *42*, 3491−3494. Reduction of sulfonates: Chen, Q. Y.; He, Y. B.; Yang, Z. Y. *Tetrahedron Lett.* **1986**, *27*, 1452−1453. Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1986**, *27*, 5541−5544.

(20) This ortho proton is part of an AA′BB′XX′ spin system: A = ortho ^{1}H, B = meta ^{1}H, X = ^{31}P. Consequently, there is a relatively large number of unresolved lines. The NMR numbering system corresponds to that used for X-ray results.

(21) Tschoerner, M.; Pregosin, P. S. *Inorg. Chim. Acta* **1999**, *290*, 95−99. Tschoerner, M.; Kunz, P. W.; Pregosin, P. S. *Magn. Reson. Chem.* **1999**, *37*, 91−97. Martinez-Viviente, E.; Pregosin, P. S.; Tschoerner, M. *Magn. Reson. Chem.* **2000**, *38*, 23−28.

(22) Tschoerner, M.; Pregosin, P. S.; Albinati, A. *Organometallics* **1999**, *18*, 670−678.

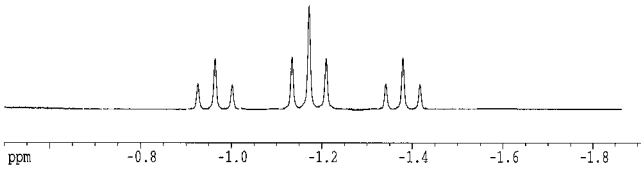
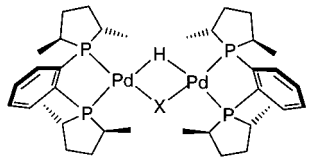


Figure 8. Bridging hydride signal for the unknown dinuclear complex (benzene-d_6, 400 MHz).

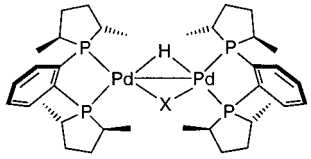
Scheme 1

$PdCl_2$(**1**) + 4 $NaBH_4$ ⟶ unknown (A or B)

Structural Fragments for the Unknown Complex



12



13

PhI, the product of oxidative addition, PdI(Ph)(**1**) (**8**) is obtained. However, when **11** is treated with 4 equiv of $NaBH_4$, a new (but relatively unstable) yellow complex is isolated in good yield (see Experimental Section). In methylene chloride solvent the new complex decomposes to $PdCl_2$(**1**) (**11**). However, the new compound is a catalyst precursor and affords the organic product of eq 1 in the normal time with an ee of ca. 60%.

We believe that this complex possesses a dinuclear structure, e.g., either **12** or **13**,[23] of the type shown in Scheme 1. The ^{31}P spectrum shows a simple AX spin system. At ambient temperature, there is a broad triplet bridging hydride ^{1}H resonance at δ −0.56, which at 253 K (see Figure 8) is observed as a triplet of triplets, with one relatively large $^2J(P,H)_{trans}$ = 160 Hz, suggesting a pseudo-trans orientation of these spins.[24] The second ^2J(P,H) value is 29 Hz. Further, one finds a broad two proton singlet at δ 8.67, which might arise from complexed water. A 2-D exchange spectrum reveals that (a) these two spin types are exchanging slowly on the NMR time scale at room temperature and (b) the four methyl groups of **1** undergo pairwise exchange within each ligand. These latter dynamic data are consistent with X-bridge opening of **13**, isomerization, and subsequent re-formation of the dinuclear species.[25]

The bridging hydride chemical shift, multiplicity, and $^2J(P,H)_{trans}$ value are sufficient to support the basic structure shown: i.e, two ligands, two metals, and one bridging hydride.[26] Further, there are numerous strong signals in both the FAB and MALDI TOF mass spectra at *m/e* >800, in agreement with this assignment. However, we do not find a signal consistent with the molecular ion expected for, e.g., **13** (X = H_2O). Moreover, elemental analyses clearly show four boron atoms per two Pd atoms, consistent with the high reaction yield; i.e., we lose very little mass.

The IR spectrum of this unknown material shows a strong signal at ν 2300 cm^{-1} and a shoulder at 2360 cm^{-1} consistent with B−H stretching modes. Moreover, there are broad proton NMR signals at δ 4.64 and δ 1.71, each integrated to one proton, which might well be B−H resonances. We have been unable to obtain a boron NMR spectrum, presumably because the boron anion is complexed, thereby increasing its correlation time and thus strongly broadening the lines. It seems likely that ligand X is a small negatively charged boron cluster which forms under the reaction conditions in the presence of additional borohydride reagent. Unfortunately, although the synthesis of the new material is reproducible, we have not been able to determine its structure. Both **12** and **13** remain as possibilities; however, on the basis of the observed chemistry and dynamics, we lean toward **12**.

Conclusions. Although **1** does not intrude in many places within the Pd(II) coordination sphere, the structural analyses prove that the proximate methyl groups are placed sufficiently close to where one would expect to find a complexed substrate. The hydroarylation reaction requires both complexed olefin and aryl ligands so that, although **1** is small, it is well within reach of these ligands and, as indicated by the observed ee's, readily biases one diastereomeric transition state relative to the other.

Experimental Section

General Considerations. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Flash chromatography was performed using Silicagel 60 (Fluka, particle size 40−63 μm); detection was made by UV light (254 nm) or with iodine. All solvents (Fluka, Merck, Aldrich) were of purissimum p.A. quality and were used as such or distilled under argon over an appropriate drying agent following standard procedures. Deuterated solvents ($CDCl_3$, CD_2Cl_2, C_6D_6, D_2O) were purchased from Dr Glaser AG or from Cambridge Isotope Laboratories. Routine ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded with Bruker DPX-300 and 400 MHz spectrometers. Chemical shifts are given in ppm, and coupling constants (J) are given in Hertz. The two-dimensional ^{1}H NOESY and X,^{1}H correlation experiments were carried out at 400 MHz or at 500 MHz. HPLC was performed at 25 °C on a Hewlett-Packard Series 1050 chromatograph equipped with a variable-wavelength detector and Daicel Chiralcel OJ-H column (0.46 cm × 25 cm, particle size 5 μm). Elemental analyses were carried out by the Laboratory of Microelemental Analysis (ETH Zürich). Mass spectra were measured by the MS service of the Laboratorium für Organische Chemie (ETH Zürich) using a ZAB VSEQ mass spectrometer with a 3-NOBA (3-nitrobenzyl alcohol) matrix and Xe atom beam with a transational energy of 8 keV for FAB$^+$ MS.

Crystallography. White crystals of **2** and yellow crystals of **4** were obtained by slow diffusion of ether into a solution of

(23) Our method of synthesis might lead to a Pd(I) dimer in that unstable PdHCl(**1**) (**14**), formed from hydride displacement of chloride, could lose HCl to form Pd(**1**), which could then react with a second molecule of **14** to give the product.

(24) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979; Vol. 16. Albinati, A.; Lianza, F.; Pasquali, M.; Sommovigo, M.; Leoni, P.; Pregosin, P. S.; Ruegger, H. *Inorg. Chem.* **1991**, *30*, 4690−4692.

(25) Valentini, M.; Selvakumar, K.; Wörle, M.; Pregosin, P. S. *J. Organomet. Chem.* **1999**, *587*, 244−251. Feiken, N.; Pregosin, P. S.; Trabesinger, G. *Organometallics* **1998**, *17*, 4510−4518.

(26) Albinati, A.; Venanzi, L. M. *Coord. Chem. Rev.* **2000**, *200−202*, 687−715 and references therein.

the compound in dichloromethane. Diffraction data were collected on a Syntex P21 four-circle diffractometer at room temperature. The structure was solved by the Patterson method of SHELXS-86.[27] All non-hydrogen atomic positions were refined in the anisotropic mode by full-matrix least-squares calculations (SHELXL-93[28]) on F^2. Air-stable, pale yellow crystals of **3**, **5**, and **6** were also obtained by slow diffusion of ether into a saturated CH_2Cl_2 solution. A prismatic single crystal for each complex was mounted on a glass capillary and data sets covering a hemisphere were collected on a Siemens SMART platform diffractometer equipped with a CCD detector. Data reduction plus corrections for Lorentz polarization and absorption were performed using the programs SAINT[29] and SADABS.[30] The structures were solved by direct methods and refined by full-matrix least squares (versus F^2) with the SHELXTL program package.[31] Crystals of compound **6** were of poor quality; this is reflected in the relatively high R value. The SbF_6 molecules are disordered and were described as rigid groups. In addition, the carbons C(1), C(15), C(16), and C(18) of the MeDuphos ligand had half-occupancies. Where refinement with disordered positions did not improve the result of the refinement with nonsplit positions, the group was described as rigid; alternatively the disorder was described via splitting. Crystal data and structure refinements are summarized in Table 2.

[PdBr(4-cyanophenyl)(1)] (2). Ligand **1** (15.1 mg, 0.05 mmol) and [PdBr(TMEDA)(*p*-cyanophenyl)] (20 mg, 0.05 mmol) were dissolved in 2 mL of THF and then stirred at 60 °C for 16 h. The solution was filtered, and the solvent was removed in vacuo. The residue was washed with Et_2O (5 × 2 mL) and the crude white product recrystallized from CH_2Cl_2 and Et_2O (by allowing Et_2O to diffuse into a CH_2Cl_2 solution of the product). Over a period of 24 h crystals were formed, which were washed with Et_2O and dried in vacuo. Yield: 23 mg (78.2%) of **2** as white crystals. Anal. Calcd (found) for $C_{25}H_{32}BrNP_2Pd$ (mol wt 594.81): C, 50.48 (50.61); H, 5.42 (5.46); N, 2.35 (2.24). MS (FAB^+, *m/e*): 594 $[M]^+$, 514 $[M - Br]^+$, 493.1 $[PdBr(1)]^+$, 412.1 $[Pd(1)]^+$. ^{31}P NMR: (121.5 MHz, CD_2Cl_2): δ 72.9 (d, $^2J_{PP} = 24$ Hz), 69.3 (d, $^2J_{PP} = 24$ Hz). $^{13}C\{^1H\}$ NMR: (75.47 MHz, CD_2Cl_2): δ 14.5 (d, $J_{PC} = 10$ Hz, 2C), 16.2 (d, $J_{PC} = 7$ Hz), 17.4 (d, $J_{PC} = 11$ Hz), 34.8 (d, $J_{PC} = 29$ Hz), 35.6 (d, $J_{PC} = 6$ Hz), 36.4 (d, $J_{PC} = 22$ Hz), 36.8, 36.9, 37.8 (d, $J_{PC} = 2$ Hz), 42.3 (d, $J_{PC} = 22$ Hz), 43.2 (d, $J_{PC} = 30$ Hz), 106.6 (d, $J_{PC} = 1$ Hz, C4′), 120.7 (s, C≡N), 129.3 (d, $J_{PC} = 9$ Hz), 131.8 (dd, $J_{PC} = 6$, 2 Hz), 131.9 (dd, $J_{PC} = 4$, 2 Hz), 133.1 (dd, $J_{PC} = 16$, 2 Hz), 133.6 (d, $J_{PC} = 15$ Hz), 138.8 (virtual t, $J_{PC} = 2$ Hz), 141.7 (dd, C12, $J_{PC} = 31$, 28 Hz), 143.4 (dd, C7, $J_{PC} = 44$, 38 Hz), 174.0 (dd, C1L, $J_{PC} = 138$, 2 Hz). ^1H NMR (300 MHz, CD_2Cl_2): δ 0.65−0.85 (m, 1H), 0.95 (dd, 3H, CH_3, $^3J_{PH} = 14.8$, $^3J_{HH} = 7.2$ Hz), 1.00 (dd, 3H, CH_3, $^3J_{PH} = 16.0$, $^3J_{HH} = 7.2$ Hz), 1.32 (dd, 3H, CH_3, $^3J_{PH} = 19.3$, $^3J_{HH} = 7.0$ Hz), 1.57 (dd, 3H, CH_3, $^3J_{PH} = 18.9$, $^3J_{HH} = 7.0$ Hz), 1.6−1.7 (m, 1H), 1.75−2.35 (m, 6H), 2.63−2.7 (m, 2H, H5 and H17), 3.02−3.08 (m, 1H, H2), 3.45−3.50 (m, 1H, H14), 7.37 (dd, 1H, $J = 8.2$, 2.2 Hz, H3′), 7.66−7.81 (m, 5H).

[PdBr(C_6F_5)(1)], 3. With [PdBr(C_6F_5)(TMEDA)] as the starting material, the same reaction conditions as given for **2** were used: THF, 60 °C, 16 h. Yield: 28 mg (85%) as pale yellow crystals from CH_2Cl_2/Et_2O. Anal. Calcd (found) for $C_{24}H_{28}BrF_5P_2Pd$ (mol wt 659.8): C, 43.69 (43.85); H, 4.28 (4.53). MS (FAB^+, *m/e*): 578.8 $[M - Br]^+$, 492.8 $[M - C_6F_5]^+$. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 85.12 (d, $^2J_{PP} = 10$ Hz), 78.9 (m, 6 line multiplet, $^2J_{PP} = 10$ Hz). $^{13}C-^{19}F$ HMQC: δ 122.1 (C1L), 135.0/136.5 (C3L/C5L), 138.5 (C4L), 144.1/148.3 (C2L/C6L). $^{13}C\{^1H\}$ NMR: (75.47 MHz, CD_2Cl_2): δ 13.56 (d, $J_{PC} = 21.4$ Hz), 13.58 (d, $J_{PC} = 20.9$ Hz), 15.53 (dd, $J_{PC} = 7.4$, 5.4 Hz), 16.26 (d, $J_{PC} = 8.2$ Hz), 35.1 (d, $J_{PC} = 5.6$ Hz), 36.0 (d, $J_{PC} = 3.5$ Hz), 36.2, 36.5, 37.0 (d, $J_{PC} = 1.2$ Hz), 37.8 (dd, $J_{PC} = 29$, 3.2 Hz), 42.3 (d, $J_{PC} = 30.2$ Hz), 43.1 (d, $J_{PC} = 27.5$ Hz), 131.6−132.3 (6 doublets, 3C), 132.7 (d, $J_{PC} = 16.2$ Hz), 142.1 (dd, $J_{PC} = 38.2$, 39.5 Hz), 142.4 (dd, $J_{PC} = 33.1$, 34.8 Hz). ^{19}F NMR (376 MHz, CD_2Cl_2): δ −112.13 (m, 1F), −119.16 (m, 1F), −161.6 (t, 1F, $J = 18.8$), −163.66 (m, 2F). (The complexity arises from $^2J(P,P)$ plus ^{19}F spin−spin coupling.) ^1H NMR (300 MHz, CD_2Cl_2): δ 1.00 (dd, 3H, CH_3, $^3J_{PH} = 15.2$, $^3J_{HH} = 7.1$ Hz),1.05 (dd, 3H, CH_3, $^3J_{PH} = 15.2$, $^3J_{HH} = 7.1$ Hz), 1.37 (dd, 3H, CH_3, $^3J_{PH} = 19.5$, $^3J_{HH} = 7.2$ Hz), 1.57 (dd, 3H, CH_3, $^3J_{PH} = 19$,$^3J_{HH} = 7$ Hz), 1.66−1.93 (m, 2H), 2.07−2.52 (m, 6H), 2.6−2.78 (m, 2H), 2.9−3.0 (m, 1H), 7.70−7.76 (m, 4H).

[PdI(C_6F_5)(1)] (4). Starting from [PdI(C_6F_5)(TMEDA)] the same reaction conditions as given for **2** were used: THF, 60 °C, 24 h. Yield: 21.5 mg (61%) as yellow crystals from CH_2Cl_2/Et_2O. Anal. Calcd (found) for $C_{24}H_{28}F_5IP_2Pd$ (mol wt 706.75): C, 40.79 (40.99); H, 3.99 (4.14). MS (FAB^+, *m/e*): 579.1 $[M - I]^+$, 539 $[M - C_6F_5]^+$, 412 $[Pd(1)]^+$. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 82.44 (d, $J_{PP} = 11.4$ Hz), 78.09 (m, 6 line multiplet, $J_{PP} = 11.4$ Hz). $^{13}C-^{19}F$ HMQC: δ 122.1 (C1L), 135.0/136.5 (C3L/C5L), 138.5 (C4L), 144.1/148.3 (C2L/C6L). $^{13}C\{^1H\}$ NMR: (75.47 MHz, CD_2Cl_2): δ, 14.41 (d, $J_{PC} = 35.4$ Hz), 14.43 (d, $J_{PC} = 35.4$ Hz), 15.91 (dd, $J_{PC} = 7.3$, 5.7 Hz), 17.34 (d, $J_{PC} = 8.1$ Hz), 35.99 (d, $J_{PC} = 5.4$ Hz), 36.38 (d, $J_{PC} = 3.1$ Hz), 36.85, 37.98, 38.02 (dd, $J_{PC} = 27.6$, 2.6 Hz), 39.06 (d, $J_{PC} = 27$ Hz), 43.43 (d, $J_{PC} = 28.6$ Hz), 44.36 (d, $J_{PC} = 27.4$ Hz), 132−133 (6 doublets, 3C), 133.6 (d, $J_{PC} = 16.4$ Hz), 142.1 (dd, $J_{PC} = 38.2$, 39.5 Hz), 142.4 (dd, $J_{PC} = 33.1$, 34.8 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ −110.36 (m, 1F), −118.31 (m, 1F), −161.6 (t, 1F, $J = 19.8$), −163.91 (m, 2F). (The complexity arises from $^2J(P,P)$ plus ^{19}F spin−spin coupling.) ^1H NMR (300 MHz, CD_2Cl_2): δ 0.98 (dd, 3H, CH_3, $^3J_{PH} = 16.5$, $^3J_{HH} = 7.2$ Hz), 1.03 (dd, 3H, CH_3, $^3J_{PH} = 16.5$, $^3J_{HH} = 7.2$ Hz), 1.38 (dd, 3H, CH_3, $^3J_{PH} = 19.7$, $^3J_{HH} = 7.1$ Hz), 1.57 (dd, 3H, CH_3, $^3J_{PH} = 18.99$, $^3J_{HH} = 6.9$ Hz), 1.66−1.97 (m, 2H), 2.13−2.90 (m, 8H), 3.45−4.0 (m, 1H), 7.70−7.81 (m, 4H).

[Pd($OAc)_2$(1)] (5). Ligand **1** (109.2 mg, 0.356 mmol) and $Pd(OAc)_2$ (80 mg, 0.356 mmol) were dissolved in 2 mL of CH_2Cl_2 and the resulting solution stirred at room temperature for 1 h. The solution was filtered and concentrated to 0.5 mL. Addition of Et_2O led to the precipitation of **5**. The residue was washed with Et_2O (5 × 2 mL) and the crude yellow product recrystallized from CH_2Cl_2 and Et_2O as described for **2**. Over a period of 24 h crystals were formed, which were washed with Et_2O and dried under vacuum. Yield: 180 mg (95%) of pale yellow crystals. Anal. Calcd (found) for $C_{22}H_{34}O4P_2Pd{\cdot}H_2O$ (mol wt 549): C, 48.09 (48.08); H, 6.56 (6.63). MS (FAB^+, *m/e*): 471 $[M - OAc]^+$, 412.1 $[Pd(1)]^+$, 307.1 $[(1)]^+$. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 90.3. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 14.1 (s, 2C), 16.4 (t, $^2J_{PC} = 3.3$ Hz, 2C), 24.4 (s, 2C, OC(O)*CH*$_3$), 35.7 (t, $J_{PC} = 2.6$ Hz, 2C), 36.8 (s, 4C), 132.4−132.9 (m, 4C), 140.1−141.0 (m, C12 and C7), 176.9 (s, 2C, O*C*(O)CH$_3$). ^1H NMR (400 MHz, CD_2Cl_2): δ 0.94 (dd, $^3J_{PH} = 16.8$ Hz, $^3J_{HH} = 7.1$ Hz, 6H, CH_3), 1.63 (dd, $^3J_{PH} = 19.4$ Hz, $^3J_{HH} = 6.9$ Hz, 6H, CH_3), 1.67−1.83 (m, 4H), 1.96 (s, 6H, OC(O)*CH*$_3$), 2.24−2.44 (m, 4H), 2.52−2.69 (m, 2H), 3.42−3.57 (m, 2H), 7.61−7.68 (m, 2H), 7.71−7.76 (m, 2H).

[Pd($NCCH_3)_2$(1)]($PF_6)_2$ and [Pd(μ-$PO_2F_2)_2$(1)]$_2$($PF_6)_2$ (6 and 7). Complex **11** (150 mg, 0.310 mmol) was dissolved in 3 mL of CH_3CN at room temperature and reacted with $AgPF_6$ (156.8 mg, 0.620 mmol). The suspension that resulted was stirred at room temperature for 3 h and then filtered through Celite, and the filtrate was evaporated to dryness in vacuo. The residue was washed with ether (5 × 2 mL) and the crude

(27) Sheldrick, G. M. SHELXS-86: Program for the Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1985.
(28) Sheldrick, G. M. SHELXS-93: Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1993.
(29) SAINT, Version 4; Siemens Analytical X-ray Systems, Inc., Madison, WI.
(30) Sheldrick, G. SADABS; University of Göttingen, Göttingen, Germany, 1997.
(31) SHELXL Program Package, Version 5.1; Bruker AXS, Inc.: Madison, WI.

yellow product recrystallized from CH_2Cl_2 and Et_2O (by allowing Et_2O to diffuse into a CH_2Cl_2 solution of the product). Over a period of 48 h crystals were formed, which were washed with Et_2O and dried in vacuo. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 100.5 (s) −143.3 (7, $^1J_{PF}$ = 710 Hz, PF_6) for **6**; δ 106.0 (s), −13.8 (3, $^1J_{PF}$ = 969 Hz, PF_2O_2). −143.3 (7, $^1J_{PF}$ = 710 Hz, PF_6) for **7**.

[PdI(Ph)(1)] (8). Ligand **1** (57.5 mg, 0.187 mmol) and [PdI(phenyl)(TMEDA)] (80 mg, 0.187 mmol) were dissolved in 2 mL of THF and stirred at 40 °C for 45 min. The solution was filtered, and the solvent was removed in vacuo. The residue was washed with pentane (5 × 2 mL) and the crude yellow product recrystallized from CH_2Cl_2 and pentane as described for **2**. Yield: 110 mg (95%). Anal. Calcd (found) for $C_{24}H_{33}IP_2Pd$ (mol wt 616.8): C, 46.74 (47.25); H, 5.39 (5.91). MS (FAB$^+$, *m/e*): 539 [M − Ph]$^+$, 489 [M − I]$^+$, 412 [Pd(1)]$^+$. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 65.8 (d,$^2J_{P,P}$ = 26.5 Hz), 69.6 (d,$^2J_{P,P}$ = 26.5 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 14.6 (d, $^2J_{PC}$ = 27.7 Hz, 2C, C1 and C13), 15.8 (d, $^2J_{PC}$ = 7.2 Hz, C18), 17.6 (d, $^2J_{PC}$ = 11.3 Hz, C6), 33.7 (d, $^1J_{PC}$ = 27.6 Hz, C14), 35.5 (d, $^2J_{PC}$ = 5.2 Hz, C16), 36.8 (d, $^2J_{PC}$ = 13 Hz, 2C, C15 and C4), 37.6 (d, $^1J_{PC}$ = 22 Hz, C2), 38.0 (C3), 42.6 (d, $^1J_{PC}$ = 21.1 Hz, C5), 43.7 (d, $^1J_{PC}$ = 28.9 Hz, C17), 122.9 (C4L), 127 (d, $^4J_{PC}$ = 8.1 Hz, 2C, C3L and C5L), 131.3−133.8 (4C, C8, C9, C10, and C11), 139 (br, 2C, C2L and C6L), 142.0−144.0 (2C, C7 and C12), 158.7 (d, $^2J_{PC}$ = 135 Hz, C1L). ^1H NMR (400 MHz, CD_2Cl_2): δ 0.75 (m, 1H, H16), 0.95 (dd, 3H, CH_3 1, $^3J_{PH}$ = 15.4, $^3J_{HH}$ = 7.3 Hz), 0.98 (dd, 3H, CH_3 13, $^3J_{PH}$ = 16, $^3J_{HH}$ = 7.3 Hz), 1.36 (dd, 3H, CH_3 18, $^3J_{PH}$ = 19.1, $^3J_{HH}$ = 7.0 Hz), 1.56 (dd, 3H, CH_3 6, $^3J_{PH}$ = 18.7, $^3J_{HH}$ = 7.0 Hz), 1.65 (m, 1H, H15), 1.83−2.01 (m, 2H, H3 and H5′), 2.03−2.21 (m, 3H, H4, H4′, and H15′), 2.39 (m, 1H, H3′), 2.53−2.70 (m, 3H, H5, H17, and H16′), 3.15 (m, 1H, H14), 3.7 (m, 1H, H2), 6.91 (m, 1H, H4L), 7.08−7.14 (m, 2H, H3L and H5L), 7.46−7.56 (m, 2H, H2L and H6L), 7.61−7.83 (m, 4H, H8 H9, H10, and H11).

[PdCl$_2$(1)] (11). Ligand **1** (23.6 mg, 0.077 mmol) and [$PdCl_2(CH_3CN)_2$] (20 mg, 0.077 mmol) were dissolved in 1 mL of CH_2Cl_2 and stirred at room temperature for 1 h. The white precipitate that formed was collected by filtration, washed with Et_2O (5 × 2 mL), and dried in vacuo. The product was recrystallized from CH_2Cl_2 as white crystals. Yield: 34 mg (91.3%). Anal. Calcd (found) for $C_{18}H_{28}Cl_2P_2Pd$ (mol wt 483.69): C, 44.7 (44.1); H, 5.83 (5.96). MS (FAB$^+$, *m/e*): 449.1 [PdCl(1)]$^+$, 412.1 [Pd(1)]$^+$. $^{31}P\{^1H\}$ NMR: (121.5 MHz, $CDCl_3$): δ 95.86. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 14.3 (Me), 17.4 (virtual t, $J_{PC} + J_{PC}$ = 5.8 Hz), 36.0 (virtual t), 37.3, 38.6 (virtual t, $J_{PC} + J_{PC}$ = 40 Hz), 43.2 (virtual t, $J_{PC} + J_{PC}$ = 41 Hz), 132.7 (virtual t, $J_{PC} + J_{PC}$ = 29 Hz), 133.1 (br), 141.4 (t, J_{PC} = 37.4). ^1H NMR (300 MHz, $CDCl_3$): δ 0.96 (dd, 6H, $^3J_{PH}$ = 16.9, $^3J_{HH}$ = 7.2 Hz), 1.64 (dd, 6H, $^3J_{PH}$ = 19.9, $^3J_{HH}$ = 6.9 Hz), 1.72−1.83 (m, 2H), 2.23−2.2.47 (m, 6H), 2.61−2.70 (m, 2H), 3.65−3.75 (m, 2H), 7.64−7.75 (m, 4H).

[Pd(μ-H)(μ-X)(1)]$_2$ (12 and 13). Complex **11** (180 mg, 0.372 mmol) was dissolved in 2 mL of THF at room temperature and subsequently treated with $NaBH_4$ (28 mg, 0.744 mmol). The colorless solution turned into a dark red-brown suspension that was stirred at room temperature overnight. During this time the color of the suspension changed to yellow. The reaction mixture was then filtered through Celite, and the filtrate was evaporated to dryness in vacuo. The residue was washed with pentane (5 × 2 mL) and the crude yellow product precipitated from THF and pentane to afford 120 mg of yellow powder. This compound is not stable for prolonged periods in solution. $^{31}P\{^1H\}$ NMR (202.46 MHz, benzene-d_6): δ 67.3 (br d, $^2J_{P,P}$ = 18.0 Hz), 49.8 (br). $^{13}C\{^1H\}$ NMR (125.77 MHz, CD_2Cl_2): δ 15.3 (C13), 15.8 (C1), 19.1 (C18), 20.7 (C6), 33.7, 35.5, 36.8, 37.6, 38.0, 41.1, 42.3, 128.6, 129.0, 133.8, 134.2. ^1H NMR (500 MHz, CD_2Cl_2): δ −0.56 (br, 1H), 0.76 (dd, 6H, CH_3 1, $^3J_{PH}$ = 12.4, $^3J_{HH}$ = 7.3 Hz), 0.97 (dd, 6H, CH_3 13, $^3J_{PH}$ = 13.6, $^3J_{HH}$ = 7.3 Hz), 1.59−1.64 (m, 3H), 1.70 (dd, 6H, CH_3 18, $^3J_{PH}$ = 18.1, $^3J_{HH}$ = 7.0 Hz), 1.73 (dd, 6H, CH_3 6, $^3J_{PH}$ = 17.7,$^3J_{HH}$ = 7.0 Hz), 1.89−1.98 (m, 4H), 2.04 (m, 2H), 2.07−2.18 (m, 4H), 2.35 (m, 2H), 2.45 (m, 2H), 2.66 (m, 2H), 2.69−2.77 (m, 4H), 3.82 (m, 2H), 4.64 (br, 1H), 7.22−7.26 (m, 4H), 7.64−7.72 (m, 4H), 8.67 (br, 2H).

Hydroarylation Catalysis. A typical procedure for the catalytic reaction is as follows. To a solution of **5** (13.8 mg, 0.02599 mmol) in dry DMF (6 mL) were added phenyl iodide (96 μL, 0.8607 mmol), norbornene (262.5 mg, 2.7878 mmol), triethylammine (390 μL, 2.798 mmol) and formic acid (84 μL, 2.226 mmol). The mixture was stirred under argon at room temperature for 24 h. The resulting solution was treated with 6 mL of water and the mixture then extracted with pentane (3 × 12 mL). The combined organic phase was dried over $MgSO_4$ and filtered. After evaporation of the solvent the product was purified by chromatography on silica gel using pentane as eluent. The enantiomeric excesses were determined by HPLC analysis with a chiral stationary phase column (Chiracel OJ column, 9/1 hexane/2-propanol, 3 mL/min).

Transfer Hydrogenation Reaction. To a solution of **5** (13.8 mg, 0.02599 mmol) were added 3-methyl-2-cyclohexenone (98 μL, 0.8607 mmol), triethylamine (390 μL, 2.798 mmol), and formic acid (84 μL, 2.226 mmol). The mixture was stirred under argon at 50 °C for 24 h. The resulting solution was treated with 6 mL of water and the mixture then extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was dried over $MgSO_4$ and filtered. After evaporation of the solvent the product was purified by chromatography on silica gel using 3/1 CH_2Cl_2/ether as eluent. Yield: 38 mg (ca. 40%, the remaining material is unreacted 3-methylcyclohexenone); ee = 30%.

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Supporting Information Available: A figure giving the NOESY spectrum of **8** and tables giving X-ray crystallographic data for **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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