Chiral Palladium(0) *trans*-Stilbene Complexes: Synthesis, Structure, and Oxidative Addition of Phenyl Iodide

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Received February 17, 2005

The chiral Pd(0) *trans*-stilbene complexes Pd(diphos*)(*trans*-stilbene) (diphos* = (*R*,*R*)-Me-Duphos, (*R*,*R*)-Et-Duphos, (*R*,*R*)-i-Pr-Duphos, (*R*,*R*)-Me-BPE, (*S*,*S*)-Me-FerroLANE, (*S*,*S*)-Me-DuXantphos, (*S*,*S*)-Et-FerroTANE, (*R*,*S*)-CyPF-t-Bu, (*R*,*S*)-PPF-t-Bu, (*R*,*S*)-BoPhoz) and Ni((*R*,*R*)-Me-Duphos)(*trans*-stilbene) were prepared by $NaBH(OMe)_3$ reduction of the corresponding M(diphos*)Cl_2 compounds in the presence of *trans*-stilbene. The rate of oxidative addition of phenyl iodide to the stilbene complexes, which gave Pd(diphos*)(Ph)(I), depended on the ligand (larger for increased ligand bite angles and reduced steric bulk) and was markedly faster than oxidative addition to mixtures of $Pd(dba)_2$ and diphos*. The complexes Pd(diphos*)(Ph)(I) were prepared independently by treatment of $PdL_2(Ph)(I)$ (L_2 = TMEDA, $(PPh_3)_2$) with diphos*. Oxidative addition of PhI to the complexes M((*R*,*R*)-Me-Duphos)(*trans*-stilbene) occurred in the rate order Pd > Ni ≫ Pt. The complexes Pd(diphos*)Cl_2, Pd(diphos*)-(*trans*-stilbene), and Pd(diphos*)(Ph)(I), as well as some analogous Ni compounds, were structurally characterized by X-ray crystallography.

Introduction

Pd(0) complexes are catalysts for many synthetically valuable reactions.[1] The commercially available zerovalent PdL_4 (L = PPh_3) is often used as a catalyst precursor. However, for other phosphines and diphosphines, catalysts are commonly produced in situ. When precursors such as $Pd(OAc)_2$ are used, catalyst productivity and selectivity depend not only on the properties of the ligand but also on the details of the activation step, reduction of Pd(II) to Pd(0).[2] Using the zerovalent precursors $Pd(dba)_2$ and $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone) avoids this complication, but the activated olefin dba often binds tightly to Pd, slowing oxidative addition,[3] and it can undergo side reactions.[4]

Replacing dba with less functionalized olefins might limit these problems, but little is known about simple alkene complexes of Pd(0), in contrast to the well-developed chemistry of Ni and Pt.[5,6] Such Pd compounds have been reported to contain labile alkene ligands. For example, Pd(diop)(ethylene)[7] and the analogous dppe complex[8] readily decomposed in solution in the absence of ethylene, and in Pd(dppf)(methyl acrylate), rapid exchange of free and bound olefin occurred on the NMR time scale.[9] However, the sterically demanding *alkylphosphine* complexes $Pd(R_2PCH_2CH_2PR_2)(C_2H_4)$ (R = t-Bu, i-Pr) were stable in solution in the absence of ethylene.[10]

In addition to stabilizing Pd alkene complexes, related chelating alkylphosphines might be useful for catalytic reactions in which it is crucial that the diphosphine does not dissociate from the metal, even in the presence of an excess of competing ligands. Such processes include

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10.1021/om050115h CCC: $30.25
Publication on Web 04/22/2005

Pd-catalyzed asymmetric phosphination[11] and Pt-catalyzed asymmetric hydrophosphination, for which the bulky alkylphosphine Me-Duphos was a useful ligand.[12] We previously described the well-defined catalyst precursor Pt(Me-Duphos)(*trans*-stilbene) and related Pt(diphos)(*trans*-stilbene) compounds.[13] Here we report a series of analogous chiral Pd *trans*-stilbene complexes, which in many cases are robust crystalline compounds stable on storage.[14] Varying the diphosphine ligand and the metal (Ni, Pd, Pt) revealed trends in selectivity of binding of one stilbene enantioface.[13,15]

Oxidative addition of an aryl or vinyl halide or sulfonate to Pd(0), the first step in popular cross-coupling or Heck reactions, has been studied in detail.[16] To investigate effects of the diphosphine ligand on this step, we studied the oxidative addition of PhI to the stilbene complexes and compared the rates of these reactions to those of Pd(diphos*)(dba), generated in situ. Structural effects of the different ligands were probed by X-ray structure determinations of three classes of complexes: Pd(diphos*)Cl_2, Pd(diphos*)(*trans*-stilbene), and Pd(diphos*)(Ph)(I), as well as some analogous Ni compounds.

Results and Discussion

Treatment of Pd(COD)Cl_2 (COD = cyclooctadiene) with the chiral diphosphines shown in Scheme 1 (all are commercially available except for Me-FerroLANE and Me-DuXantphos) gave the air-stable complexes Pd(diphos*)Cl_2 (diphos* = (*R*,*R*)-Me-Duphos (**1a**), (*R*,*R*)-Et-Duphos (**1b**), (*R*,*R*)-i-Pr-Duphos (**1c**), (*R*,*R*)-Me-BPE (**1d**), (*S*,*S*)-Me-FerroLANE (**1e**),[17] (*S*,*S*)-Me-DuXantphos (**1f**),[18] (*S*,*S*)-Et-FerroTANE (**1g**), (*R*,*S*)-CyPF-t-Bu (**1h**), (*R*,*S*)-PPF-t-Bu (**1i**), (*R*,*S*)-BoPhoz (**1j**)[19,20]), which were characterized by NMR spectroscopy and elemental analyses.

Scheme 1

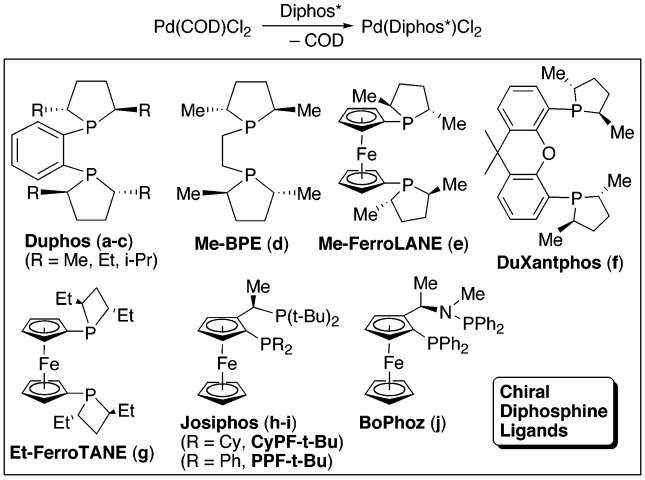

Table 1. Selected Bond Lengths (Å) and Angles (deg) (Average Values) in the Complexes Pd(diphos*)Cl_2

	1a·CH_2Cl_2	[**1b**]$_3$·2(acetone)	**1e**	**1g**
diphos	Me-Duphos[a]	Et-Duphos[b]	Me-Ferro-LANE	Et-Ferro-TANE
Pd−P	2.2183(15)	2.215(3)	2.2734(7)	2.2726(5)
Pd−Cl	2.3637(16)	2.355(3)	2.3535(7)	2.3600(5)
P−Pd−P	87.04(5)	87.26(13)	100.16(2)	98.799(17)
Cl−Pd−Cl	94.37(5)	93.81(14)	88.59(3)	87.237(17)
P−Pd−Cl	89.26(5)	90.56(14)	85.85(2)	87.098(18)
	175.81(6)	175.23(10)	172.26(2)	172.92(18)

[a] Average values. See the Supporting Information of ref 11b for data. [b] The asymmetric unit contains 1.5 Pd molecules; average bond lengths and angles are reported.

Little is known about the Pd coordination chemistry of some of these ligands;[21] thus, the $PdCl_2$ complexes of Et-Duphos, Et-FerroTANE, and Me-FerroLANE were further characterized by X-ray crystallography (Table 1 and the Supporting Information). Apart from the expected larger bite angles for the ferrocene-based ligands, the structures are quite similar, with the Pd−P bond distances slightly greater for **1e**,**g**.

The DuXantphos complex **1f** displayed unusual NMR behavior. At room temperature in CD_2Cl_2 or $CDCl_3$, the ^{1}H NMR spectrum contained broad peaks, and the ^{31}P NMR spectrum (CD_2Cl_2) included a sharp low-intensity singlet at δ 31.8 (<5%) plus two broad signals at δ 48.8 and 37.3. When the temperature was lowered to −20 °C, these broad signals sharpened to two doublets (J = 9 Hz) at δ 49.2 and 36.6. At this temperature, the ^{1}H NMR spectrum contained signals for six inequivalent methyl groups.

These observations are consistent with the existence (at room temperature) of a small amount of the trans

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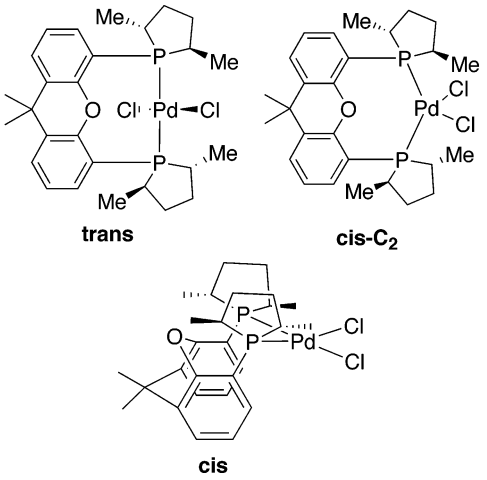
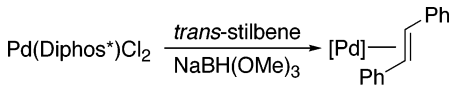
Chart 1. Trans and Cis Isomers of Pd(Me-DuXantphos)Cl_2 (1f)



Scheme 2[a]



[a] [Pd] = Pd(diphos*).

isomer and a fluxional major cis isomer. The C_2-symmetric cis isomer, which requires a planar xanthane ring system (Chart 1), would have equivalent P nuclei and three pairs of equivalent Me groups, but molecular modeling suggests that this conformation induces greater steric repulsions than others in which the ring is puckered. With such an envelope conformation in the C_2-symmetric cis isomer, the P nuclei and all six Me groups are inequivalent, as observed at low temperature. These NMR observations are consistent with the NMR and X-ray crystallographic results of Osborn et al. on a Pd cyclohexenyl cation with a closely related ligand.[18] The fluxional process may involve interconversion of different ligand ring conformations via the C_2-symmetric isomer; related observations in a variety of Pd−Xantphos complexes have been described recently.[18b,22]

As in analogous Pt chemistry,[13] reduction of dichloride precursors **1a**−**j** with an excess (typically 3 equiv) of $NaBH(OMe)_3$ in THF in the presence of *trans*-stilbene gave the title stilbene complexes Pd(diphos*)(*trans*-stilbene) **2a**−**j** (Scheme 2).[11a] After the THF was removed in vacuo, extraction with toluene removed unidentified brown material, and **2a**−**j** were purified by recrystallization. For the Duphos complexes **2a**−**c**, using an excess (2−3 equiv) of stilbene reduced the amount of brown impurity and simplified the workup, but it was difficult to separate the excess stilbene from the Pd complexes. With 1 equiv of stilbene, more brown material was formed; yields were reduced and purification was more difficult, but Pd complexes free of excess stilbene could be obtained. Because small amounts of free stilbene did not affect oxidative addition of PhI to the stilbene complexes (see below) or their performance as precursors for catalytic asymmetric phosphination (to be described separately), it is more convenient to use excess stilbene in the synthesis of **2a**−**c**. A slight excess of *trans*-stilbene (ca. 1.1 equiv) was used to prepare complexes of the other diphosphines. In all cases, analogous toluene-insoluble material was observed; yields and ease of purification depended on the ligand.

Stilbene complexes **2a**−**j** were isolated as greenish yellow, orange, or brown crystalline solids. In most cases, they were stored in a freezer under nitrogen as a precaution; under these conditions they were stable for months. For comparison to other Pd alkene complexes, we also investigated their stability in solution and in the solid state at room temperature, which depended on the diphosphine ligand. Freshly recrystallized **2a**, a bright canary yellow solid, gradually changed color to greenish yellow and then gray yellow on standing in the solid state under nitrogen. When a pentane solution of this material was filtered through Celite to remove a gray precipitate (presumably Pd metal) and then concentrated, **2a** could be recovered as a yellow solid. Heating a solution of **2a** in toluene to 100 °C overnight caused some decomposition to Pd metal, but a ^{31}P NMR spectrum of the yellow solution showed that **2a** survived. The Et-FerroTANE complex **2g** was stable as a solid and decomposed slowly in solution over several days; the Me-FerroLANE complex **2e** was formed in higher yield with less byproduct and was more stable in solution as well. The Me-BPE complex **2d** was the most sensitive in this Pd phospholane series, decomposing slowly even on storage as a solid in the glovebox freezer (−25 °C; yellow crystals formed a brown solid); in C_6D_6 solution some decomposition was observed in just a few hours.

$NaBH(OMe)_3$ reduction of Pd(Me-DuXantphos)Cl_2 in the presence of stilbene led to formation of free Me-DuXantphos as well as a material believed to be Pd(Me-DuXantphos)(*trans*-stilbene) (**2f**). Like the other Me-DuXantphos complexes described here, **2f** showed broad room-temperature ^1H and ^{31}P NMR spectra. Low-temperature ^1H NMR spectra revealed resonances characteristic of coordinated stilbene (see the Experimental Section), but **2f** could not be isolated in pure form to enable study of its fluxionality in solution.

The Josiphos complexes **2h**,**i** were robust both as solids and in solution, but the BoPhoz derivative **2j** decomposed at room temperature even in the solid state, so that we could not obtain correct elemental analyses for this complex. However, it could be stored as a solid at −30 °C under nitrogen without decomposition.

The nickel complex Ni(Me-Duphos)(*trans*-stilbene) (**Ni-2a**), which is highly air-sensitive in solution but stable as a solid, was prepared similarly.[23] Although treatment of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) with *trans*-stilbene in the presence of triarylphosphines gave $Ni(PAr_3)_2$(*trans*-stilbene),[24] a similar reaction of Ni(COD)$_2$ with Me-Duphos and stilbene gave instead Ni(Me-Duphos)(COD) (**4**), along with a small amount of

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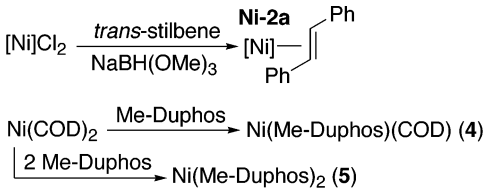
Table 2. Selected NMR Data for M(diphos*)(*trans*-stilbene) Complexes[a]

compd	diphos	diastereomer ratio	$\delta(^{31}P)$	$\delta(^{1}H)$[b]	$\delta(^{13}C)$[c]
2a	Me-Duphos	5.6:1	57.6	5.50 (d, $J = 2$)	60.6 (t, $J = 10$)
			50.8	5.25 (d, $J = 2$)	64.2 (m)
2b	Et-Duphos	7.8:1	51.5	5.46 (d, $J = 2$)	60.2 (t, $J = 10$)
			46.4	5.24 (d, $J = 2$)	64.0
2c	i-Pr-Duphos	38:1	44.7	5.34 (d, $J = 2$)	62.9 (t, $J = 11$)
			47.6	5.18	d
2d	Me-BPE	2.5:1	55.8	5.44 (d, $J = 2$)	62.6 (t, $J = 11$)
			45.3	5.40 (d, $J = 2$)	60.7 (t, $J = 10$)
2e	Me-FerroLANE	6.4:1	36.2	5.02 (m)	63.6 (m)
			32.5	5.00 (m)	*d*
2g	Et-FerroTANE	10.3:1	44.1	5.33	64.8 (t, $J = 10$)
			37.7	5.30	*d*
2h	CyPF-t-Bu	40:1	76.5, 20.3[e]	4.78 (br), 4.68 (m)[f]	66.3 (d, $J = 28$), 63.7 (dd, $J = 27, 5$)
			82.9, 18.6	*d*	*d*
2i	PPF-t-Bu	25:1	77.5, 9.6[e]	4.97, 4.33[f]	69.9 (dd, $J = 23, 5$), 68.6 (d, $J = 28$)
			d	*d*	*d*
2j	BoPhoz	2:1	89.8, 8.6[e]	5.33, 5.19[f]	71.9 (m), 66.5 (m)[g]
			90.2, 8.1	5.86 (br), 5.52 (br)	*d*
Ni-2a	Me-Duphos	55:1	68.9	4.67	52.5 (t, $J = 9$)
			60.9	4.32	*d*
Pt-2a[h]	Me-Duphos	3:1	71.4	4.64 (m)	50.3 (t, $J = 16$)
			66.3	4.45 (m)	53.4 (t, $J = 16$)

[a] Solvent: C_6D_6. Chemical shifts are given in ppm and coupling constants in Hz. Data for the major diastereomer is given first. [b] Stilbene C*H*. [c] Stilbene *C*H. [d] Not observed. [e] For the unsymmetrical complexes **2h**−**j**, J_{PP} values in Hz for the major and minor diastereomers, respectively, are as follows: for **2h**, 5, not observed; for **2i**, 14, not observed; for **2j**, 23, 21. [f] For **2h**−**j**, $J_{HH} = 10$ Hz. J_{PH} values (Hz) are as follows: for **2h**, (δ 4.68) 4.5, 5.0, (δ 4.78) 5.0, 4.5; for **2i**, (δ 4.33) 4.5, 8.0; (δ 4.97) 4.7, 6.3. for **2j**, J_{PH} appeared to be similar in magnitude, but the broadness of the peaks precluded precise simulations. For **2h**−**j**, the similar magnitudes of the two J_{PH} couplings prevented us from making assignments of the stilbene CH ^{1}H NMR signals to specific protons. [g] In toluene-d_8, these peaks were better resolved and showed doublet couplings of 20 and 27 Hz, respectively. [h] Reference 13.

Scheme 3[a]



[a] [Ni] = Ni(Me-Duphos).

Ni(Me-Duphos)$_2$ (**5**).[25] Complexes **4** and **5** were prepared directly from Ni(COD)$_2$ and 1 or 2 equiv of Me-Duphos (Scheme 3).

Characteristic NMR data for the *trans*-stilbene complexes are summarized in Table 2. No exchange of free and bound stilbene was observed on the NMR time scale. In the Pd complexes, the coordinated *trans*-stilbene gave rise to ^{1}H NMR signals around 5 ppm and ^{13}C NMR alkene resonances near 60 ppm. Interestingly, in **Ni-2a** and **Pt-2a**, these ^{1}H peaks appeared at lower chemical shift than in the Pd analogue **2a**, near 4.5 ppm, as did the ^{13}C signals, near 50 ppm.

Because the Josiphos and BoPhoz ligands in **2h**−**j** are not C_2 symmetric, the stilbene CH protons and carbons are inequivalent. Selective ^{31}P-decoupling experiments and simulation of the ^{1}H NMR spectra with gNMR[26] enabled assignment of the J_{HH} and J_{PH} coupling constants for coordinated stilbene (see Table 2). In comparison to *trans*-stilbene itself,[27] or unsymmetrical stilbenes ArCH=CHAr′, where $J_{HH} \approx 16$ Hz,[28] in complexes **2h**−**j** J_{HH} is reduced to ~10 Hz, consistent with a change in hybridization of the stilbene carbons on binding to Pd.[29]

The ratio of diastereomers for the *trans*-stilbene complexes depended on the ligand, increasing significantly in the Duphos series **a**−**c** as the ligand substituents increase in size. As the metal is varied in the series M(Me-Duphos)(*trans*-stilbene), selectivity of stilbene binding decreased down the group (Ni (55:1) > Pd (5.6:1) > Pt (3:1)). Nickel's position as the most selective is readily rationalized in terms of its smaller size, which magnifies Duphos−stilbene steric interactions, but the difference between the Pd and Pt complexes, where the metals are presumably similar in size, is less easy to explain.

The crystal structures of the palladium stilbene complexes **2c**,**g**,**h**, the nickel stilbene complex **Ni-2a**, and the nickel cyclooctadiene complex **4** are shown in Figures 1−5; see Tables 3 and 4 for crystallographic details and selected bond lengths and angles.

As mentioned above, palladium alkene complexes have been less investigated than those of nickel and platinum. Previous work suggested that the affinity of Pd for alkene ligands is weaker than that of the other metals.[30,31] Structural characterization of **Ni-2a**, **2c**, and **Pt-2a** permits comparison of metal−stilbene binding in

(25) For other Ni(diphos)(COD) complexes, see: (a) Spielvogel, D. J.; Davis, W. M.; Buchwald, S. L. *Organometallics* **2002**, *21*, 3833−3836. (b) Pawlas, J.; Nakao, Y.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 3669−3679. (c) van Soolingen, J.; Brandsma, L.; Kruse, C. G. Eur. Pat. Appl. 613719, 1993.

(26) gNMR (Budzelaar, P. gNMR v3.6.5; Cherwell Scientific, 1992−1996) is commercial software for the simulation and analysis of NMR spectra.

(27) Mucci, A.; Parenti, F.; Schenetti, L. *Eur. J. Org. Chem.* **2002**, 938−940.

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(31) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669−2676.

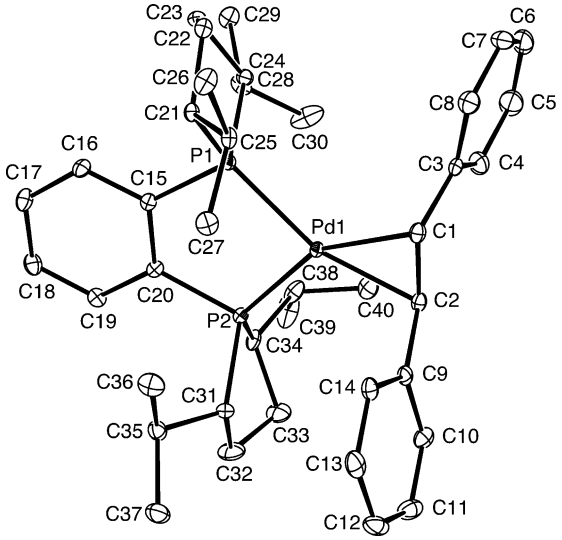


Figure 1. ORTEP diagram of Pd((*R*,*R*)-i-Pr-Duphos)(*trans*-stilbene) (**2c**).

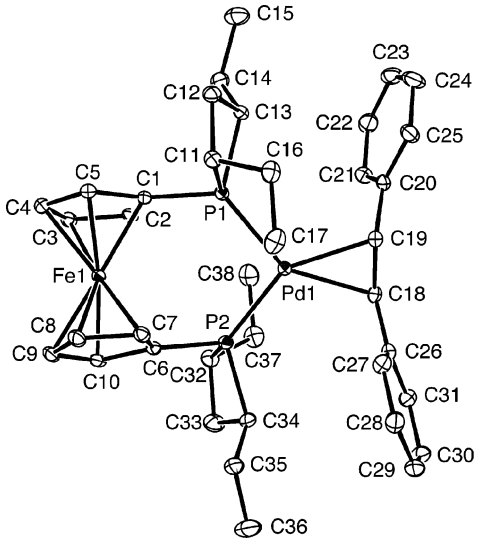


Figure 2. ORTEP diagram of Pd((*S*,*S*)-Et-FerroTANE)(*trans*-stilbene) (**2g**).

the series. As expected, the complex of the smaller Ni atom featured the shortest M−C and M−P bonds. Weaker Pd−C interactions, with reduced back-bonding in comparison to the other metals, would be expected to result in longer Pd−C and C=C (stilbene) distances, but the differences observed are small or not significant. We have not attempted further comparative structural analysis of the metal−stilbene bonding,[32] because steric effects of the larger i-Pr-Duphos ligand in **2c** may obscure electronic effects of the different metals.

Comparison of structures with the same metal suggests that varying the diphosphine ligand has little effect on the metal−stilbene interaction. For the Pd complexes **2c**,**g**,**h**, although the FerroTANE and CyPF-t-Bu bite angles are considerably larger than that of i-Pr-Duphos (106.673(18), 100.29(8), and 89.01(2)°, respectively), the structures are otherwise very similar. Likewise, the complex Ni(dtbpm)(*trans*-stilbene) (dtbpm = $(t\text{-Bu})_2PCH_2P(t\text{-Bu})_2$) features an unusually small bite

(32) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33−61.

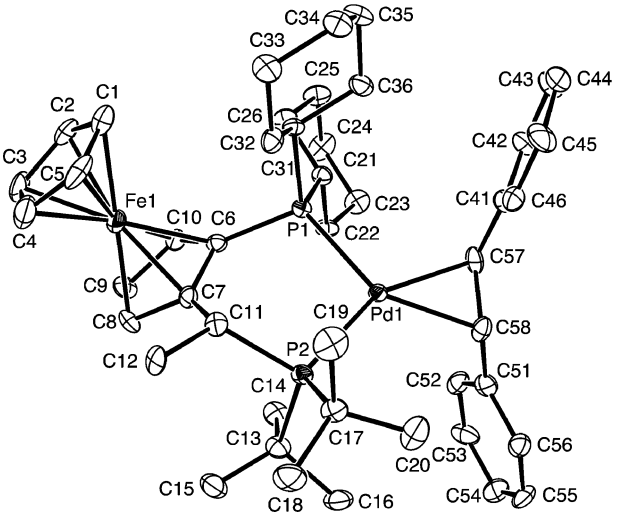


Figure 3. ORTEP diagram of Pd((*R*,*S*)-CyPF-t-Bu)(*trans*-stilbene) (**2h**).

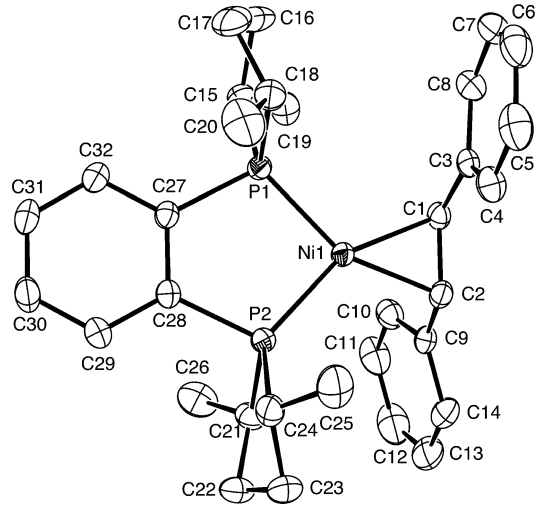


Figure 4. ORTEP diagram of Ni((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (**Ni-2a**).

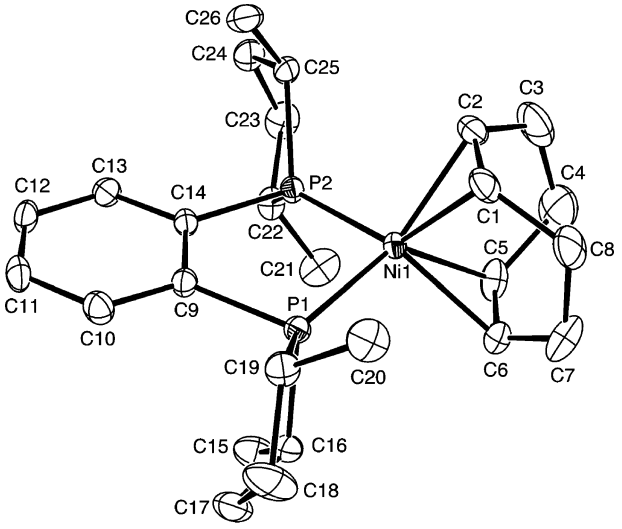


Figure 5. ORTEP diagram of Ni((*R*,*R*)-Me-Duphos)(COD) (**4**).

angle (79.6(1)°) in comparison to that in **Ni-2a** (91.84(3)°).[23b] The shorter Ni−C and longer C=C (stilbene) distances in **Ni-2a** might be attributed to a stronger

Table 3. Crystallographic Data for Complexes 2c,g,h, Ni-2a, 3a, 3g·0.33C_7H_8, 3i·CH_2Cl_2, and 4

	2c	2g	2h	Ni-2a	3a	3g·0.33C_7H_8	3i·CH_2Cl_2	4
formula	$C_{40}H_{56}P_2Pd$	$C_{38}H_{48}FeP_2Pd$	$C_{46}H_{64}FeP_2Pd$	$C_{32}H_{40}NiP_2$	$C_{30}H_{39}IP_2Pd$	$C_{32.33}H_{43.67}FeIP_2Pd$	$C_{39}H_{47}Cl_2FeIP_2Pd$	$C_{26}H_{40}NiP_2$
fw	705.19	728.95	841.16	545.29	694.85	783.43	937.76	473.23
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P4_3$	$P2_1$	$P2_12_12$
a, Å	10.8583(6)	11.5878(6)	14.4666(12)	11.9233(19)	9.8739(6)	17.7091(6)	9.612(3)	17.4446(8)
b, Å	15.3242(9)	15.2320(8)	18.2168(15)	12.158(2)	16.9699(10)	17.7091(6)	15.196(5)	18.0140(9)
c, Å	22.2132(13)	19.4887(10)	18.3127(16)	20.517(4)	10.0976(6)	30.6787(19)	13.524(5)	7.8476(4)
β, deg	90	90	90	90	116.8340(10)	90	92.40(3)	90
V, Å^3	3696.2(4)	3439.9(3)	4826.0(7)	2974.2(9)	1509.75(16)	9621.2(8)	1973.7(11)	2466.1(2)
Z	4	4	4	4	2	12	2	4
D(calcd), g/cm^3	1.267	1.408	1.158	1.218	1.529	1.623	1.578	1.275
μ(MoKα), mm^{-1}	0.614	1.062	0.766	0.778	1.759	2.095	1.848	0.927
temp, K	100(2)	150(2)	203(2)	213(2)	173(2)	100(2)	252(2)	213(2)
$R(F)$, %[a]	0.0330	0.0217	0.0669	0.0352	0.0199	0.0438	0.0349	0.0397
R(wF^2), %[a]	0.0650	0.0526	0.1599	0.0837	0.0439	0.0876	0.0873	0.0816

[a] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o,0)]/3$.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in the Complexes M(diphos*)(*trans*-stilbene)

	Ni-2a	2c	Pt-2a	2g	2h	Ni-dtbpm
diphos	Me-Duphos	i-Pr-Duphos	Me-Duphos[a]	Et-FerroTANE	CyPF-t-Bu	dtbpm[b]
M−P	2.1240(6)	2.2787(7)	2.235(4)	2.2927(5)	2.314(2)	2.222(1)
	2.1267(6)	2.2859(7)	2.240(3)	2.3012(5)	2.344(2)	2.218(1)
M−C	1.965(2)	2.136(3)	2.102(12)	2.1498(17)	2.125(8)	1.982(4)
	1.975(2)	2.134(3)	2.113(12)	2.1599(19)	2.156(8)	1.979(4)
C−C	1.417(3)	1.419(4)	1.436(18)	1.417(3)	1.430(13)	1.430(7)
P−M−P	91.84(3)	89.01(2)	88.49(13)	106.673(18)	100.29(8)	79.6(1)
C−M−C	42.16(9)	38.83(11)	39.8(5)	38.39(7)	39.0(3)	42.3(2)
P−M−C	113.75(7)	117.09(8)	115.5(4)	107.56(5)	107.0(3)	118.7(2)
	112.27(7)	114.75(8)	116.2(4)	107.45(5)	113.8(2)	120.2(1)
	154.14(7)	153.37(8)	155.3(4)	145.72(5)	145.5(2)	159.2(10)
	155.88(7)	155.79(8)	155.9(4)	145.87(5)	152.7(3)	161.0(2)
(P−M−P)−(C−M−C)[c]	4.6	5.0	3.9	4.1	7.2	14.4

[a] Reference 13. [b] Reference 23b. [c] Dihedral angle between these planes.

Table 5. Selected Bond Distances (Å) and Angles (deg) for the Complexes Ni((*R*,*R*)-Me-Duphos)(COD) (4) and Ni(*S*-BINAP)(COD)[a]

	Ni((*R*,*R*)-Me-Duphos)(COD)	Ni(*S*-BINAP)(COD)
Ni−C (av)	2.0987(3)	2.110(10)
Ni−P (av)	2.1529(7)	2.174(3)
C−C (av)	1.365(5)	1.394(13)
P−Ni−P	90.48(3)	97.37(10)
C−Ni−C (av)	37.95(14)	38.6(4)

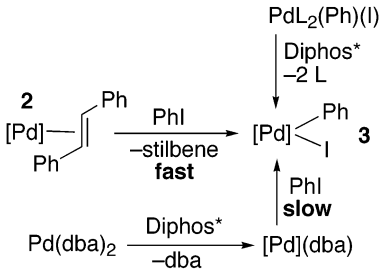
[a] Reference 25a.

Ni−C bond with greater back-bonding, but these observations, as well as the longer Ni−P bonds in the dtbpm complex, could also result from greater steric crowding.

Details of a similar comparison of Ni(Me-Duphos)(COD) (**4**) with the analogous BINAP complex[25a] are shown in Table 5. As expected, the less sterically demanding, better donor ligand Me-Duphos resulted in shorter Ni−P bonds, and the BINAP bite angle was larger than that of Me-Duphos. However, Ni−COD bonding does not differ significantly in these structures.

Oxidative addition of PhI to the stilbene complexes was studied in NMR tube scale experiments in toluene (Scheme 4 and Table 6). For the Duphos complexes, oxidative addition occurred in minutes to hours, more quickly for the smaller ligands, in the order Me-Duphos > Et-Duphos > i-Pr-Duphos. A trace of the complex Pd(Me-Duphos)I_2 was observed as a byproduct from **2a**, with increasing amounts of impurities assumed to be the analogous diiodide complexes seen for the larger Et-Duphos (ca. 6%) and i-Pr-Duphos (ca. 26%) complexes.[33] In contrast, no diiodide impurities were observed for the faster (minutes) oxidative additions of BPE, FerroLANE, and FerroTANE complexes **2d**,**e**,**g**. Treatment of the impure Me-DuXantphos complex **2f** with PhI also led to oxidative addition within minutes to yield *trans*-Pd(Me-DuXantphos)(Ph)(I) (**3f**; see below). Oxidative addition to the Josiphos and BoPhoz complexes **2h**−**j** also proceeded quickly.

Scheme 4[a]



[a] [Pd] = Pd(Diphos*); L_2 = $(PPh_3)_2$, TMEDA.

In summary, the large bite angle ligands (ferrocene-based, or DuXantphos) led to fast oxidative addition. Results in the Duphos/BPE series showed that reduced steric bulk also promoted oxidative addition. Further analysis of these structural trends would require de-

(33) These diiodide complexes were identified by ^{31}P NMR spectroscopy in comparison to the well-characterized Pd(Me-Duphos)I_2.[11b] ^{31}P NMR chemical shifts (toluene): for Pd(Et-Duphos)I_2, δ 84.5; for Pd(i-Pr-Duphos)I_2, δ 81.7.

Table 6. Oxidative Addition of PhI to M(diphos*)(*trans*-stilbene) Complexes and to Mixtures of Pd(dba)$_2$ and diphos*[a]

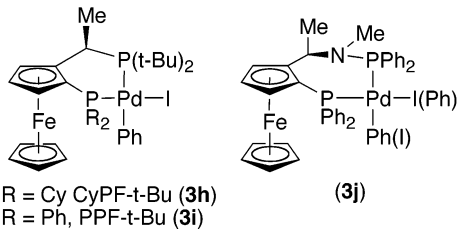
compd	Diphos*	approx reacn time[b,c]	byproduct
2a **2a-dba**	Me-Duphos	<25 min NR (70 h)[c]	[Pd]I_2 (trace)
2b **2b-dba**	Et-Duphos	3 h NR (70 h)	[Pd]I_2 (6%)
2c **2c-dba**	i-Pr-Duphos	9 h (70 h)	[Pd]I_2 (26%) [Pd]I_2[d]
2d **2d-dba**	Me-BPE	15 min NR (28 h)	*e*
2e **2e-dba**	Me-FerroLANE	5 min 37% (74 h)	*e*
2f **2f-dba**	DuXantphos	5 min 2 h	*e*
2g **2g-dba**	Et-FerroTANE	5 min 56% (51 h)	*e*
2h **2h-dba**	CyPF-t-Bu	<60 min NR (24 h)[f]	*e*
2i **2i-dba**	PPF-t-Bu	<45 min 72 h, 50 °C	*e*
2j **2j-dba**	BoPhoz	<30 min 24 h	*e*
Ni-2a	Me-Duphos	100 min	*e*
Pt-2a	Me-Duphos	*g*	[Pt]I_2 (major product)

[a] Conditions: room temperature, ~1.5 equiv of PhI, toluene. Reactions were monitored by ^{31}P NMR spectroscopy. [b] Time for complete conversion to the product [M](Ph)(I) and byproducts, [M]I_2. In cases where conversion was not complete, the reaction time and percent conversion are reported. [c] NR = no reaction. [d] Yield was not determined. [e] No byproducts were observed. [f] No reaction after 24 h at room temperature or after 48 h at 60 °C. [g] No reaction at room temperature; heating to 60 °C gave a small amount of **Pt-3a** and Pt(Me-Duphos)I_2 as the major product.

tailed knowledge of the mechanism of oxidative addition, which we have investigated in only one case. Added *trans*-stilbene clearly slowed the rate of oxidative addition of PhI to Pd(Me-Duphos)(*trans*-stilbene) (**2a**). Reaction was complete in <1 h for pure **2a** but required 5 h when 5 equiv of stilbene was added and >24 h with 10 equiv. These results are consistent with an important contribution from a dissociative pathway, as reported for PhI oxidative addition to Pd(diphos)(dba).[3a] Similarly, we previously observed that added *trans*-stilbene slowed conversion of one diastereomer of Pt(Tol-Binap)(*trans*-stilbene) into the other, which suggested isomerization occurred by a dissociative mechanism involving loss of stilbene and binding of the other enantioface.[13]

For comparison, mixtures of Pd(dba)$_2$ and a chiral diphosphine were prepared. These solutions presumably contain Pd(diphos*)(dba), consistent with their ^{31}P NMR spectra (see Table 9 in the Experimental Section), but they were not characterized further. Under comparable conditions (toluene, room temperature, ca. 1.5 equiv of PhI), their reactions with PhI were much slower than those of the stilbene complexes. Pd(dba)$_2$/Duphos mixtures with PhI led either to no reaction (Me-Duphos, Et-Duphos) or to the formation of a small amount of Pd(i-Pr-Duphos)I_2. The FerroLANE and FerroTANE dba complexes reacted slowly with PhI to give the oxidative addition products. In contrast, a mixture of Me-DuXantphos and Pd(dba)$_2$ reacted rapidly with PhI in toluene to yield *trans*-Pd(Me-DuXantphos)(Ph)(I) (see below), and Pd(dba)$_2$/BoPhoz underwent PhI oxidative addition overnight. When Josiphos/Pd(dba)$_2$ mixtures were treated with PhI, no reaction occurred with the CyPF-t-Bu ligand, and slow oxidative addition occurred on heating for PPF-t-Bu. Slow oxidative addition of aryl halides to Pd(diphos)(dba) complexes has been observed previously and rationalized by the reluctance of the dba ligand to dissociate from Pd to afford the reactive intermediate Pd(diphos).[3b,34]

Chart 2. Josiphos Complexes 3h,i and BoPhoz Complex 3j[a]



R = Cy CyPF-t-Bu (**3h**)
R = Ph, PPF-t-Bu (**3i**)

(**3j**)

[a] The complexes **3h,i** were formed as single diastereomers, but complex **3j** was an 8:1 mixture.

As stated by a reviewer, "oxidative addition of Pd(0) complexes to PhI is generally fast and kinetically irrelevant in most mechanistic cycles of practical relevance." However, these results show that the rate of PhI oxidative addition depends strongly on the precursor, at least under the mild (room-temperature) conditions studied here. For several chiral diphosphines, oxidative addition occurred slowly or not at all when Pd(dba)$_2$/diphos mixtures were used. Since this reaction proceeded more quickly with stilbene complexes **2**, they may be preferable catalyst precursors in some cases.

The oxidative addition products Pd(diphos*)(Ph)(I) (**3a**–**j**) were prepared independently by ligand substitution reactions of $PdL_2(Ph)(I)$ (L_2 = TMEDA,[35] $(PPh_3)_2$[36]).[37] For Me-Duphos, synthesis via the TMEDA complex, even at low temperature in the dark, led to the formation of traces of Pd(Me-Duphos)$_2$ and Pd(Me-Duphos)I_2; thus, the alternative route was preferred.[11b] For the non-C_2-symmetric Josiphos and BoPhoz complexes, two regioisomers could be formed (Chart 2). Only one was observed for Josiphos complexes **3h**,**i**. X-ray crystallographic structure determinations (see below) showed that the Ph group was trans to the P(t-Bu)$_2$ ligand, consistent with Hartwig's observations on related Josiphos phenyl bromide complexes.[16a,d] For the BoPhoz compound **3j**, both diastereomers were observed, in a 8:1 ratio. Although **3j** appeared to be relatively stable in solution, it underwent partial decomposition on attempted isolation; for details, see the Experimental Section.[38]

As observed for dichloride **1f**, the Me-DuXantphos complex **3f** displayed broad NMR spectra in CD_2Cl_2 at

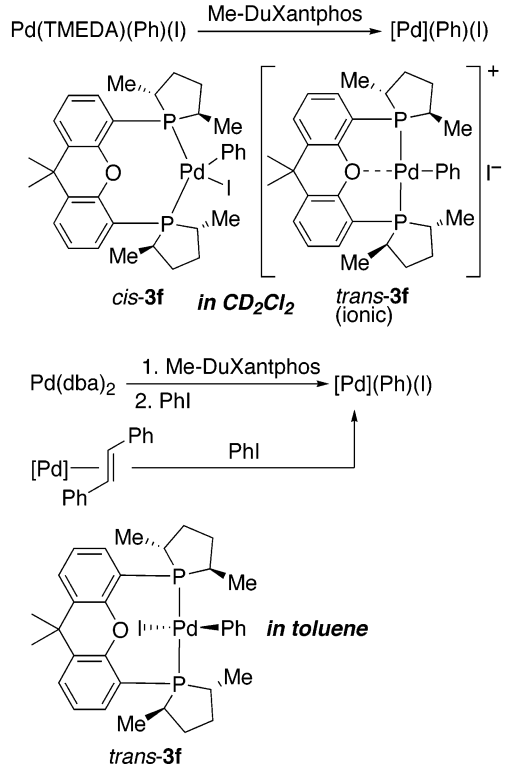
(34) Reid, S. M.; Mague, J. T.; Fink, M. J. *J. Organomet. Chem.* **2000**, *616*, 10–18.

(35) (a) de Graaf, W.; van Wegen, J.; Boersma, J.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 275–277. (b) Markies, B. A.; Canty, A. J.; de Graaf, W.; Boersma, J.; Janssen, M. D.; Hogerheide, M. P.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1994**, *482*, 191–199.

(36) (a) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287–291. (b) Fitton, P.; Johnson, M. P.; McKeon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 6–7.

(37) We reported FerroTANE complex **3g** previously,[21] and the Me-Duphos complex **3a** was described in both ref 11a and ref 20a.

Scheme 5[a]

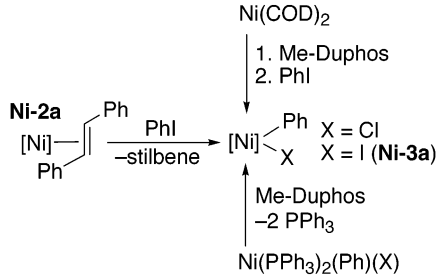


[a] [Pd] = Pd(Me-DuXantphos).

room temperature, characteristic of a fluxional process. Low-temperature ^{31}P and ^{1}H NMR spectroscopy were consistent with the existence of two isomers of this complex, the C_1-symmetric *cis*-**3f** and C_2-symmetric *trans*-**3f**, formulated as a cation with a Pd−O interaction by analogy to related Pd-Xantphos complexes (Scheme 5).[22] Once purified, this material did not dissolve in toluene. These isomers are different from that observed in toluene as a result of oxidative addition of PhI to Pd(dba)$_2$/Me-DuXantphos or to impure Pd(Me-DuXantphos)(stilbene). It showed a characteristic AB pattern in the ^{31}P NMR spectrum, assigned to *neutral trans*-**3f**. When the toluene was removed and this material was dissolved in CD_2Cl_2, it displayed a ^{31}P NMR spectrum identical with that of the isolated material, cationic *trans*-**3f**. This is consistent with ionization of the iodide being favored in the more polar solvent.

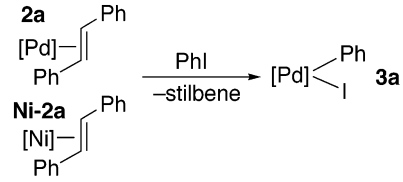
Oxidative addition of PhI to Ni(Me-Duphos)(*trans*-stilbene) (**Ni-2a**) quickly gave Ni(Me-Duphos)(Ph)(I) (**Ni-3a**) (Scheme 6), although this complex could not be isolated in pure form (see the Experimental Section). It could also be generated as the major product by treatment of Ni(COD)$_2$ with Me-Duphos and PhI. In another approach, oxidative addition of PhI to Ni(PPh$_3$)$_4$ gave Ni(PPh$_3$)$_2$(Ph)(I). This complex has been reported several times in the literature, but without details of its characterization.[39] Its NMR spectra (see the Experimental Section) suggested the presence of paramagnetic materials, as commonly observed for Ni(II), and decomposition in solution. In any case, treatment of Ni(PPh$_3$)$_2$(Ph)(I) with Me-Duphos also gave impure **Ni-3a**. In contrast, reaction of the well-behaved Ni(PPh$_3$)$_2$(Ph)(Cl)[40] with Me-Duphos gave Ni(Me-Duphos)(Ph)(Cl), which was isolated in good yield and characterized crystallographically (see the Experimental Section and the Supporting Information).

Scheme 6[a]



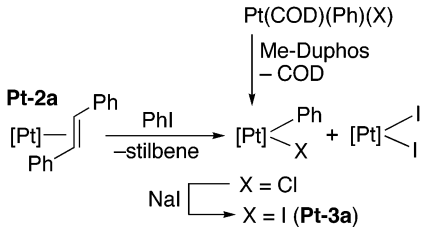
[a] [Ni] = Ni(Me-Duphos).

Scheme 7[a]



[a] [M] = M(Me-Duphos).

Scheme 8[a]



[a] [Pt] = Pt(Me-Duphos).

In separate experiments, oxidative addition of PhI to the Pd complex **2a** was somewhat faster than that to **Ni-2a**. In a competition experiment, a mixture of **2a** and **Ni-2a** was treated with PhI (Scheme 7). Oxidative addition of PhI to the Pd complex occurred more quickly; it was complete before formation of **Ni-3a**, consistent with the individual rates.

In contrast, the Pt analogue Pt(Me-Duphos)(*trans*-stilbene) (**Pt-2a**) did not react with PhI at room temperature. When the temperature was raised to 60 °C, some Pt(Me-Duphos)(Ph)(I) (**Pt-3a**) formed; further heating gave large amounts of Pt(Me-Duphos)I$_2$ (prepared independently; see the Experimental Section) as the major product (Scheme 8). Complex **Pt-3a** was also prepared either by treatment of Pt(COD)(Ph)(I)[41] with

(38) The instability of **3j** may be due to the seven-membered Pd(BoPhoz) ring, as observed in analogous complexes with related chelates. (a) Pd(Diop)(Ph)(I) exists in a concentration-dependent equilibrium with chelate ring-opened oligomeric species (de Graaf, W.; Boersma, J.; van Koten, G.; Elsevier: C. J. *J. Organomet. Chem.* **1989**, *378*, 115−124; see also reference 26 therein). (b) Pd(MeO-Biphep)(Ph)(I) decomposes quickly to yield Pd(MeO-Biphep)I$_2$.[3b]

(39) (a) Schoenberg, A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 7761−7764. (b) Fauvarque, J. F.; Jutand, A. *J. Organomet. Chem.* **1979**, *177*, 273−281. (c) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115−4127. (d) Giannoccaro, P.; Pannacciulli, E. *J. Organomet. Chem.* **1987**, *319*, 119−127. (e) Reference 49 is often cited for the preparation of this complex, but it describes only the related chemistry of aryl chlorides and bromides.

(40) Zeller, A.; Herdtweck, E.; Strassner, T. *Eur. J. Inorg. Chem.* **2003**, 1802−1806.

(41) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411−428.

Table 7. Selected NMR Data for the Complexes M(diphos*)(Ph)(I)[a]

compd	diphos	$\delta(^{31}P)$	$\delta(^{13}C)$ (Pd−C_6H_5)
3a	Me-Duphos	67.8, 64.7 (J = 27)	159.3 (d, J = 138)
3b	Et-Duphos	61.4, 58.5 (J = 26)	158.2 (d, J = 138)
3c	i-Pr-Duphos	62.4, 57.0 (J = 23)	156.4 (d, J = 134)
3d	Me-BPE	72.9, 61.5 (J = 25)	158.9 (d, J = 132)
3e	Me-FerroLANE	41.0, 23.9 (J = 32)	153.5 (dd, J = 122, 3)
3f	Me-DuXantphos[b]	31.7 (trans)	nd
		36.2, 27.1 (J = 32, cis)	
3g	Et-FerroTANE	46.4, 32.8 (J = 29)	155.9 (dd, J = 127, 5)
3h	CyPF-t-Bu	78.0, 13.0 (J = 35)	152.0
3i	PPF-t-Bu	74.3, 18.9 (J = 40)	nd
3j	BoPhoz[c]	79.6, −4.5 (J = 32) (major)	148.7 (m)
		81.8, 5.8 (J = 37) (minor)	nd
Ni-3a	Me-Duphos	75.0, 68.7 (J = 26)	nd
Pt-3a[d]	Me-Duphos	63.6, 56.8 (J = 6)	158.9 (dd, J = 115, 7)

[a] Solvent: $CDCl_3$ for **3c**,**e**,**g**−**j**, C_6D_6 for **3a**,**b**,**d** and **Ni-3a**. Chemical shifts are given in ppm and coupling constants in Hz. n.d. = not determined. [b] CD_2Cl_2, −50 °C. The trans to cis ratio is 3.2:1. However, in toluene, a neutral trans complex was observed (−20 °C): δ 30.8, 25.3 (AB quartet, J = 417). [c] 8:1 diastereomer ratio, from ^{31}P NMR integration. [d] In C_6D_6, J_{Pt-P} = 1616 and 3754 Hz, respectively.

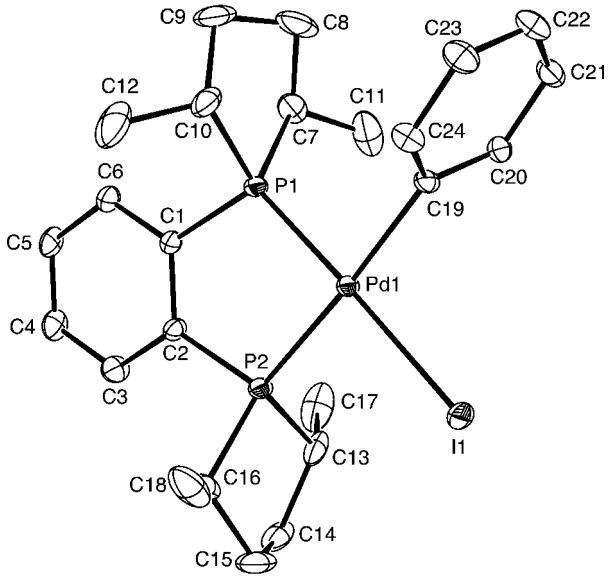


Figure 6. ORTEP diagram of Pd((*R*,*R*)-Me-Duphos)(Ph)(I) (**3a**).

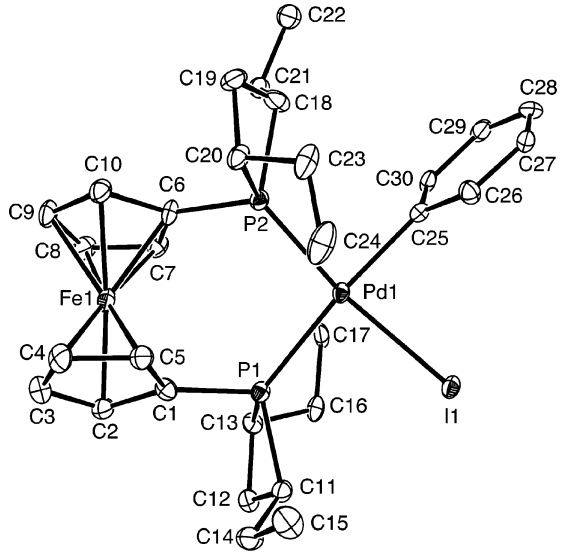


Figure 7. ORTEP diagram of one of the three independent molecules in the unit cell of Pd((*S*,*S*)-Et-FerroTANE)(Ph)(I)·0.33toluene (**3g**·0.33(toluene)). The solvent molecule and disorder in one of the ethyl groups are not shown.

Me-Duphos or by reaction of Pt(Me-Duphos)(Ph)(Cl) (prepared from Pt(COD)(Ph)(Cl)[41] and crystallographically characterized; see the Supporting Information) with excess NaI.

The trend in rates of PhI oxidative addition to the M(Me-Duphos)(*trans*-stilbene) complexes (Ni, Pd ≫ Pt) is consistent with related observations in the literature. However, the faster oxidative addition of the Pd complex **2a**, relative to **Ni-2a**, is unusual.[42] Further study of the mechanisms of oxidative addition will be required to explain these results.

Characteristic NMR data for the phenyl iodide complexes are summarized in Table 7. The ^{31}P NMR spectra showed two peaks with a small cis coupling constant (ca. 30 Hz). The Pd-bound phenyl group gave rise to a characteristic ^{13}C NMR resonance around 150 ppm with a large trans J_{PC} value (ca. 130 Hz), and little dependence on the ligand.[43]

The crystal structures of several of these complexes (**3a**,**c**,**g**,**h**) were also determined (Figures 6−8, Tables 3 and 8, and the Supporting Information). All showed

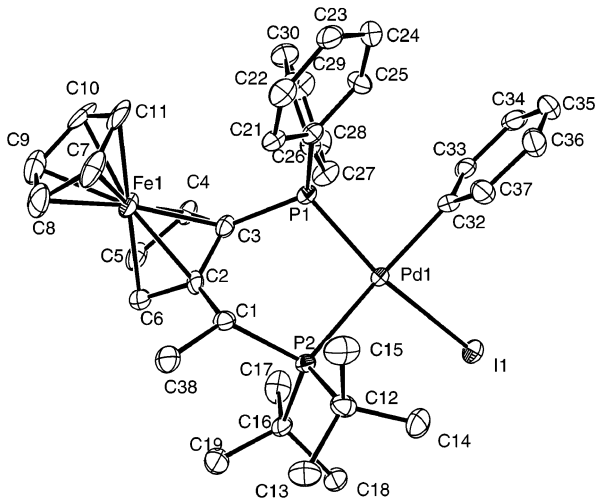


Figure 8. ORTEP diagram of Pd((*R*,*S*)-PPF-*t*-Bu)(Ph)(I)·CH_2Cl_2 (**3i**·CH_2Cl_2). Hydrogen atoms and the solvent molecule are omitted.

distorted-square-planar geometry with, in most cases, somewhat longer Pd−P and Pd−I bonds in the sterically

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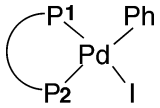
(43) Tschoerner, M.; Kunz, R. W.; Pregosin, P. S. *Magn. Reson. Chem.* **1999**, *37*, 91−97.

Table 8. Selected Bond Lengths (Å) and Angles (deg) in the Complexes Pd(diphos*)(Ph)(I)



	3a	**3c**·C_6D_6	**3g**·$0.33C_7H_8$	**3h**·CH_2Cl_2·THF	**3i**·CH_2Cl_2
diphos	Me-Duphos	i-Pr-Duphos[a]	Et-Ferro-TANE[b]	CyPF-t-Bu[a]	PPF-t-Bu
Pd−P1	2.2348(8)	2.2427(10)	2.2722(18)	2.3000(8)	2.249(2)
Pd−P2	2.3182(8)	2.3151(12)	2.3768(19)	2.4151(8)	2.439(2)
Pd−C	2.084(3)	2.032(5)	2.056(7)	2.043(3)	2.065(9)
Pd−I	2.6588(3)	2.6459(5)	2.6427(7)	2.6847(3)	2.6916(11)
P−Pd−P	86.63(3)	87.70(4)	100.54(6)	97.98(3)	97.02(8)
C−Pd−I	92.92(9)	88.10(11)	86.5(2)	83.31(9)	84.9(2)
P1−Pd−C	89.11(9)	91.40(12)	85.6(2)	87.76(9)	84.5(2)
P2−Pd−C	175.41(8)	178.88(15)	169.0(2)	162.80(10)	161.4(3)
P1−Pd−I	177.96(2)	179.40(5)	166.40(5)	149.52(2)	155.47(7)
P2−Pd−I	91.34(2)	92.79(3)	89.18(5)	99.07(2)	100.03(6)

[a] See the Supporting Information. [b] Average values; three independent molecules in the unit cell.

crowded Josiphos complexes **3h**,**i**. Significant deviations of the P1−Pd−I angle from the ideal 180° (166.40(5), 149.52(2), and 155.47(7)°) occurred in complexes **3g**−**i**, consistent with the larger bite angles of the diphosphines (100.54(6), 97.98(3), and 97.02(8)°, respectively). The structures of **3h**,**i** are very similar to those of the analogous bromide complexes Pd(PPF-t-Bu)(Ph)(Br) and Pd(CyPF-t-Bu)(Ph)(Br).[16a] As expected from the relative trans influences of the ligands, the Pd−P bonds trans to the phenyl group were longer than those trans to iodide.[44]

Conclusions

The complexes Pd(diphos*)(*trans*-stilbene) (**2**) were prepared by reduction of the precursors Pd(diphos*)Cl_2 (**1**) in the presence of the alkene. These complexes, convenient sources of the zerovalent Pd(diphos*), are catalyst precursors for asymmetric phosphination,[11] and we expect they will find other applications in asymmetric catalysis. Their stability and the enantioface selectivity in binding of *trans*-stilbene depended strongly on the diphosphine. The rate of oxidative addition of PhI to **2** to give the complexes Pd(diphos*)(Ph)(I) (**3**) also depended on the diphosphine, being faster for ligands with large bite angles and reduced steric bulk. These oxidative additions were significantly faster than those of Pd(diphos*)(dba), which was generated in situ. Oxidative addition of PhI to the complexes M(Me-Duphos)(*trans*-stilbene) (M = Ni, Pd, Pt) occurred in the rate order Pd > Ni ≫ Pt. Crystallographic studies of complexes **1**−**3** revealed a surprisingly small structural dependence on the nature of the diphosphine.

Experimental Section

General Experimental Details. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at room temperature in a drybox, or using standard Schlenk techniques. Petroleum ether (bp 38−53 °C), ether, THF, CH_2Cl_2, and toluene were dried and degassed using columns containing activated alumina.[45]

NMR spectra were recorded on Varian 500 or 300 MHz spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported relative to Me_4Si and were determined by reference to the residual ^{1}H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported relative to H_3PO_4 (85%), used as an external reference. All *J* values are given in Hz. Unless otherwise noted, peaks in NMR spectra are singlets; other abbreviations used are d = doublet, t = triplet, q = quartet, m = multiplet, and quat = quaternary. Infrared spectra were recorded on KBr pellets with a Perkin-Elmer 1600 series FTIR instrument and are reported in cm^{-1}. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory, or by Quantitative Technologies, Inc. Mass spectra were obtained at the University of Illinois Urbana-Champaign.

Literature procedures were used to prepare Pd((*R*,*R*)-Me-Duphos)Cl_2,[11b] Pd(COD)Cl_2,[46] Pd(dba)$_2$,[47] Pd(TMEDA)(Ph)(I),[35] Pd$(PPh_3)_2$(Ph)(I),[36] Pd(PPF-t-Bu)Cl_2 (**1i**),[16d] Ni((*R*,*R*)-Me-Duphos)Cl_2,[48] Ni$(PPh_3)_2$(Ph)(Cl),[49] Ni$(PPh_3)_4$,[50] Pt(COD)(Ph)(Cl) and Pt(COD)(Ph)(I),[41] Me-FerroLANE,[17] Me-DuXantphos,[18] and Pt(Me-Duphos)(*trans*-stilbene).[13]

The complexes Pd(diphos*)Cl_2 were prepared from Pd(COD)Cl_2 and the appropriate diphosphine. One example is described below, and synthetic details for the analogous compounds are given in the Supporting Information.

Pd((*R*,*R*)-Et-Duphos)Cl_2 (1b). To a stirred slurry of Pd(COD)Cl_2 (201 mg, 0.704 mmol) in CH_2Cl_2 (2 mL) was added (*R*,*R*)-Et-Duphos (260 mg, 0.717 mmol) as a solution in CH_2Cl_2 (2 mL). The precipitate dissolved immediately, and the reaction mixture turned canary yellow. After it was stirred for 1 h, the solution was concentrated to 0.5 mL and layered with petroleum ether. Cooling at −30 °C overnight resulted in a yellow oil that solidified upon trituration with petroleum ether. The yellow solid was dried in vacuo, giving 352 mg (93%) of the desired compound. Recrystallization from THF/petroleum ether gave analytically pure yellow crystals. Recrystallization from acetone gave crystals of an acetone solvate suitable for X-ray analysis.

Anal. Calcd for $C_{22}H_{36}P_2Cl_2Pd$: C, 48.95; H, 6.72. Found: C, 49.06; H, 6.84. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 90.2. ^{1}H NMR ($CDCl_3$): δ 7.78−7.72 (m, 2H, Ar), 7.69−7.62 (m, 2H, Ar), 3.45−3.34 (m, 2H, CH), 2.55−2.28 (m, 6H, CH, CH_2), 2.24−2.00 (m, 6H, CH_2), 1.70−1.59 (m, 2H, CH_2), 1.30−1.19 (m, 2H, CH_2), 1.19−1.06 (m, 2H, CH_2), 0.93 (t, *J* = 7.5, 6H, Me), 0.85 (t, *J* = 7.5, 6H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.1 (t, *J* = 37, quat), 132.9 (m, Ar), 132.8 (t, *J* = 10, Ar), 50.3 (m, CH), 44.9 (m, CH), 34.2 (CH_2), 33.1 (CH_2), 25.5 (t, *J* = 3, CH_2), 23.3 (CH_2), 14.7 (t, *J* = 6, Me), 13.8 (t, *J* = 6, Me).

Pd((*R*,*R*)-*i*-Pr-Duphos)Cl_2 (1c). Anal. Calcd for $C_{26}H_{44}P_2Cl_2Pd$: C, 52.41; H, 7.44. Found: C, 52.38; H, 7.66. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 85.1. ^{1}H NMR ($CDCl_3$): δ 7.78−7.73 (m, 4H, Ar), 3.48−3.34 (m, 2H, CH), 2.76−2.56 (m, 2H, CH), 2.52−2.14 (m, 8H, CH_2), 1.90−1.58 (m, 4H, CH), 1.12 (d, *J* = 6.6, 6H, Me), 1.05 (d, *J* = 6.6, 6H, Me), 0.80 (d, *J* = 6.6, 6H, Me), 0.72 (d, *J* = 6.6, 6H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.9 (t, *J* = 35, quat), 133.1 (t, *J* = 10, Ar), 132.8 (m, Ar), 56.4 (m, CH), 51.1 (m, CH), 31.1 (CH_2), 30.7 (m, CH_2), 29.9 (m, CH), 28.2 (CH), 26.2 (t, *J* = 4, Me), 24.9 (t, *J* = 4, Me), 21.6 (t, *J* = 5, Me), 20.7 (t, *J* = 3, Me).

Pd((*R*,*R*)-Me-BPE)Cl_2 (1d). Anal. Calcd for $C_{14}H_{28}P_2PdCl_2$: C, 38.60; H, 6.48. Found: C, 38.53; H, 6.72. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 102.3. ^{1}H NMR ($CDCl_3$): δ 3.52 (m, 2H), 2.37−2.08 (overlapping m, 6H), 2.00−1.77 (overlapping m, 6H),

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(50) Ittel, S. D. *Inorg. Synth.* **1977**, *17*, 117−125.

1.58 (dd, J = 19, 7, 6H, Me), 1.49−1.36 (m, 2H), 1.26 (dd, J = 16, 7, 6H, Me). The low solubility of the complex precluded obtaining its ^{13}C NMR spectrum.

Pd((*S*,*S*)-Me-FerroLANE)Cl$_2$ (1e). Anal. Calcd for $C_{22}H_{32}FeP_2PdCl_2$: C, 44.67; H, 5.45. Found: C, 44.45; H, 5.38. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 57.0. ^1H NMR ($CDCl_3$): δ 4.69 (2H, Cp), 4.47 (2H, Cp), 4.34 (2H, Cp), 4.28 (2H, Cp), 3.95−3.85 (m, 2H), 2.69−2.59 (m, 2H), 2.27−2.17 (m, 2H), 2.02−1.93 (m, 2H), 1.88 (dd, J = 20, 7, 6H, Me), 1.84−1.73 (m, 2H), 1.32−1.24 (m, 2H), 0.91 (dd, J = 17, 7, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 76.0 (apparent t, J = 4, Cp CH), 75.3 (apparent t, J = 8, Cp CH), 74.6 (Cp CH), 72.9 (apparent t, J = 3, Cp CH), 68.1 (d, J = 47, Cp quat), 39.6 (m, CH), 35.8 (CH_2), 35.3 (m, CH), 35.1 (CH_2), 21.4 (apparent t, J = 4, Me), 14.9 (Me).

Pd((*S*,*S*)-Me-DuXantphos)Cl$_2$ (1f). Anal. Calcd for $C_{27}H_{36}P_2OPdCl_2{\cdot}CH_2Cl_2$: C, 47.99; H, 5.47. Found: C, 48.12; H, 5.77. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ 49.2 (d, J = 9), 36.6 (d, J = 9). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ 48.8 (br), 37.3 (br), 31.8. ^1H NMR (CD_2Cl_2, −20 °C): δ 7.60−7.56 (m, 3H, Ar), 7.34 (t, J = 7, 1H, Ar), 7.28 (t of d, J = 8, 2, 1H, Ar), 7.20 (t of d, J = 8, 1, 1H, Ar), 3.60−3.56 (m, 1H), 3.12−3.06 (m, 1H), 2.92−2.86 (m, 2H), 2.49−2.39 (m, 1H), 2.33−2.25 (m, 1H), 2.01−1.95 (m, 3H), 1.94 (overlapping previous m, dd, J = 14, 7, 3H, phospholane Me), 1.85 (3H, Xant Me), 1.83−1.65 (overlapping m, 3H), 1.60 (dd, J = 21, 7, 3H, phospholane Me), 1.40 (3H, Xant Me), 1.36 (dd, J = 19, 7, 3H, phospholane Me), 0.88 (dd, J = 14, 7, 3H phospholane Me).

Pd((*S*,*S*)-Et-FerroTANE)Cl$_2$ (1g). Anal. Calcd for $C_{24}H_{36}P_2FePdCl_2$: C, 46.52; H, 5.86. Found: C, 46.53; H, 5.74. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 57.3. ^1H NMR ($CDCl_3$): δ 4.76 (2H), 4.59−4.57 (overlapping singlets, 4H), 4.32−4.27 (m, 2H), 4.21 (2H), 2.62−2.57 (m, 2H), 2.47−2.24 (m, 6H), 2.18−2.07 (m, 2H), 1.26 (t, J = 7, 6H, Me), 1.16−1.09 (m, 4H), 0.73 (t, J = 7, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 76.6 (t, J = 4, CH), 76.1−75.9 (m, CH), 74.1 (CH), 73.6 (CH), 66.4−66.1 (m, quat), 41.3−40.6 (m, CH), 35.8−35.7 (m, CH_2), 26.4 (CH_2), 24.8 (t, J = 2, CH_2), 14.1−13.9 (m, Me), 12.0−11.8 (m, Me). IR: 3082, 2955, 2856, 1456, 1383, 1300, 1169, 1039, 818, 628, 571, 493.

Pd((*R*,*S*)-CyPF-t-Bu)Cl$_2$ (1h). Anal. Calcd for $C_{32}H_{52}FeP_2PdCl_2(CH_2Cl_2)_{0.8}$: C, 49.26; H, 6.75. Found: C, 49.02; H, 6.92. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 114.4 (d, J = 11), 32.6 (br). ^1H NMR ($CDCl_3$): δ 4.91 (1H), 4.58 (1H), 4.56 (1H), 4.30 (5H), 3.10 (m, 1H), 2.60 (br, 1H), 2.39−2.34 (m, 1H), 2.26 (br, 2H), 2.13−2.11 (m, 1H), 2.04−2.01 (5H), 1.99 (br, 2H), 1.92−1.85 (m, 2H), 1.77 (br, 6H), 1.69 (d, J = 13, 9H), 1.42 (br, 5H), 1.29 (d, J = 14, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 110.0 (Cp), 72.3 (Cp), 70.0 (Cp), 69.6 (Cp), 69.5 (Cp), 66.1 (Cp), 41.9, 40.9 (d, J = 12), 34.7 (d, J = 9), 34.3, 32.3, 31.4, 30.3, 29.5, 28.4, 27.9, 27.6, 27.1 (d, J = 14), 26.5, 25.9, 22.6, 18.3, 15.5, 14.3.

Pd((*R*,*S*)-BoPhoz)Cl$_2$ (1j). Anal. Calcd for $C_{37}H_{35}NFeP_2PdCl_2(CH_2Cl_2)_{0.3}$: C, 55.02; H, 4.41; N, 1.72. Found: C, 55.52; H, 4.68; N, 1.68. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 85.2 (d, J = 25), 14.5 (d, J = 25). ^1H NMR ($CDCl_3$): δ 8.05 (br, 2H), 7.73 (br, 2H), 7.54 (br, 6H), 7.43−7.39 (br, 5H), 7.31 (br, 1H), 7.05 (br, 2H), 6.83 (br, 2H), 5.42 (br, 1H), 4.58 (br, 1H), 4.38 (br, 1H), 4.04 (5H), 3.72 (1H), 2.15 (d, J = 7, 3H), 0.93 (br, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.4 (d, J = 10, Ar), 134.4 (d, J = 11, Ar), 134.2 (d, J = 11, Ar), 133.5 (Ar), 133.2 (d, J = 10, Ar), 133.1 (d, J = 5, Ar), 131.9 (Ar), 131.5 (Ar), 131.3 (Ar), 131.0 (d, J = 2, Ar), 130.7 (Ar), 129.1 (d, J = 11, Ar), 128.6 (Ar), 128.3 (d, J = 7, Ar), 128.2 (d, J = 7, Ar), 127.1 (d, J = 12, Ar), 76.1 (Cp), 72.3 (Cp), 71.9 (Cp), 71.2 (Cp), 70.3 (d, J = 7, Cp), 69.4 (d, J = 7, Cp), 53.2 (d, J = 16), 29.3 (d, J = 6), 13.9.

The complexes Pd(diphos*)(*trans*-stilbene) were prepared by treatment of Pd(diphos*)Cl$_2$ with NaBH(OMe)$_3$ in the presence of stilbene in THF. A representative procedure is included below, with synthetic details for the analogous compounds in the Supporting Information.

Pd((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (2a). To a stirred slurry of Pd((*R*,*R*)-Me-Duphos)Cl$_2$ (295 mg, 0.61 mmol) in THF (2 mL) was added *trans*-stilbene (111 mg, 0.616 mmol) as a solution in THF (2 mL) followed by NaBH(OMe)$_3$ (233 mg, 1.83 mmol, 3 equiv) dissolved in THF (5 mL). The mixture turned dark yellow-green immediately, and gas was evolved. After the reaction mixture was stirred for 1 h at room temperature, when it was completely homogenized, the solvent was removed in vacuo and the residue was extracted with toluene (30 mL) and filtered. The toluene was removed in vacuo, and the yellow solid was dissolved in hexane and filtered again. Cooling of the solution overnight (−25 °C) gave 240 mg (66%) of a 5.6:1 (a:b) mixture of diastereomers as a bright yellow solid. When 2 equiv of stilbene was used, the yield was comparable. The NMR spectra are reported as a mixture of diastereomers, unless otherwise indicated. Recrystallization from pentane gave a sample for elemental analysis which contained 0.5 equiv of pentane.

Anal. Calcd for $C_{32}H_{40}P_2Pd(C_5H_{12})_{0.5}$: C, 65.87; H, 7.37. Found: C, 65.97; H, 7.02. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 57.6 (a), 50.8 (b). ^1H NMR (C_6D_6): δ 7.43 (d, J = 8, 4H, Ar), 7.33−7.27 (m, 2H, Ar), 7.21−7.14 (m, 4H, Ar), 7.02−6.97 (m, 2H, Ar), 6.88−6.83 (m, 2H, Ar), 5.50 (d, J = 2, 2H, CH=CH, a), 5.25 (d, J = 2, 2H, CH=CH, b), 2.58−2.51 (m, 2H, CH, b), 2.40−2.28 (m, 2H, CH, a), 2.26−2.16 (m, 2H, CH, b), 2.04−1.92 (m, 2H, CH, a), 1.92−1.80 (m, 4H, CH_2, b), 1.66−1.57 (m, 4H, CH_2, a), 1.57−1.48 (m, 2H, CH_2, a), 1.38 (dd, J = 20, 7, 6H, Me, a), 1.36−1.16 (m, 4H, CH_2), 0.63 (dd, J = 13, 7, 6H, Me, b), 0.55 (dd, J = 19, 7, 6H, Me, b), 0.36 (dd, J = 14, 7, 6H, Me, a). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.4−147.3 (m, quat, Ar), 146.8−146.1 (m, quat, Ar), 133.4 (m, CH, Ar, b), 133.2 (apparent t, J = 5, CH, Ar, a), 128.9 (CH, Ar, a), 128.8 (CH, Ar, b), 128.2 (apparent t, J = 2, CH, Ar), 125.1 (m, CH, Ar, b), 124.4 (apparent t, J = 2, CH, Ar, a), 122.3 (m, CH, Ar, b), 121.9 (apparent t, J = 2, CH, Ar, a), 64.2 (m, CH=CH, b), 60.6 (apparent t, J = 10, CH=CH, a), 39.9 (m, CH, b), 39.8 (m, CH, b), 38.1 (apparent t, J = 7, CH, a), 37.1 (CH_2, b), 36.9 (m, CH_2, a), 36.7 (m, CH_2, a), 36.6 (apparent t, J = 7, CH, a), 20.5 (apparent t, J = 12, Me, a), 17.5 (Me, b), 15.1 (Me, b), 15.0 (Me, a).

Pd((*R*,*R*)-Et-Duphos)(*trans*-stilbene) (2b). Anal. Calcd for $C_{36}H_{48}P_2Pd(C_6H_{14})_{0.5}$: C, 67.67; H, 8.01. Found: C, 67.66; H, 7.66. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 51.5 (a), 46.4 (b). ^1H NMR (C_6D_6): δ 7.42−7.32 (m, 6H, Ar), 7.20−7.14 (m, 4H, Ar), 7.04−6.98 (m, 2H, Ar), 6.95−6.90 (m, 2H, Ar, b), 6.87−6.82 (m, 2H, Ar, a), 5.45 (d, J = 2, 2H, CH=CH, a), 5.23 (d, J = 2, 2H, CH=CH, b), 2.44−2.36 (m, 2H, b), 2.26−2.14 (m, 2H, a), 2.14−1.92 (m, 2H), 1.94−1.70 (m, 5H), 1.40−1.26 (m, 4H), 1.26−1.14 (m, 2H), 0.97 (t, J = 7.5, 6H, Me, a), 0.88−0.76 (m, 3H), 0.71−0.61 (m, 2H, overlapped), 0.65 (t, J = 7, 6H, b, overlapped), 0.55 (t, J = 7.5, 6H, Me, b), 0.48 (t, J = 7.5, 6H, Me, a). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.1 (t, J = 3, quat), 146.6 (t, J = 29, quat), 133.6 (t, J = 4, Ar), 128.8 (Ar, a), 128.7 (Ar, b), 128.2 (t, J = 2, Ar), 124.9 (Ar, b), 124.3 (t, J = 2, Ar, a), 122.1 (Ar, b), 121.6 (t, J = 2, Ar, a), 63.5 (CH=CH, b), 60.2 (t, J = 10, CH=CH), 48.0 (CH, b), 47.4 (CH, b), 46.6 (t, J = 7, CH, a), 44.0 (t, J = 7, CH, a), 34.7 (CH_2, b), 34.3 (CH_2, a), 34.2 (CH_2, a), 33.8 (CH_2, b), 29.3 (t, J = 12, CH_2), 24.3 (CH_2, b), 23.8 (CH_2, a), 14.6 (t, J = 6, Me), 14.3 (t, J = 4, Me).

Pd((*R*,*R*)-*i*-Pr-Duphos)(*trans*-stilbene) (2c). Anal. Calcd for $C_{40}H_{56}P_2Pd$: C, 68.13; H, 8.00. Found: C, 68.00; H, 8.07. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 47.6 (b), 44.7 (a). ^1H NMR (C_6D_6): δ 7.46−7.36 (m, 6H, Ar), 7.22−7.16 (m, 4H, Ar), 7.01−6.97 (m, 2H, Ar), 6.89−6.85 (m, 2H, Ar), 5.34 (d, J = 2, 2H, CH=CH, a), 5.18 (d, J = 2, 2H, CH=CH, b), 2.31−2.22 (m, 2H), 2.16−2.07 (m, 2H), 2.07−1.96 (m, 2H), 1.86−1.76 (m, 2H), 1.52−1.34 (m, 4H), 1.31 (d, J = 6.5, 6H, Me), 1.26−1.18 (m, 2H), 1.16−1.07 (m, 2H), 1.02 (d, J = 6.5, 6H, Me), 0.48 (d, J = 6.5, 6H, Me), 0.36 (d, J = 6.5, 6H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.4 (dd, J = 28, 27, quat), 146.7 (apparent t, J = 2, quat), 133.9 (apparent t, J = 4, Ar), 128.7 (Ar), 128.3 (Ar), 124.5 (apparent t, J = 2, Ar), 121.7 (Ar), 62.9 (apparent t, J = 11, CH=CH), 52.8 (apparent t, J = 6, CH), 50.6 (apparent t, J = 7, CH), 32.5 (CH_2), 31.7 (apparent t, J = 9, CH), 28.9 (CH_2),

28.6 (CH), 24.7 (apparent t, $J = 4$, Me), 24.3 (apparent t, $J = 5$, Me), 21.5 (apparent t, $J = 3$, Me), 19.8 (apparent t, $J = 5$, Me).

Pd(Me-BPE)(*trans*-stilbene) (2d). Anal. Calcd for $C_{28}H_{40}P_2Pd$: C, 61.71; H, 7.40. Found: C, 61.50; H, 7.52. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 55.8 (A), 45.3 (B) (diastereomer ratio 2.5:1). ^1H NMR (C_6D_6): δ 7.40 (m, 4H, Ar, A and B), 7.15 (m, 4H, Ar, A and B), 6.89 (m, 2H, Ar, A and B), 5.44 (apparent d, $J = 2$, 2H, stilbene C*H*, A), 5.40 (apparent d, $J = 2$, 2H, stilbene C*H*, B), 2.28−2.22 (m, 2H, B), 1.85−1.77 (m, 2H, A), 1.70−1.66 (m, 2H, B), 1.64−1.52 (m, 4H, A), 1.50−1.42 (m, 2H, A), 1.39−1.34 (m, 2H, B), 1.28 (dd, $J = 20$, 8, 6H, Me), 1.27−1.20 (partially obscured m, 2H, A), 1.14−1.06 (m, B), 1.05−0.95 (m, 4H, A), 0.91 (dd, $J = 13$, 8, 6H, Me, B), 0.71−0.66 (m, 2H, A), 0.56 (dd, $J = 13$, 7, 6H, A), 0.45 (dd, $J = 19$, 8, 6H, B). Not all the protons associated with B could be identified due to peak overlap. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.8 (apparent t, $J = 2$, Ar quat, B), 147.4 (apparent t, $J = 2$, Ar quat, A), 128.3 (Ar CH, B), 128.2 (Ar CH, A), 125.0 (t, $J = 2$, Ar CH, B), 124.5 (t, $J = 2$, Ar CH, A), 122.1 (Ar CH, B), 121.9 (t, $J = 2$, Ar CH, A), 62.6 (t, $J = 11$, stilbene CH, B), 60.7 (t, $J = 10$, stilbene CH), 38.6 (apparent t, $J = 6$, CH B), 36.8 (apparent t, $J = 7$, CH A), 36.3 (CH_2 B), 36.2 (CH_2 B), 36.1 (apparent t, $J = 8$, CH B), 36.0 (CH_2 A), 35.9 (CH_2 A), 34.0 (apparent t, $J = 6$, CH A), 24.0 (apparent t, $J = 16$, CH_2 A), 23.0 (apparent t, $J = 16$, CH_2 B), 21.1 (apparent t, $J = 11$, Me, A), 18.9 (apparent t, $J = 11$, Me, B), 14.5 (Me, B), 14.2 (Me A).

Pd((*S,S*)-Me-FerroLANE)(*trans*-stilbene) (2e). Anal. Calcd for $C_{36}H_{44}FeP_2Pd$: C, 61.69; H, 6.33. Found: C, 61.73; H, 6.60. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 36.2 (A), 32.5 (B) (diastereomer ratio 6.4:1). ^1H NMR (C_6D_6): δ 7.43 (d, $J = 8$, 4H, Ar, A), 7.37 (d, $J = 8$, 4H, Ar, B), 7.19 (partially obscured, 4H, Ar, B), 7.18 (t, $J = 8$, 4H Ar, A), 7.00 (t, $J = 8$, 2H, Ar, B), 6.93 (t, $J = 8$, 2H, Ar, A), 5.02 (m, 2H, stilbene CH, A), 5.00 (m, 2H, stilbene CH, B), 4.21 (m, 1H, Cp, B), 4.13 (m, 1H, Cp, B), 4.08 (overlapping m, 2H, Cp, A), 3.95 (partially obscured m, 1H, Cp, B), 3.93 (m, 1H, Cp, A), 3.78 (m, 1H, Cp, B), 3.74 (m, 1H, Cp, A), 2.45−2.36 (m, 2H, A), 2.31−2.24 (m, 2H, B), 2.13−2.05 (m, 2H, A), 1.94−1.89 (m, 2H, B), 1.82−1.71 (m, 2H, A), 1.69−1.61 (m, 2H, A), 1.58 (dd, $J = 20$, 7, 6H, Me, A), 1.30−1.22 (m, 2H, A), 1.20−1.11 (m, 2H, A), 1.08 (dd, $J = 13$, 7, 6H, Me, B), 0.88−0.83 (m, 2H, B), 0.59 (dd, $J = 19$, 7, 6H, Me, B), 0.37 (dd, $J = 14$, 7, 6H, Me, A). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.1 (m, Ar quat, B), 146.8 (apparent t, $J = 2$, Ar quat, A), 128.5 (Ar, B), 128.1 (Ar, A), 125.0 (Ar, B), 124.8 (apparent t, $J = 2$, Ar, A), 122.9 (Ar, B), 122.7 (Ar, A), 78.3 (m, Cp quat, B), 78.1 (m, Cp quat, A), 77.4 (m, Cp, A), 72.7 (m, Cp, B), 72.5 (apparent t, $J = 4$, Cp, A), 71.6 (m, Cp, B), 71.3 (apparent t, $J = 2$, Cp, A), 69.6 (Cp, A), 64.7 (m, stilbene CH B), 63.6 (m, stilbene CH, A), 38.3 (m, CH, B), 36.3 (CH_2, B), 36.0 (CH_2, A), 35.9 (m, CH, A), 35.7 (d, $J = 2$, CH_2, A), 35.6 (m, CH_2 B), 34.6 (CH, B), 33.8 (m, CH, A), 23.4 (m, Me, A), 22.7 (Me, B), 14.9 (Me, B), 13.7 (Me, A). Only those resonances from B that could be distinguished are listed.

In certain syntheses, subsequent crops of material contained a variable, but small (less than 7%), amount of an unknown impurity that was observed by ^1H NMR spectroscopy. ^1H NMR (C_6D_6): δ 4.62 (m, Cp), 4.60 (m, Cp), 4.46 (m, Cp), 3.87 (m, Cp), 1.35 (dd, $J = 17$, 7, Me), 0.61 (dd, $J = 14$, 7, Me).

Pd(Me-DuXantphos)(*trans*-stilbene) (2f). Pd(Me-DuXantphos)Cl_2 (48 mg, 7.3×10^{-5} mol) and *trans*-stilbene (15 mg, 8.3×10^{-5} mol) were slurried in THF (2 mL), and $NaBH(OMe)_3$ (28 mg, 2.2×10^{-4} mol) was added as a solid in small portions. Immediately on addition the solution turned red-brown and H_2 evolution was observed. Residual $NaBH(OMe)_3$ was added to the mixture in THF (1 mL), and then the solution was stirred for 1 h. All volatiles were then removed in vacuo, and the residue was extracted with toluene (6 mL). The solution was filtered through Celite, and again all volatiles were removed in vacuo to yield a dark brown solid. The solid was extracted with petroleum ether (6 mL), the extract was filtered, and the solution was pumped to dryness in vacuo to give 49 mg of crude material. This was characterized by NMR spectroscopy and showed resonances consistent with two diastereomers of Pd(Me-DuXantphos)(*trans*-stilbene). In separate experiments, small amounts of free ligand were always observed in the crude product.

$^{31}P\{^1H\}$ NMR (C_6D_6, 21 °C): δ 31.6 (A, br), 26.5 (B, v. br) (two sharp singlets at 27.0 and 26.1 were reproducibly observed in separate experiments overlying the resonance due to B); ratio A:B 2.8:1. $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, −30 °C): δ 30.9 (A), 26.7 (B); ratio A:B 4.0:1. Selected ^1H NMR (C_6D_6, 21 °C): δ 4.9 (br, stilbene CH, A), 4.7 (br, stilbene CH, B). Selected ^1H NMR ($C_6D_5CD_3$, −30 °C): δ 4.81 (m, stilbene CH, A), 4.72 (m, stilbene CH, B); ratio A:B 4.3:1.

Attempts to recrystallize this material from hexane, toluene/hexane, or diethyl ether/hexane mixtures were unsuccessful and resulted in decomposition, as indicated by additional peaks in the $^{31}P\{^1H\}$ NMR spectrum; in particular, an additional sharp peak was observed at δ 35.2 ($C_6D_5CD_3$). To further characterize the crude product, it was treated with PhI. Crude Pd(Me-DuXantphos)(*trans*-stilbene) (27 mg, 3.7×10^{-5} mol) was dissolved in toluene (1 mL), and PhI (6.7 μL, 6.0×10^{-5} mol, 1.6 equiv) was added by microliter syringe. The reaction mixture was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After 5 min peaks consistent with *trans*-Pd(Me-DuXantphos)(Ph)(I) (**3f**) were observed and the spectrum did not change for a further 1 h after the addition. See below, and the Results and Discussion, for details of the characterization of **3f**.

Pd((*S,S*)-Et-FerroTANE)(*trans*-stilbene) (2g). Anal. Calcd for $C_{38}H_{48}FeP_2Pd$: C, 62.61; H, 6.64. Found: C, 62.45; H, 6.47. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 44.1 (a), 37.7 (b) (diastereomer ratio 10.3:1). ^1H NMR (C_6D_6): δ 7.48−7.46 (m, 4H, Ar), 7.34−7.31 (m, 4H, Ar), 7.01 (m, 2H, Ar), 5.33 (CH=CH, 2H, a), 5.30 (CH=CH, 2H, b), 4.33 (Cp, 2H), 4.24 (Cp, 2H), 4.19 (m, Cp, 4H), 2.44−2.40 (m, 2H), 2.34−2.30 (m, 6H), 2.09−2.05 (m, 2H), 2.04−1.99 (m, 2H), 1.47 (t, $J = 7$, 6H, Me), 1.08−1.00 (m, 2H), 0.99−0.88 (m, 2H), 0.48 (t, $J = 7$, 6H, Me). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 146.4, 129.2 (b), 128.33, 128.28 (b), 125.4 (b), 125.0, 122.8, 77.8 (m), 77.4 (apparent t, $J = 12$), 73.4 (b), 73.2 (apparent t, $J = 4$), 71.9 (b), 71.3, 70.1 (b), 70.0, 64.8 (apparent t, $J = 10$, stilbene CH), 36.3 (apparent t, $J = 6$), 35.1 (m), 34.5 (b), 33.9 (m), 28.5 (apparent t, $J = 7$), 25.6, 22.8 (b), 14.6 (apparent t, $J = 6$), 14.3 (b), 12.6 (b) 11.7 (apparent t, $J = 4$).

Pd(CyPF-t-Bu)(*trans*-stilbene) (2h). Anal. Calcd for $C_{46}H_{64}FeP_2Pd(C_{14}H_{12})_{0.25}$: C, 67.08; H, 7.62. Found: C, 67.12; H, 8.04. $^{31}P\{^1H\}$ NMR (C_6D_6; two diastereomers, 40:1 ratio): δ 76.5 (d, $J = 5$), 20.3 (br) (major); 82.9, 18.6 (minor). ^1H NMR (C_6D_6): δ 7.43 (d, $J = 8$, 2H), 7.37 (d, $J = 8$, 2H), 7.21 (t, $J = 8$, 2H), 7.18−7.14 (m, 2 H, overlapping with solvent), 6.97 (t, $J = 7$, 1H), 6.91 (t, $J = 7$, 1H), 4.78 (br, 1H), 4.68 (m, 1H), 4.26 (Cp, 1H), 4.09 (Cp, 1H), 4.06 (Cp, 5H), 4.04 (Cp, 5H, minor), 3.97 (t, $J = 3$, Cp, 1H), 2.98 (m, 1H), 2.16 (br, 2H), 1.93−1.77 (m, 8H), 1.73 (t, $J = 7$, 3H), 1.58 (m, 5H), 1.53 (d, $J = 12$, 9H), 1.42−1.00 (m, 7H), 0.63 (d, $J = 12$, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 149.1 (m, Ar), 148.6 (dd, $J = 6$, 2, Ar), 128.7−128.2 (m, overlapping C_6D_6 peaks, Ar), 125.8 (d, $J = 2$, Ar), 125.2 (d, $J = 3$, Ar), 122.9 (d, $J = 2$, Ar), 122.7 (d, $J = 3$, Ar), 110.5 (Ar), 98.0 (dd, $J = 6$, 21, Cp), 76.3 (Cp), 73.3 (Cp), 70.1 (Cp), 70.0 (Cp, minor), 69.7 (Cp), 67.9 (d, $J = 4$, Cp), 66.3 (d, $J = 28$, stilbene CH), 63.7 (dd, $J = 5$, 27, stilbene CH), 38.0 (d, $J = 4$), 37.4 (d, $J = 5$), 37.3 (d, $J = 5$), 36.8 (t, $J = 4$), 36.7, 35.5 (m), 34.8, 31.6 (br), 30.6 (br), 30.0 (d, $J = 7$), 29.8, 28.1 (m), 27.8, 27.6 (d, $J = 6$), 27.5, 26.4, 18.3 (d, $J = 6$), 12.0. $^1H\{^{31}P\}$ NMR (C_6D_6) (selected peaks): δ 4.75 (d, $J = 10$), 4.65 (d, $J = 10$), 1.67 (d, $J = 10$), 1.32 (9H), 0.60 (9H).

Selective $^1H\{^{31}P\}$ decoupling experiments enabled identification of the ^{31}P NMR resonances for both **2h** and **2i**. Here, decoupling the P(t-Bu)$_2$ signal at δ 76.5 collapsed the t-Bu signals into singlets as well as simplifying the CHMe resonance, while decoupling the other peak did not affect these signals.

Pd(PPF-t-Bu)(*trans*-stilbene) (2i). Anal. Calcd for $C_{46}H_{52}FeP_2Pd$: C, 66.64; H, 6.32. Found: C, 66.03; H, 6.53. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 77.4 (d, J = 14), 9.6 (d, J = 14). The minor diastereomer was not observed in the ^{31}P NMR spectrum, perhaps because of peak overlap. ^1H NMR (C_6D_6): δ 7.53 (t, J = 8, 2H), 7.34 (d, J = 8, 2H), 7.30−7.26 (m, 2H), 7.21 (m, 2H), 7.18−7.14 (m, 2H), 7.10 (t, J = 7, 1H), 7.06−6.98 (m, 6H), 6.84−6.79 (m, 3H), 4.97 (m, 1H), 4.33 (m, 1H), 4.26 (m, Cp, 1H), 4.09 (Cp, 1H), 3.99 (m, Cp, 1H), 3.51 (Cp, minor diastereomer, 5H), 3.43 (Cp, 5H), 3.33 (m, 1H), 1.69 (t, J = 7, 3H), 1.53 (d, J = 12, 9H), 0.75 (d, J = 12, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.9 (dd, J = 6, 2, Ar), 146.5 (dd, J = 5, 2 Ar), 141.5 (dd, J = 30, 4, Ar), 140.0 (d, J = 25, Ar), 135.9 (d, J = 18, Ar), 131.4 (d, J = 12, Ar), 129.2 (Ar), 128.4 (d, J = 1, Ar), 128.3 (Ar), 128.2−127.7 (m, overlapping C_6D_6 peaks), 127.5 (Ar), 125.1 (d, J = 2, Ar), 124.4 (d, J = 2, Ar), 122.9 (Ar), 122.1 (Ar), 97.9 (dd, J = 6, 26, Cp), 79.6 (dd, J = 2, 20, Cp), 74.6 (Cp), 70.2 (Cp), 69.6 (d, J = 8, Cp), 69.5 (dd, J = 5, 23), 68.6 (br, d, J = 28), 67.8 (d, J = 4, Cp), 36.7 (dd, J = 4, 1), 36.3 (d, J = 7), 36.0 (t, J = 4.5), 31.2 (d, J = 9), 30.9 (d, J = 8), 17.6 (d, J = 3).

Pd(BoPhoz)(*trans*-stilbene) (2j). $^{31}P\{^1H\}$ NMR (C_6D_6; two diastereomers, in 2:1 ratio): major, δ 90.0 (d, J = 23), 8.6 (d, J = 23); minor, δ 90.1 (d, J = 21), 8.2 (d, J = 21). ^1H NMR (C_6D_6): δ 8.03 (br, 1H, Ar), 7.84 (d, J = 8, 2H, Ar), 7.81 (t, J = 8, 2H, Ar), 7.62 (t, J = 8, 2H, Ar), 7.26−7.22 (m, 4H, Ar), 6.91−6.84 (m, 4H, Ar), 6.81 (br, 5H, Ar), 6.75 (m, 5H, Ar), 6.56 (t, J = 6, 2H, Ar), 6.35−6.31 (m, 1H, Ar), 6.29−6.28 (m, Cp-C*H*(Me)), 6.01 (t, J = 9, 2H, Ar), 5.86 (m, 1H, minor stilbene CH), 5.52 (br, 1H, minor stilbene CH), 5.35−5.31 (m, 1H, stilbene CH), 5.21−5.16 (m, 1H, stilbene CH), 4.13 (1H, Cp), 4.08 (1H, Cp), 4.03 (1H, Cp, minor), 3.96 (1H, Cp, minor), 3.73 (5H, Cp, minor), 3.60 (1H, Cp, minor), 3.58 (1H, Cp), 3.46 (5H, Cp), 2.18 (d, J = 7, 3H, minor), 2.11 (d, J = 7, 3H), 1.33 (d, J = 7, 3H), 1.13 (d, J = 7, 3H, minor). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 148.2 (m, Ar), 144.9 (m, Ar), 140.8 (m, Ar), 140.1 (d, J = 9, Ar), 139.7 (Ar), 139.5 (Ar), 135.2 (d, J = 17, Ar), 132.9 (d, J = 16, Ar), 132.6 (d, J = 16, Ar), 132.3 (d, J = 17, Ar), 130.3 (d, J = 15, Ar), 129.5 (Ar), 129.2 (Ar), 129.0 (Ar), 128.5 (Ar), 128.3 (Ar), 128.2−127.9 (m, overlapping C_6D_6 peaks), 127.7 (d, J = 15, Ar), 127.5 (d, J = 7, Ar), 125.9 (m, Ar), 125.6 (m, Ar, minor), 124.6 (m, Ar, minor), 124.4 (m, Ar), 123.7 (Ar), 122.8 (m, Ar), 97.7 (m, Cp), 75.5 (Cp), 73.2 (m, Cp), 71.9 (m, stilbene CH), 70.3 (Cp, 5C, major), 70.2 (Cp, 5C, minor), 69.1 (m, Cp), 68.2 (m, Cp), 66.5 (m, stilbene CH), 57.7 (m, Cp *CH*(Me)N−), 30.4 (Me, major), 30.2 (Me, minor), 29.4 (N−Me, major), 29.0 (N−Me, minor). Note: only selected peaks of the minor diastereomer are reported.

Ni((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (Ni-2a). Ni((*R*,*R*)-Me-Duphos)Cl_2 (150 mg, 0.34 mmol) and *trans*-stilbene (68 mg, 0.38 mmol) were stirred as a slurry in THF (4 mL). $NaBH(OMe)_3$ (132 mg, 1.03 mmol) was added as a solid, and any residual borohydride was then washed into the reaction mixture with THF (2 mL). The reaction mixture immediately turned brown, and gas evolved. Stirring was continued for a further 1.5 h, and then all volatiles were removed in vacuo. The mixture was extracted with toluene (8 mL) and filtered through Celite, and the resulting dark brown solution was pumped to dryness in vacuo. The orange residue was then extracted with petroleum ether (12 mL), filtered through Celite, and reduced in volume to ca. 6 mL in vacuo. After storage overnight at −30 °C, the product was isolated as fine orange needles (90 mg), suitable for X-ray crystallography. Concentration of the supernatant to 3 mL in volume and cooling to −30 °C yielded a second crop of solid. Total yield (two crops): 110 mg (0.20 mmol, 59%). Despite repeated attempts, we were unable to get satisfactory elemental analyses for this complex.

Anal. Calcd for $C_{32}H_{40}P_2Ni$: C, 70.48; H, 7.39. Found: C, 69.42; H, 7.63. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 68.9 (a), 60.9 (b); diastereomer ratio (a):(b) 55:1. ^1H NMR (C_6D_6): δ 7.36 (d, J = 7, 4H, stilbene Ar), 7.24 (m, 2H, Ar), 7.17 (t, J = 7, 4H, stilbene Ar), 6.99 (m, 2H, Ar), 6.90 (t, J = 7, 2H, stilbene Ar), 4.67 (2H, stilbene C*H* (a)), 4.32 (2H, stilbene C*H* (b)), 2.35 (m, 2H), 1.97 (m, 2H), 1.66 (m, 2H), 1.45 (m, 6H, Me), 1.45−1.32 (m, 2H), 1.32−1.24 (m, 4H), 0.38 (m, 6H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.8 (apparent t, J = 2, stilbene Ar quat), 147.3 (apparent t, J = 31, Ar quat), 131.8 (apparent t, J = 6, Ar), 128.7 (Ar), 128.3 (Ar), 123.9 (apparent t, J = 2, Ar), 121.4 (apparent t, J = 2, Ar), 52.5 (apparent t, J = 9, stilbene CH), 38.3 (apparent t, J = 12, CH), 37.20 (CH_2), 37.16 (CH_2), 35.4 (apparent t, J = 10, CH), 19.8 (apparent t, J = 9, Me), 15.0 (Me).

Ni((*R*,*R*)-Me-Duphos)(COD) (4). $Ni(COD)_2$ (50 mg, 0.18 mmol) was stirred as a slurry in hexane (1 mL), and a solution of (*R*,*R*)-Me-Duphos (55 mg, 0.18 mmol) in hexane (2 mL) was added dropwise. Immediately all the solid dissolved and an orange solution formed; it was stirred for 20 min and then filtered through Celite. The solution was reduced to ca. 2 mL in vacuo and stored at −30 °C overnight to yield the product as orange crystalline blocks, suitable for X-ray crystallography, which were isolated and dried in vacuo. Concentration of the supernatant and cooling to −30 °C yielded a second crop of solid. Yield: 60 mg (in 2 crops, 72%).

Anal. Calcd for $C_{26}H_{40}P_2Ni$: C, 65.99; H, 8.52. Found: C, 63.01; H, 8.64. Despite several attempts using crystalline material, a satisfactory C analysis could not be obtained. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 62.9. ^1H NMR (C_6D_6): δ 7.44−7.41 (m, 2H, Ar), 7.09−7.07 (m, 2H, Ar), 5.32−5.27 (m, 2H, alkene C*H*), 4.09−4.03 (m, 2H, alkene C*H*), 2.76−2.70 (m, 4H), 2.68−2.61 (m, 2H), 2.49−2.42 (m, 2H), 2.37−2.33 (m, 2H), 2.30−2.23 (m, 2H), 2.18−2.11 (m, 2H), 1.90−1.85 (m, 2H), 1.58−1.48 (m, 4H), 1.37 (dd, J = 16, 7, 6H, Me), 0.58 (dd, J = 12, 7, 6H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 149.0 (m, Ar quat), 131.4 (apparent t, J = 6, Ar), 128.1 (Ar), 83.9 (t, J = 2, alkene CH), 79.0 (t, J = 4, alkene CH), 40.4 (apparent t, J = 9, CH), 37.8 (dd, J = 9, 11, CH), 37.6 (CH_2), 35.8 (CH_2), 35.3 (apparent t, J = 6, CH_2), 30.2 (apparent t, J = 2, CH_2), 19.9 (apparent t, J = 8, Me), 14.6 (Me).

Ni((*R*,*R*)-Me-Duphos)$_2$ (5). $Ni(COD)_2$ (50 mg, 0.18 mmol) was stirred as a slurry in hexane (1 mL), and a solution of (*R*,*R*)-Me-Duphos (111 mg, 0.36 mmol) in hexane (2 mL) was added dropwise. Immediately all the solid dissolved and an orange solution formed; it was transferred to an ampule, which was sealed and heated at 50 °C for 5 h. The orange solution was then cooled to room temperature and filtered through Celite. The solution was reduced to ca. 2 mL in vacuo and stored at −30 °C overnight to yield the product as dark orange crystals, whose high solubility reduced the yield (66 mg in 2 crops, 54%). A solution of this complex decomposed quickly in air.

Anal. Calcd for $C_{36}H_{56}P_4Ni$: C, 64.40; H, 8.41. Found: C, 63.71; H, 8.64. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 68.5. ^1H NMR (C_6D_6): δ 7.49 (m, 4H, Ar), 7.09 (m, 4H, Ar), 2.48 (m, 4H), 2.26−2.21 (m, 8H), 1.97 (m, 4H), 1.66−1.55 (overlapping m, 8H), 1.26−1.20 (m, 12H, Me), 0.88−0.85 (m, 12H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 132.0 (m, Ar quat), 130.1 (br, Ar), 127.0 (Ar), 41.0 (quintet, J = 9), 36.93 (quintet, J = 6), 36.88, 36.5, 20.9 (m, Me), 15.8 (Me).

Addition of PhI to Pd(Diphos*)(*trans*-stilbene) Complexes. Sample Procedure. To a solution of Pd((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (**2a**; 40.7 mg, 0.069 mmol) in toluene (1 mL) was added PhI (12 μL, 21.9 mg, 0.107 mmol, 1.5 equiv) via syringe. The progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR. With this and other diphos* ligands, oxidative addition occurred to give Pd(Diphos*)(Ph)(I) as the major product; with the Duphos ligands an impurity formulated as Pd(Duphos)I_2 was also formed.[33] See Table 6 for details. In some experiments, additional *trans*-stilbene was added to **2a** before treatment with PhI.

Formation of Pd(L*)(dba) in Situ and Oxidative Addition of PhI. Sample Procedure. $Pd(dba)_2$ (17 mg, 0.03

Table 9. ^{31}P NMR Spectroscopic Data for the Complexes Pd(diphos*)(dba) Generated in Situ and Rates of Oxidative Addition of PhI to Pd(dba)$_2$/diphos* Mixtures

	Pd(diphos*)(dba)		
diphos*	^{31}P{^{1}H} NMR (δ, toluene)	formation reacn time (h)	extent of formation of Pd(diphos*)(Ph)(I) (%)
Me-Duphos	63.4 (br), 43.2 (br)[a]	30[b]	0 (70 h)
Et-Duphos	57.2 (br), 54.3 (br)	4.5 (40 °C)	0 (70 h)
i-Pr-Duphos	49.9 (br), 47.2 (br)	40	0 (70 h)[c]
Me-BPE	61.9 (v br), 59.2 (v.br)[d]	0.5	0 (28 h)
Me-FerroLANE	37.3 (br), 35.8 (br)	1	37 (74 h)
Me-DuXantphos	35.1 (br), 31.9 (br)[e]	23	100 (2 h)
Et-FerroTANE	45.5 (br), 43.2 (br)[f]	24	56 (51 h)
CyPF-t-Bu	79.3 (br), 23.0 (br)[g]	72 (60 °C)	0 (24 h, then 48 h at 60 °C)
PPF-t-Bu	80.8 (br), 11.7 (br)[h]	72 (50 °C)	100 (72 h, 50 °C)
BoPhoz	88.2 (br), 8.8 (br)[i]	72	100 (24 h)

[a] Pd(Me-Duphos)$_2$ (~15%; see ref 11b) was also observed. [b] 7 h at 40 °C, followed by 23 h at room temperature. [c] A small amount of what is believed to be Pd(i-Pr-Duphos)I$_2$ (see Table 6 and ref 33) was observed, along with signals attributed to Pd(i-Pr-Duphos)(dba). [d] After 30 min the reaction mixture contained 55% Pd(Me-BPE)(dba) and 45% of another material, believed to be Pd(BPE)$_2$ (δ 55.3); after 28 h, it was 66% Pd(Me-BPE)(dba) and 34% Pd(BPE)$_2$. [e] After 23 h, the reaction mixture contained ~5% Me-DuXantphos. [f] After 24 h, the reaction mixture contained ~14% Et-FerroTANE. [g] These peaks were observed initially; later, signals at δ 49.8 and 42.6 were also observed. None of these signals were affected by treatment with PhI. [h] In addition to these signals, peaks at δ 60.9, 47.7, and 29.6 were observed; they were unaffected by treatment with PhI. [i] In addition to these signals, peaks at δ 29.7 and 27.4 were observed; they were unaffected by treatment with PhI.

mmol) was slurried in toluene (0.5 mL), and a solution of diphos* (1 equiv) in toluene (1 mL) was added. The reaction mixture was transferred to an NMR tube and monitored by ^{31}P{^{1}H} NMR spectroscopy until free ligand was no longer observed. In some cases, the mixture was heated to speed up the reaction. The tube was then brought back into the glovebox; in some cases, the solution was filtered through Celite to remove unreacted Pd(dba)$_2$ and Pd black. PhI (5 μL, 0.05 mmol, 1.5 equiv) was then added via microliter syringe, and the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy. Table 6 summarizes the results of these experiments; additional spectroscopic data and details are given in Table 9.

Oxidative Addition of PhI to Ni(Me-Duphos)(*trans*-stilbene). Ni(Me-Duphos)(*trans*-stilbene) (38 mg, 0.069 mmol) was dissolved in toluene (1 mL), and PhI (11.6 μL, 0.10 mmol) was added via microliter syringe. The solution was then transferred to an NMR tube and monitored periodically by ^{31}P{^{1}H} NMR spectroscopy.

Competition Experiment: Oxidative Addition of PhI to *trans*-Stilbene Complexes of Ni(Me-Duphos) and Pd(Me-Duphos). Ni(Me-Duphos)(*trans*-stilbene) (17.0 mg, 0.031 mmol) and Pd(Me-Duphos)(*trans*-stilbene) (18.5 mg, 0.031 mmol) were dissolved in toluene (1 mL). PhI (11.2 μL, 0.10 mmol) was then added via microliter syringe, and the solution was transferred to an NMR tube. The reaction was then periodically monitored by ^{31}P{^{1}H} NMR spectroscopy.

A spectrum obtained 5 min after the addition of PhI showed the presence of Pd(Me-Duphos)(Ph)(I) and Ni(Me-Duphos)(*trans*-stilbene) (both diastereomers) only. The spectrum remained unchanged on continued monitoring, although after 30 min a small quantity of solid precipitated from the reaction mixture.

Reaction of Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (Pt-2a) with PhI. To a yellow solution of Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (30 mg, 0.04 mmol) in toluene (0.5 mL) was added PhI (7.9 μL, 0.07 mmol) with a microliter syringe. The reaction mixture was transferred into an NMR tube and monitored by ^{31}P{^{1}H} NMR. No reaction was observed after 1 day at room temperature. After the reaction mixture was heated to 60 °C for 15 min, oxidative addition of PhI was observed, yielding a small amount of Pt((*R*,*R*)-Me-Duphos)(Ph)(I) along with unreacted Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene). After the reaction mixture was heated to 60 °C for 1 h, some Pt((*R*,*R*)-Me-Duphos)I$_2$ was also observed, along with Pt((*R*,*R*)-Me-Duphos)(Ph)(I) and unreacted Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene). Heating the reaction mixture at 100 °C for 10 min gave more Pt((*R*,*R*)-Me-Duphos)I$_2$, although Pt((*R*,*R*)-Me-Duphos)(Ph)(I) and unreacted Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) were still present. During this process the color changed from bright yellow to pale yellow.

The complexes Pd(diphos*)(Ph)(I) were prepared by treatment of Pd(TMEDA)(Ph)(I) or Pd(PPh$_3$)$_2$(Ph)(I) with diphos*. Typical procedures are given below, with details for the analogous compounds being given in the Supporting Information.

Pd((*R*,*R*)-Me-Duphos)(Ph)(I) (3a). To a slurry of Pd(PPh$_3$)$_2$(Ph)(I) (159.2 mg, 0.191 mmol) in THF (5 mL) in a vial wrapped in aluminum foil was added (*R*,*R*)-Me-Duphos (64.1 mg, 0.21 mmol, 1.1 equiv) as a solution in THF (2 mL). Upon addition the solid dissolved and the reaction mixture changed color from yellow to red-brown. After it was stirred for 2 h at room temperature, the reaction mixture was filtered through Celite, concentrated to ~0.5 mL, and layered with petroleum ether. After this mixture was cooled overnight at −30 °C, the resulting orange oily residue was triturated with petroleum ether and dried in vacuo to give 85.2 mg (72%) of the desired compound as a yellow-orange solid. No Pd((*R*,*R*)-Me-Duphos)I$_2$ was observed by ^{31}P NMR.

Slow diffusion of petroleum ether into a THF solution of the compound yielded a yellow oil which solidified upon trituration with petroleum ether to yield an analytically pure solid. The solid was stable when stored at −25 °C in the dark but became pink at room temperature in the light. In solution, the compound slowly decomposed to form Pd metal and Pd((*R*,*R*)-Me-Duphos)I$_2$. A sample suitable for crystallographic analysis was obtained by slow evaporation of C_6D_6.

Anal. Calcd for $C_{24}H_{33}IP_2Pd\cdot$THF: C, 48.73; H, 5.97. Found: C, 49.09; H, 6.13. The presence of solvent was confirmed by ^{1}H NMR. ^{31}P{^{1}H} NMR (C_6D_6): δ 67.8 (d, J = 27), 64.7 (d, J = 27). ^{1}H NMR (C_6D_6): δ 7.87 (br, 2H, Ar), 7.26−7.19 (m, 3H, Ar), 7.10−7.00 (m, 4H, Ar), 4.00−3.92 (m, 1H, CH), 3.15−3.06 (m, 1H, CH), 2.40−2.32 (m, 1H, CH), 2.19−2.05 (m, 2H, CH$_2$), 1.96−1.78 (m, 2H, CH$_2$), 1.64 (dd, $^3J_{PH}$ = 19, $^3J_{HH}$ = 7, 3H, Me), 1.59−1.32 (m, 3H, CH, CH$_2$), 1.27 (dd, $^3J_{PH}$ = 19, 7, 3H, Me), 1.30−1.24 (m, 2H, overlapping with previous peak, CH$_2$), 0.70−0.63 (overlapping dd, $^3J_{HH}$ = 7, 7, $^3J_{PH}$ = 14, 15, 6H, 2Me). ^{13}C{^{1}H} NMR (C_6D_6): δ 159.3 (d, J = 138, Ar, quat), 144.1 (dd, J = 44, 35, Ar, quat), 143.4 (dd, J = 33, 26, Ar, quat), 139.9 (br, Ar, CH), 133.9 (d, J = 14, Ar, CH), 133.4 (d, J = 15, Ar, CH), 131.9−131.8 (m, Ar, CH), 128.7−128.3 (m, Ar, CH, obscured by residual solvent peaks), 127.5 (d, J = 9, Ar, CH), 123.4 (d, J = 7, Ar, CH), 43.6 (dd, J = 29, 10, CH), 42.8 (dd, J = 21, 8, CH), 38.1 (br, CH$_2$), 37.7 (dd, J = 21, 10, CH), 36.9 (br m, 2 CH$_2$), 35.7 (m, CH$_2$), 33.7 (dd, J =

27, 8, CH), 18.2−18.0 (m, Me), 16.2−16.1 (m, Me), 15.1−15.0 (m, Me), 14.8−14.7 (m, Me). IR: 3044, 2922, 2855, 1650, 1622, 1556, 1450, 1378, 1244, 1156, 1111, 1056, 1017, 756, 728, 694, 528, 456.

Pd((*R,R*)-Et-Duphos)(Ph)(I) (3b). Anal. Calcd for $C_{28}H_{41}IP_2Pd{\cdot}C_6H_6$: C, 54.38; H, 6.31. Found: C, 54.12; H, 6.52. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.4 (d, $J = 26$), 58.5 (d, $J = 26$). ^1H NMR (C_6D_6): δ 7.91 (br, 2H, Ar), 7.27−7.25 (m, 3H, Ar), 7.12−7.11 (m, 1H, Ar), 7.06−7.01 (m, 3H, Ar), 3.85−3.78 (m, 1H, CH), 3.02−2.94 (m, 1H, CH), 2.46−2.39 (m, 1H, CH), 2.30−2.18 (m, 2H, CH_2), 2.13−1.93 (m, 5H, 2 CH_2, CH), 1.87−1.53 (m, 4H, 2 CH_2), 1.37−1.10 (m, 4H, 2 CH_2), 1.03−0.93 (m, 2H, CH_2), 0.92 (overlapping dd, $^3J_{HH} = 7, 7$, 3H, Me), 0.79 (overlapping dd, $^3J_{HH} = 7, 7$, 3H, Me), 0.74 (overlapping dd, $^3J_{HH} = 7, 7$, 3H, Me), 0.69 (overlapping dd, $^3J_{HH} = 7, 7$, 3H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 158.2 (d, $J = 138$, Ar, quat), 144.8 (dd, $J = 52, 33$, Ar, quat), 144.6 (dd, $J = 34, 24$, Ar, quat), 140.1 (br, Ar, CH), 134.0 (d, $J = 15$, Ar, CH), 133.2 (d, $J = 16$, Ar, CH), 131.1−131.0 (m, Ar, CH), 130.9 (d, $J = 5$, Ar, CH), 127.6 (d, $J = 9$, Ar, CH), 123.6 (Ar, CH), 51.3 (d, $J = 27$, CH), 50.8 (d, $J = 19$, CH), 44.4 (d, $J = 20$, CH), 40.5 (d, $J = 26$, CH), 35.2 (d, $J = 2$, CH_2), 34.4 (d, $J = 3$, CH_2), 34.3 (CH_2), 32.9 (d, $J = 6$, CH_2), 26.7 (d, $J = 11$, CH_2), 24.9 (d, $J = 8$, CH_2), 24.3 (d, $J = 1$, CH_2), 24.2 (d, $J = 2$, CH_2), 15.2 (d, $J = 11$, Me), 15.0 (d, $J = 12$, Me), 14.3 (d, $J = 8$, Me), 14.2 (d, $J = 9$, Me).

Pd((*R,R*)-*i*-Pr-Duphos)(Ph)(I) (3c). Anal. Calcd for $C_{32}H_{49}IP_2Pd$: C, 52.72; H, 6.78. Found: C, 52.81; H, 6.98. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 62.4 (d, $J = 23$), 57.0 (d, $J = 23$). ^1H NMR ($CDCl_3$): δ 7.81−7.75 (m, 1H, Ar), 7.69−7.68 (m, 1H, Ar), 7.61−7.51 (m, 4H, Ar), 7.09−7.07 (m, 2H, Ar), 6.90−6.87 (m, 1H, Ar), 3.46−3.41 (m, 1H, CH), 2.83−2.77 (m, 1H, CH), 2.69−2.60 (m, 1H, CH), 2.44−2.19 (m, 5H, 2 CH_2, CH), 2.06−1.89 (m, 4H, CH_2, 2CH), 1.69−1.49 (m, 3H, CH_2, CH), 1.34−1.23 (m, 1H, CH), 1.12 (d, $^3J_{HH} = 6$, 3H, Me), 1.06 (d, $^3J_{HH} = 6$, 3H, Me), 0.93 (d, $^3J_{HH} = 6$, 3H, Me), 0.89 (d, $^3J_{HH} = 6$, 3H, Me), 0.86 (d, $^3J_{HH} = 6$, 3H, Me), 0.74−0.71 (two overlapping d, $J_{HH} = 7$, 6H, Me), 0.66 (d, $^3J_{HH} = 6$, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.4 (d, $J = 134$, Ar, quat), 144.9 (dd, $J = 31, 16$, quat), 144.6 (dd, $J = 32, 5$, quat), 134.7 (d, $J = 15$, Ar, CH), 133.6 (d, $J = 17$, Ar, CH), 131.8 (m, Ar, CH), 131.4 (m, Ar, CH), 127.7 (d, $J = 8$, Ar, CH), 123.4 (Ar, CH), 56.7−56.6 (m, CH), 51.6 (d, $J = 18$, CH), 47.2 (d, $J = 33$, CH), 32.9 (d, $J = 2$, CH_2), 32.35 (d, $J = 3$, CH_2), 32.04 (CH_2), 32.02 (d, $J = 10$, CH), 30.9 (d, $J = 6$, CH_2), 30.1 (d, $J = 7$, CH), 29.6 (d, $J = 2$, CH), 28.6 (CH), 26.9 (d, $J = 8$, Me), 26.7 (d, $J = 4$, Me), 26.0 (d, $J = 6$, Me), 25.1 (d, $J = 6$, Me), 22.7 (d, $J = 7$, Me), 22.6 (d, $J = 8$, Me), 21.6 (d, $J = 6$, Me), 21.5 (d, $J = 7$, Me).

Pd((*R,R*)-Me-BPE)(Ph)(I) (3d). Pd(TMEDA)(Ph)(I) (53 mg, 0.12 mmol) was slurried in THF (1 mL), and a solution of (*R,R*)-Me-BPE (32 mg, 0.12 mmol) in THF (1 mL) was added slowly. All the solid dissolved initially; then a white precipitate formed. The reaction mixture was stirred for 45 min, and then all volatiles were removed in vacuo to give a pale orange solid, which was washed with petroleum ether (3 mL). The residue was dried and then redissolved in CH_2Cl_2 (3 mL) and filtered. Layering this solution with Et_2O (12 mL) and storage at −30 °C for 1 week yielded a fine white fluffy solid (pure by NMR spectroscopy) as well as some larger yellow crystalline pieces which were suitable for elemental analysis. Yield: 50 mg (0.088 mmol, 70%).

Anal. Calcd for $C_{20}H_{33}P_2PdI$: C, 42.24; H, 5.85. Found: C, 42.16; H, 6.14. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 72.9 (d, $J = 25$), 61.5 (d, $J = 25$). ^1H NMR ($CDCl_3$): δ 7.41 (t, $J = 7$, 2H, Ph), 7.05 (t of d, $J = 8, 3$, 2H, Ph), 6.84 (t of d, $J = 8, 1$, 1H, Ph), 3.44 (m, 1H), 2.32−2.20 (m, 2H), 2.14−1.71 (overlapping m, 8H), 1.65−1.56 (m, 1H), 1.51 (dd, $J = 18, 7$, 3H, Me), 1.46 (partially obscured m, 2H), 1.41 (dd, $J = 19, 7$, 3H, Me), 1.38−1.25 (m, 1H), 1.22 (dd, $J = 14, 7$, 3H, Me), 1.18 (dd, $J = 15, 7$, 3H, Me), 1.05−0.95 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.9 (d, $J = 132$, Ph quat), 137.6 (Ph), 127.2 (d, $J = 9$, Ph), 122.5 (Ph), 39.2 (d, $J = 26$, CH), 39.1 (d, $J = 19$, CH), 36.8 (d, $J = 3$, CH_2), 36.0 (d, $J = 1$, CH_2), 35.6 (d, $J = 3$, CH_2), 35.0 (CH_2), 33.5 (d, $J = 20$, CH), 31.7 (d, $J = 29$, CH), 25.7 (apparent t, $J = 22$, CH_2), 21.2 (dd, $J = 16, 12$, CH_2), 20.0 (d, $J = 11$, Me), 19.0 (d, $J = 8$, Me), 14.6 (d, $J = 1$, Me), 13.8 (d, $J = 1$, Me).

Pd((*S,S*)-Me-FerroLANE)(Ph)(I) (3e). Anal. Calcd for $C_{28}H_{37}FeIP_2Pd$: C, 46.41; H, 5.15. Found: C, 46.22; H, 5.07. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.0 (d, $J = 32$), 23.9 (d, $J = 32$). ^1H NMR ($CDCl_3$): δ 7.41 (apparent t, $J = 8$, 1H, Ar), 7.31 (apparent t, $J = 8$, 1H, Ar), 7.10 (apparent t, $J = 8$, 1H, Ar), 7.04 (apparent t, $J = 8$, 1H, Ar), 6.81 (apparent t, $J = 7$, 1H, Ar), 4.57 (m, 1H, Cp), 4.53 (m, 1H, Cp), 4.44 (m, 1H, Cp), 4.40 (m, 3H, Cp), 4.21 (m, 1H, Cp), 4.13 (m, 1H, Cp), 3.95−3.87 (m, 1H), 2.79−2.72 (m, 1H), 2.63−2.56 (m, 1H), 2.24−2.10 (m, 2H), 2.00−1.94 (m, 1H), 1.96 (dd, $J = 7, 1$, 3H, Me), 1.92 (d, $J = 7$, 3H, Me), 1.82−1.74 (m, 1H), 1.65−1.55 (m, 1H), 1.36−1.11 (m, 3H), 1.10−1.02 (m, 1H), 0.90 (dd, $J = 15, 7$, 3H, Me), 0.51 (dd, $J = 16, 7$, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.5 (dd, $J = 122, 3$, Ar quat), 138.1 (apparent t, $J = 3$, Ar), 135.8 (d, $J = 5$, Ar), 128.4 (d, $J = 9$, Ar), 127.8 (d, $J = 8$, Ar), 122.7 (Ar), 75.0 (Cp CH), 74.9 (Cp CH), 74.3 (Cp CH), 74.1 (d, $J = 2$, Cp CH), 73.6 (dd, $J = 33, 7$, Cp quat), 72.5 (Cp CH), 72.3 (d, $J = 2$, Cp CH), 71.9 (d, $J = 2$, Cp CH), 71.6 (d, $J = 2$, Cp CH), 70.7 (dd, $J = 21, 3$, Cp quat), 38.3 (d, $J = 21$, CH), 36.7 (d, $J = 28$, CH), 36.4 (overlapping, 2 × CH_2), 36.2 (d, $J = 3$, CH_2), 35.3 (d, $J = 32$, CH), 34.7 (d, $J = 22$, CH), 34.2 (CH_2), 21.6 (d, $J = 13$, Me), 21.1 (d, $J = 11$, Me), 14.7 (Me), 14.2 (Me).

Pd((*S,S*)-Me-DuXantphos)(Ph)(I) (3f). Anal. Calcd for $C_{33}H_{41}P_2OIPd(CH_2Cl_2)_{0.5}$: C, 50.84; H, 5.35. Found: C, 50.64; H, 5.53. The presence of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −50 °C): δ 31.7 (A); 36.2 (d, $J = 32$), 27.1 (d, $J = 32$) (B); ratio A:B 3.2:1. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ 31.3 (br). ^1H NMR (CD_2Cl_2, −50 °C): δ 7.71 (m, 2H, Ar, A), 7.62 (d, $J = 8$, 1H, Ar, B), 7.54 (dd, $J = 7, 1$, 1H, Ar, B), 7.54−7.32 (overlapping m, 5H, Ar, A), 7.24−7.21 (overlapping m, 2H, Ar, B), 7.20 (d, $J = 7$, 2H, Ar, B), 7.15 (t of d, $J = 7, 1$, 1H, Ar, B), 7.07 (t, $J = 7$, 2H, Ar, A), 6.96 (t, $J = 7$, 1H, Ar, A), 6.92 (t, $J = 8$, 1H, Ar, A), 6.79 (m, 1H, Ar, B), 6.69 (t, $J = 7$, 1H, Ar, B), 6.61 (br t, $J = 7$, 1H, Ar, B), 5.86 (br m, 1H, Ar, B), 3.48 (m, 1H, B), 2.92 (m, 1H, B), 2.81−2.77 (m, 2H, A), 2.65−2.60 (m, 4H, A), 2.57−2.45 (m, 2H, B), 2.38−2.27 (m, 1H, B), 2.26−2.13 (m, 2H, A), 2.12−2.06 (m, 2H, A), 2.04−2.01 (m, 1H, B), 1.92 (3H, Xant Me B), 1.83−1.76 (m, 2H, B), 1.70 (6H, Xant Me, A), 1.66−1.62 (overlapping m, 1H, B), 1.62 (dd, $J = 12, 5$, 3H, Me, B), 1.58 (dd, $J = 20, 7$, 3H, Me, B), 1.45 (dd, $J = 19, 7$, 3H, Me, B), 1.36 (3H, Xant Me B), 1.29−1.24 (m, 2H, B), 1.23−1.20 (overlapping m, 1H, B), 1.20−1.14 (m, 6H, Me, A), 1.09−1.01 (m, 2H, A), 0.92 (dd, $J = 10, 7$, Me, 6H, A), 0.27 (dd, $J = 13, 7$, 3H, Me, B).

Complex **3f** was also generated in toluene by oxidative addition of PhI to impure Pd(Me-DuXantphos)(*trans*-stilbene) or to $Pd(dba)_2$/Me-DuXantphos. In the latter experiment, at room temperature, four broadened peaks were observed in the $^{31}P\{^1H\}$ NMR spectrum, which sharpened upon cooling to −20 °C. The AB pattern (toluene, −20 °C; δ 30.8, 25.3 ($J = 417$)) was consistent with *trans*-Pd(Me-DuXantphos)(Ph)(I). Removal of the solvent in vacuo and dissolution of the residue in CD_2Cl_2 gave spectra similar to those of an authentic sample (prepared by the method above) in the same solvent.

Pd((S,S)-Et-FerroTANE)(Ph)(I) (3g). Anal. Calcd for $C_{30}H_{41}FeIP_2Pd$: C, 47.87; H, 5.49. Found: C, 48.03; H, 5.58. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 46.4 (d, $J = 29$), 32.8 (d, $J = 29$). ^1H NMR ($CDCl_3$): δ 7.65 (br t, $J = 6$, 1H, Ph), 7.13 (br, 2H, Ph) 7.03 (br, 1H, Ph), 6.85 (t of d, $J = 7, 1$, 1H, Ph), 4.65 (m, 1H, Cp), 4.62 (m, 1H, Cp), 4.50 (m, 1H, Cp), 4.48 (m, 3H, Cp), 4.35 (m, 1H, Cp), 4.26 (m, 1H, Cp), 4.14 (quintet, $J = 9$, 1H), 2.60−2.52 (m, 2H), 2.47−2.33 (m, 3H), 2.30−2.17 (m, 2H), 2.13−1.89 (m, 3H), 1.56−1.51 (m, 1H), 1.41 (t, $J = 7$, 3H, Me), 1.35 (t, $J = 7$, 3H, Me), 1.15−1.10 (m, 2H), 1.07−1.00 (m, 1H), 0.90−0.82 (m, 1H), 0.79 (t, $J = 7$, 3H, Me), 0.44 (t, $J = 7$, 3H, Me). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 155.9 (dd, $J = 127, 5$, quat Pd−C_6H_5), 141.1 (br), 137.4 (br m), 128.1 (d, $J = 9$), 123.0, 79.1 (d,

J = 2, Cp), 78.9 (d, J = 2, Cp), 77.9 (Cp), 77.8 (Cp), 75.9 (d, J = 8, Cp), 75.8 (d, J = 9, Cp), 73.4 (Cp), 73.1 (Cp), 71.6 (dd, J = 23, 6, quat Cp), 70.9 (dd, J = 16, 2, quat Cp), 42.0 (d, J = 35, CH), 37.8 (d, J = 15, CH_2), 37.3 (d, J = 37, CH), 36.9 (d, J = 31, CH), 36.2 (d, J = 30, CH), 35.9 (d, J = 15, CH_2), 27.9 (d, J = 6, CH_2), 27.6 (d, J = 4, CH_2), 26.0 (d, J = 4, CH_2), 25.7 (d, J = 5, CH_2), 15.0 (d, J = 10, Me), 14.8 (d, J = 11, Me), 12.4 (d, J = 12, Me), 12.2 (d, J = 7, Me).

Pd((*R*,*S*)-CyPF-t-Bu)(Ph)(I) (3h). Anal. Calcd for $C_{38}H_{57}FeP_2PdI(CH_2Cl_2)_{0.6}$: C, 50.62; H, 6.40. Found: C, 50.39; H, 6.77. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78.0 (d, J = 35), 13.0 (d, J = 35). ^1H NMR ($CDCl_3$): δ 7.50 (t, J = 7, 1H), 7.41 (br, 1H), 7.12 (br, 1H), 6.89 (m, 1H), 6.81 (m, 1H), 4.92 (br, 1H), 4.52 (br, 1H), 4.46 (t, J = 2, 1H), 4.26 (5H), 3.24 (m, 1H), 2.82 (br, 2H), 2.34 (m, 3H), 2.01 (t, J = 7, 3H), 1.91 (br, 7H), 1.73 (d, J = 12, 9H), 1.65−1.26 (10H), 1.20 (d, J = 13, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.0 (Ar), 134.4 (t, J = 3, Ar), 129.1 (Ar), 129.0 (Ar), 126.8 (Ar), 124.3 (d, J = 5, Ar), 97.7 (d, J = 22, Cp), 72.6 (Cp), 70.8 (Cp), 69.6 (Cp), 69.1 (d, J = 8, Cp), 68.6 (d, J = 5, Cp), 38.6 (d, J = 2), 36.2, 33.8, 33.3, 31.4, 29.9, 28.0−27.6 (m), 27.5, 27.1, 26.8, 26.2, 25.9, 18.1 (d, J = 6).

Pd((*R*,*S*)-PPF-t-Bu)(Ph)(I) (3i). ^1H NMR (CD_2Cl_2): δ 8.05−7.98 (m, 2H, Ar), 7.56−7.53 (m, 3H, Ar), 7.36−7.30 (m, 1H, Ar), 7.24−7.10 (m, 4H, Ar), 6.80 (br, 1H, Ar), 6.41 (br, 4H, Ar), 4.58−4.57 (m, 1H, Cp), 4.32−4.31 (m, 1H, Cp), 4.09−4.07 (m, 1H, Cp), 3.7 (5H, Cp), 3.42−3.32 (m, 1H, CH), 2.09 (dd, J = 8, 7, 3H, Me), 1.73 (d, J = 12, 9H, *t*-Bu), 1.37 (d, J = 13, 9H, *t*-Bu). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 74.3 (d, J = 40), 18.9 (d, J = 40). Anal. Calcd for $C_{38}H_{45}FeIP_2Pd(CH_2Cl_2)_{0.75}$: C, 50.78; H, 5.11. Found: C, 50.90; H, 5.11. The presence of solvent was confirmed by ^1H NMR spectroscopy.

Pd(BoPhoz)(Ph)(I) (3j). Anal. Calcd for $C_{43}H_{40}NFeP_2PdI$: C, 56.02; H, 4.37; N, 1.52. Found: C, 57.56; H, 4.82; N, 1.52. FD-MS: *m/z* 970.7 (Pd(BoPhoz)I_2), 921 (**3j**), 843.8 (**3j** − Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$; two diastereomers in 8:1 ratio): major, δ 79.6 (d, J = 32), −4.5 (d, J = 32); minor, δ 81.8 (d, J = 37), 5.9 (d, J = 37). ^1H NMR ($CDCl_3$): δ 7.86−7.83 (m, 2H, Ar), 7.50−7.41 (m, 10H, Ar), 7.36−7.33 (m, 2H, Ar), 7.30−7.26 (overlapping with solvent, 3H, Ar), 6.94 (t, J = 8, 2H, Ar), 6.70 (br, 1H, Ar), 6.55 (m, 2H, Ar), 6.47 (t, J = 7, 1H, Ar), 6.39 (br, 1H, Ar), 6.24 (br, 1H, Ar), 6.00−5.96 (m, 1H, minor), 5.81−5.74 (m, 1H), 4.61 (br, 1H, Cp, minor), 4.52 (br, 1H, Cp), 4.39 (t, J = 3, 1H, Cp), 4.31 (t, J = 3, 1H, Cp, minor), 4.14 (1H, Cp), 4.13 (1H, Cp, minor), 3.94 (Cp, 5H, minor), 3.89 (5H, Cp), 2.20 (d, J = 9, 3H), 2.11 (d, J = 8, 3H, minor), 1.18 (d, J = 7, 3H, minor), 1.15 (d, J = 7, 3H). The low intensity of other peaks due to the minor isomer and spectral overlap prevented their assignment. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 148.7 (m, Ar), 139.4 (m, Ar), 138.7 (m, Ar), 136.8 (m, Ar), 133.9 (d, J = 12, Ar), 133.6 (Ar), 133.1 (d, J = 11, Ar), 132.9 (d, J = 11, Ar), 132.3 (d, J = 10, Ar), 132.1 (Ar), 130.1 (d, J = 11, Ar), 129.9 (d, J = 2, Ar), 129.7 (Ar), 129.3 (Ar), 129.1 (Ar), 128.7−128.6 (m, Ar), 128.3 (d, J = 8, Ar), 128.1 (d, J = 10, Ar), 127.8 (d, J = 11, Ar), 127.1 (d, J = 10, Ar), 126.6 (m, Ar), 122.1 (Ar), 74.3 (Cp), 71.0 (Cp), 70.8 (Cp, minor), 70.6 (Cp), 70.2 (Cp), 69.1 (d, J = 4, Cp), 68.0 (d, J = 6, Cp), 54.3 (dd, J = 6, 19), 34.3, 15.2.

Ni(PPh_3)$_2$(Ph)(I). Ni(PPh_3)$_4$ (0.94 g, 0.85 mmol) was slurried in toluene (15 mL), and PhI (0.55 mL, 1.00 g, 4.9 mmol) was added by syringe. On addition, the dark orange solution became paler and a precipitate was observed after about 15 min. The reaction mixture was stirred for 2 h, and then the orange-brown precipitate was isolated by filtration under N_2. The solid was washed with Et_2O (2 × 5 mL) and dried in vacuo to yield 405 mg of product. Petroleum ether (10 mL) was added to the toluene supernatant, and the solution was cooled to −30 °C. After 5 days a further 100 mg of product was isolated, washed with petroleum ether (5 mL), and dried in vacuo; this product was identical with the initial precipitate by $^{31}P\{^1H\}$ NMR spectroscopy (C_6D_6) and was analyzed correctly for Ni(PPh_3)$_2$(Ph)(I). Total yield: 505 mg (0.64 mmol, 75%).

Anal. Calcd for $C_{42}H_{35}P_2NiI$: C, 64.08; H, 4.48. Found: C, 64.13; H, 4.70. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 25.2, 22.6 (1:1 ratio). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.3, 22.3 (1:5 ratio). ^1H NMR (C_6D_6): δ 10.1 (v br), 7.78 (br), 7.45 (d, J = 7), 7.00 (br), 6.27 (d, J = 7), 2.5 (v br).

The initial orange-brown solid product formed C_6D_6 and $CDCl_3$ solutions of the same color, whose ^1H NMR spectra contained a mixture of broadened and sharper peaks. An attempt to dissolve the orange-brown solid in THF give a dark green solution and a small amount of a gray solid, which was removed by filtration through Celite. The solution was then layered with an equal volume of petroleum ether and stored at −30 °C. After 2 weeks very dark green-black lumps of crystalline material were isolated and dried in vacuo. This material was analyzed for C and H as follows: C, 65.43; H, 4.98. It dissolved in THF-d_8 to give a brown solution, whose ^1H NMR spectrum revealed two broad peaks at 9.9 and 5.0 ppm. The same batch of solid dissolved in C_6D_6 to give a green solution, whose ^1H NMR spectrum contained broad peaks at 9.5, 5.1, and 3.3 ppm as well as two somewhat sharper peaks that could be assigned to THF (3.6 and 1.4 ppm). This solution slowly deposited a red solid.

Ni((*R*,*R*)-Me-Duphos)(Ph)(I) (Ni-3a). Method 1. Ni(COD)$_2$ (50 mg, 0.18 mmol) was slurried in hexane (1 mL), and a solution of Me-Duphos (55 mg, 0.18 mmol) in hexane (2 mL) was added. Immediately an orange solution formed. After 15 min of stirring, the mixture was filtered through Celite. PhI (31 μL, 0.27 mmol) was added to the filtrate by microliter syringe, and the solution was left to stand for 16 h. The resulting pale orange precipitate was isolated by decantation, washed with petroleum ether, and dried in vacuo. On drying the solid turned oily and became brown. The $^{31}P\{^1H\}$ NMR spectrum of this material revealed Ni((*R*,*R*)-Me-Duphos)(Ph)(I) as the major product as well as the presence of other unidentified impurities (see below). Attempts to recrystallize this material from ether or CH_2Cl_2/hexanes were unsuccessful and resulted in further decomposition.

Method 2. Ni(PPh_3)$_2$(Ph)(I) (21 mg, 2.7 × 10^{-5} mol) was slurried in toluene (1 mL), and a solution of Me-Duphos (8.5 mg, 2.7 × 10^{-5} mol) was added. The resultant yellow cloudy solution was transferred to an NMR tube and monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After 15 min, Ni((*R*,*R*)-Me-Duphos)(Ph)(I) as the major product was observed along with small amounts of impurity A and another unidentified impurity (δ 68.4), as well as some unreacted Ni(PPh_3)$_2$(Ph)(I).

$^{31}P\{^1H\}$ NMR (C_6D_6): δ 75.0 (d, J = 26), 68.7 (d, J = 26). Impurities observed: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 70.1 (d, J = 29), 67.5 (d, J = 29) (A); 67.6 (d, J = 28), 64.9 (d, J = 28) (B). In a separate experiment Ni(Me-Duphos)I_2 was observed as the only impurity: δ 100.1 (Method 1).[51] ^1H NMR (C_6D_6): δ 8.08 (br t, J = 6, 1H, Ar), 7.69 (br t, J = 6, 1H, Ar), 7.27−7.11 (overlapping m, 3H, Ar), 7.11−6.99 (m, 3H, Ar), 6.93−6.88 (m, 1H, Ar), 4.23−4.09 (m, 1H), 2.82−2.65 (m, 1H), 2.38−2.24 (m, 1H), 2.14−1.97 (m, 2H), 1.94−1.86 (overlapping m, 1H), 1.79 (dd, J = 18, 8, 3H, Me), 1.56 (dd, J = 16, 7, 3H, Me), 1.54−1.33 (overlapping m, 2H), 1.31−1.20 (m, 1H), 1.14−1.08 (m, 1H), 1.03−0.85 (m, 2H), 0.72 (dd, J = 7, 1, 3H, Me), 0.67 (d, J = 7, Me).

Ni((*R*,*R*)-Me-Duphos)(Ph)(Cl). Ni(PPh_3)$_2$(Ph)(Cl) (202 mg, 0.29 mmol) was stirred as a slurry in THF (3 mL), and a solution of (*R*,*R*)-Me-Duphos (89 mg, 0.29 mmol) in THF (2 mL) was added dropwise. During the addition the starting material dissolved and the solution darkened somewhat. The reaction mixture was stirred for 15 h, and then the orange-yellow slightly cloudy solution was pumped to dryness in vacuo. The residue was extracted with toluene (6 mL) and filtered through Celite to give a clear orange-red solution which was pumped to dryness. The sticky residue was washed with

(51) Frenzen, G.; Reim, S.; Sippel, H.; Frauenrath, H. *Z. Kristallogr. New Cryst. Struct.* **1999**, *214*, 121−122.

petroleum ether (3 mL) and dried in vacuo. The product was then dissolved in CH_2Cl_2 (4 mL), the solution was filtered, and the filtrate was layered with petroleum ether (15 mL). After storage at −30 °C for 1 week a small amount of yellow solid (14 mg) was isolated and shown to be Ni(Me-Duphos)Cl_2 by ^{31}P NMR spectroscopy.[48] The supernatant was pumped to dryness in vacuo, and the residue was redissolved in toluene (3 mL). This solution was filtered, hexane (3 mL) was added, and the solution was cooled to −30 °C. After 3 days, an orange crystalline toluene solvate was isolated and dried in vacuo. This was shown to be pure by ^{31}P and ^{1}H NMR spectroscopy. Yield: 103 mg (using the stoichiometry given below, 72%).

Anal. Calcd for $C_{24}H_{33}P_2NiCl(C_7H_8)_{0.2}$: C, 61.50; H, 7.03. Found: C, 61.56; H, 7.21. The presence of toluene was confirmed by ^{1}H NMR spectroscopy in $CDCl_3$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 69.7 (d, J = 29), 67.6 (d, J = 29). ^{1}H NMR ($CDCl_3$): δ 7.64−7.61 (m, 1H, Ar), 7.58−7.53 (m, 5H, Ar), 7.07−7.03 (m, 2H, Ar), 6.85 (t, J = 8, 1H, Ar), 3.42−3.37 (m, 1H), 2.99−2.92 (m, 1H), 2.54−2.44 (m, 2H), 2.35−2.28 (m, 1H), 2.22−2.14 (m, 1H), 2.06−1.82 (overlapping m, 3H), 1.74 (dd, J = 18, 7, 3H, Me), 1.73 (partially obscured m, 1H), 1.63 (dd, J = 18, 7, 3H, Me), 1.66−1.52 (m, 1H), 1.33−1.25 (m, 1H), 0.98 (dd, J = 7, 1, 3H, Me), 0.95 (dd, J = 7, 3, 3H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.7 (dd, J = 93, 36, Ni−Ph quat), 145.3 (dd, J = 45, 34, Ar quat), 141.8 (m, Ar quat), 132.0 (d, J = 13, Ar), 131.4 (d, J = 15, Ar), 130.8 (Ar), 130.8 (overlapping m, Ar), 126.6 (Ar), 126.5 (Ar), 122.2 (Ar), 43.3 (d, J = 30, CH), 41.4 (d, J = 23, CH), 37.5 (CH_2), 36.6 (CH_2), 36.5 (CH_2), 35.2 (d, J = 5, CH_2), 33.7 (d, J = 21, CH), 33.5 (d, J = 34, CH), 17.1 (d, J = 11, Me), 15.8 (d, J = 6, Me), 14.6 (Me), 14.5 (Me).

Pt((*R*,*R*)-Me-Duphos)(Ph)(Cl). A solution of (*R*,*R*)-Me-Duphos (306 mg, 1.0 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a solution of Pt(COD)(Ph)(Cl) (416 mg, 1.0 mmol) in CH_2Cl_2 (3 mL) to give a pale yellow solution. In the air, the solvent was removed under reduced pressure and the remaining crystals were washed with petroleum ether (3 × 2 mL) and recrystallized from THF and petroleum ether at −25 °C to yield 492 mg (80%) of white crystals.

Anal. Calcd. for $C_{24}H_{33}ClP_2Pt$: C, 46.95; H, 5.42. Found: C, 47.10; H, 5.52. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 67.6 (d, J = 6, J_{Pt-P} = 1647), 55.1 (d, J = 6, J_{Pt-P} = 4001). ^{1}H NMR ($CDCl_3$): δ 7.74−7.72 (m, 1H), 7.62−7.51 (m, 5H), 7.15 (td, J = 8, 2, 2H), 6.93 (t, J = 8, 1H), 3.40−3.28 (m, 2H), 2.81−2.76 (m, 1H), 2.63−2.58 (m, 1H), 2.42−2.27 (m, 2H), 2.14−2.01 (m, 2H), 1.93−1.84 (m, 1H), 1.77−1.67 (m, 1H), 1.61−1.55 (m, 2H), 1.49 (dd, J = 18, 7, 3H, Me), 1.21 (dd, J = 18, 7, 3H, Me), 0.96−0.83 (m, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 163.0 (dd, J = 118, 8, quat, Pt−Ph), 144.1 (dd, J = 49, 38, quat Ar), 141.9 (dd, J = 36, 25, quat Ar), 137.6 (J = 17, Ph), 132.9 (d, J = 13, Ar), 132.3 (dd, J = 15, 4, Ar), 131.4−131.2 (m, Ar), 128.8 (Ph), 127.8 (d, J = 7, J = 45, Ph), 122.9 (Ph), 41.2 (d, J = 17), 40.9 (d, J = 5), 37.3, 36.7 (d, J = 4), 36.4 (J_{Pt-C} = 42), 35.0 (d, J = 4), 34.8 (d, J = 17), 33.2 (d, J = 38, J_{Pt-C} = 52), 17.3 (d, J = 9, Me), 16.1 (d, J = 4, J_{Pt-C} = 42, Me), 14.30 (d, J = 16, Me), 14.28 (d, J = 16, Me).

Pt((*R*,*R*)-Me-Duphos)(Ph)(I) (Pt-3a). Method 1. A solution of (*R*,*R*)-Me-Duphos (161.4 mg, 0.53 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a solution of Pt(COD)(Ph)(I) (267 mg, 0.53 mmol) in CH_2Cl_2 (3 mL) to give a transparent solution. In the air, the solvent was removed under reduced pressure and the remaining crystals were washed with petroleum ether (3 × 2 mL) and recrystallized from THF and petroleum ether at −25 °C to yield 329 mg (88%) of white crystals.

Method 2. To a stirred solution of Pt((*R*,*R*)-Me-Duphos)(Ph)(Cl) (255 mg, 0.41 mmol) in acetone (30 mL) was added NaI (240 mg, 1.6 mmol). A white precipitate immediately formed. The solvent was removed by rotary evaporation. The white solid was washed with water (3 × 50 mL), filtered under vacuum, and allowed to dry on the frit. The crystals were washed with petroleum ether (3 × 2 mL) and dried on the frit, yielding 260 mg (89%) of white crystals.

Anal. Calcd for $C_{24}H_{33}IP_2Pt\cdot0.45H_2O$: C, 40.40; H, 4.79. Found: C, 40.07; H, 4.51. The amount of water was quantified by integration of the ^{1}H NMR spectrum in C_6D_6. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 63.6 (d, J = 6, J_{Pt-P} = 1616), 56.8 (d, J = 6, J_{Pt-P} = 3754). ^{1}H NMR (C_6D_6): δ 7.98−7.86 (t, J = 12, J_{Pt-H} = 63, 2H), 7.33−7.28 (m, 2H), 7.25−7.23 (m, 1H), 7.13−7.10 (m, 1H), 7.08−7.04 (m, 2H), 6.99 (t, J = 8, 1H), 4.01−3.95 (m, 1H), 3.29−3.22 (m, 1H), 2.42−2.31 (m, 2H), 2.30−2.15 (m, 1H), 1.98−1.85 (m, 2H), 1.62−1.53 (m, 1H), 1.56 (dd, J = 18, 7, 3H, Me), 1.50−1.33 (m, 2H), 1.22 (dd, J = 18, 7, 3H, Me), 1.10−1.02 (m, 1H), 0.86−0.77 (m, 1H), 0.71−0.64 (m, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.9 (dd, J = 115, 7, quat, Pt−Ph), 143.6 (2 overlapping dd, J = 48, 40; J = 35, 27, quat Ar), 138.7 (broad, Ar), 133.1 (d, J = 13, Ar), 132.3 (dd, J = 15, 3, Ar), 131.5−131.1 (m, Ar), 127.6 (d, J = 7, J_{Pt-C} = 46, Ar), 122.7 (Ar), 42.1 (d, J = 8), 41.9, 37.8, 37.1 (d, J = 29), 36.6 (d, J = 4), 36.4, 35.1 (d, J = 6), 33.2 (d, J = 36), 17.5 (d, J = 9, Me), 15.6 (d, J = 5, Me), 14.7 (d, J = 1, Me), 14.3 (d, J = 1, Me).

Pt((*R*,*R*)-Me-Duphos)I_2. Method 1. A solution of (*R*,*R*)-Me-Duphos (153.2 mg, 0.5 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a solution of Pt(COD)I_2 (278.5 mg, 0.5 mmol) in CH_2Cl_2 (3 mL) to give a pale yellow solution. In the air, the solvent was removed under reduced pressure and the remaining crystals were washed with ethyl ether (3 × 2 mL) and recrystallized from CH_2Cl_2/ether at −25 °C to yield 325 mg (86%) of pale yellow crystals suitable for X-ray crystallography (Supporting Information).

Method 2. To a stirred slurry of Pt((*R*,*R*)-Me-Duphos)Cl_2 (286.3 mg, 0.5 mmol) in acetone (30 mL) was added NaI (300 mg, 2 mmol). The reaction mixture was refluxed for 5 h, giving a pale yellow slurry. The solvent was removed by rotary evaporation. The solid was washed with water (3 × 20 mL) and then dissolved in CH_2Cl_2 (30 mL). $MgSO_4$ was added, and the mixture was filtered. The solvent was removed by rotary evaporation. The crystals were washed with ethyl ether (3 × 2 mL) and recrystallized from CH_2Cl_2/ether at −25 °C to yield 300 mg (80%) of pale yellow crystals.

Anal. Calcd for $C_{18}H_{28}I_2P_2Pt$: C, 28.63; H, 3.74. Found: C, 28.62; H, 3.68. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 71.3 (J_{Pt-P} = 3273). ^{1}H NMR ($CDCl_3$): δ 7.77−7.65 (m, 4H, Ar), 4.12−3.94 (m, 2H), 2.78−2.16 (m, 8H), 1.94−1.79 (m, 2H), 1.45 (dd, J = 19, 7, 6H, Me), 0.89 (dd, J = 17, 7, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.9 (dd, J = 47, 29, quat Ar), 132.5 (m, Ar), 132.1 (m, Ar), 42.4 (d, J = 38, J_{Pt-C} = 37), 39.4 (d, J = 38, J_{Pt-C} = 38), 37.1 (J_{Pt-C} = 35), 36.1 (d, J = 3), 17.2 (m, J_{Pt-C} = 34, Me), 14.3 (Me).

Acknowledgment. We thank the National Science Foundation for support and Solvias and Eastman for gifts of chiral phosphines.

Supporting Information Available: Text giving additional information on synthetic procedures and tables giving details of the X-ray crystallographic structure determinations; crystal data are also given as CIF files. This information is available free of charge via the Internet at http://acs.org.

OM050115H