Pt(Me-Duphos)-Catalyzed Asymmetric Hydrophosphination of Activated Olefins: Enantioselective Synthesis of Chiral Phosphines

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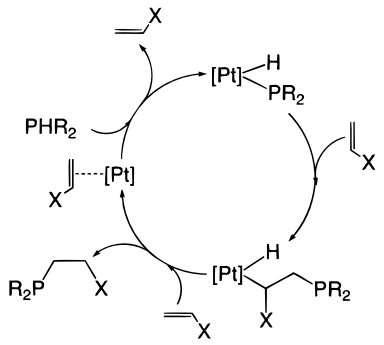
Summary: *Platinum-catalyzed asymmetric hydrophosphination of activated olefins using the catalyst precursor Pt(R,R-Me-Duphos)(trans-stilbene) (**1**) gives chiral phosphines with control of stereochemistry at phosphorus or carbon centers. Stoichiometric reactions of **1** allow observation of P−H oxidative addition, diastereoselective olefin insertion, and reductive elimination steps, which make up the proposed catalytic cycle.*

Chiral phosphines, valuable ligands for metal-catalyzed asymmetric reactions,[1] are usually prepared either by resolution or by using a stoichiometric amount of a chiral auxiliary.[2] Surprisingly little work has been reported on metal-catalyzed asymmetric syntheses.[3] We report here that Pt-catalyzed asymmetric hydrophosphination of activated olefins[4] can be used to prepare chiral phosphines with control of stereochemistry at phosphorus or carbon. Although the enantiomeric excesses (ee's) available thus far are low, mechanistic understanding may allow further development of these new reactions.

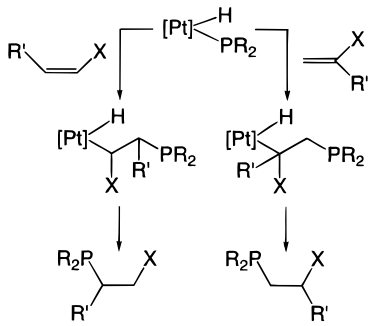
Scheme 1 shows a mechanism for Pt-catalyzed hydrophosphination, proposed on the basis of our previous studies.[5] After P−H oxidative addition, P−C bond formation occurs by selective insertion of the olefin into the Pt−P bond. Reductive elimination forms the product and regenerates Pt(0). Since the insertion step can be diastereoselective,[5,6] use of a chiral Pt catalyst could lead to enantio-enriched product. For example, a disubstituted olefin could give a phosphine (Scheme 2) with controlled stereochemistry at either of the alkene car-

Scheme 1. Proposed Mechanism for Pt-Catalyzed Hydrophosphination[a]



[a] [Pt] = Pt(diphosphine), X = CN, CO_2R, or other electron-withdrawing group.

Scheme 2. Proposed Mechanism for Pt-Catalyzed Asymmetric Hydrophosphination of Disubstituted Alkenes[a]



[a] [Pt] = Pt(chiral diphosphine), X = CN, CO_2R, or other electron-withdrawing group.

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(1) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis: the Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; Wiley: New York, 1992. (b) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley-Interscience: New York, 1994.

(2) (a) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375−1411. (b) Kagan, H. B.; Sasaki, M. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley and Sons: Chichester, England, 1990; Vol. 1; pp 51−102.

(3) An important recent exception is Burk's synthesis of Duphos ligands, which relies on Ru-Binap-catalyzed asymmetric hydrogenation of β-keto esters (Burk, M. J.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10125−10138).

(4) Pringle and co-workers have shown that Pt-catalyzed hydrophosphination can be used to prepare functionalized phosphines. (a) Costa, E.; Pringle, P. G.; Worboys, K. *Chem. Commun.* **1998**, 49−50. (b) Costa, E.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* **1997**, 4277−4282. (c) Pringle, P. G.; Brewin, D.; Smith, M. B.; Worboys, K. In *Aqueous Organometallic Chemistry and Catalysis*; Horvath, I. T., Joo, F., Eds.; Kluwer: Dordrecht, 1995; Vol. 5; pp 111−122. (d) Hoye, P. A. T.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* **1993**, *74*, 269−274. (e) Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1701−1702. (f) Harrison, K. N.; Hoye, P. A. T.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1096−1097. See also: (g) Nagel, U.; Rieger, B.; Bublewitz, A. *J. Organomet. Chem.* **1989**, *370*, 223−239. (h) Giardello, M. A.; King, W. A.; Nolan, S. P.; Porchia, M.; Sishta, C.; Marks, T. J. In *Energetics of Organometallic Species*; Martinho Simoes, J. A., Ed.; Kluwer: Dordrecht, 1992; pp 35−51.

(5) (a) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039−5040. (b) Wicht, D. K.; Kourkine, I. V.; Kovacik, I.; Glueck, D. S.; Concolino, T. E.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5381−5394.

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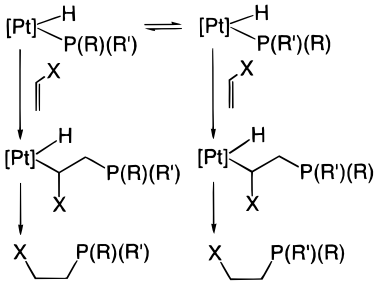
Scheme 3. Proposed Mechanism for Pt-Catalyzed Asymmetric Hydrophosphination Using Racemic Secondary Phosphines[a]



[a] [Pt] = Pt(chiral diphosphine), X = CN, CO_2R, or other electron-withdrawing group.

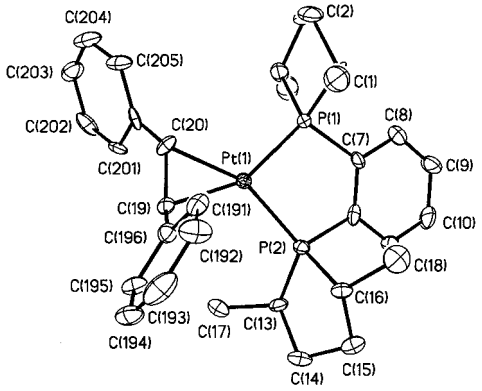
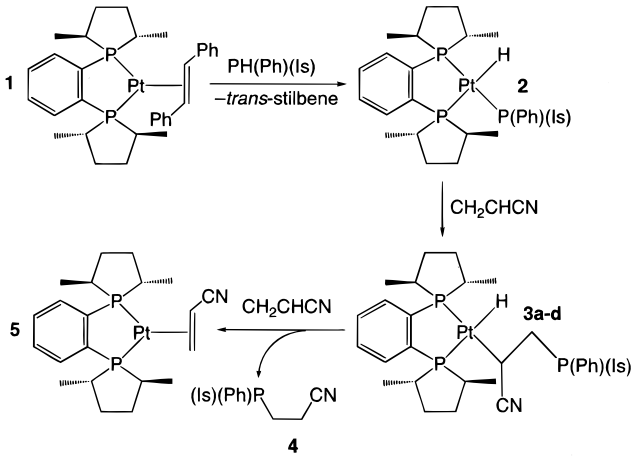


Figure 1. ORTEP diagram of Pt(Me-Duphos)(*trans*-stilbene) (**1**) with 30% thermal ellipsoids, and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt−P(1) = 2.235(4), Pt−P(2) = 2.240(3), Pt−C(19) = 2.102(12), Pt−C(20) = 2.113(12), C(19)−C(20) = 1.436(18), P(1)−Pt−P(2) = 88.49(13), C(19)−Pt−C(20) = 39.8(5), P(1)−Pt−C(19) = 155.3(4), P(1)−Pt−C(20) = 115.5(4), P(2)−Pt−C(19) = 116.2(4), P(2)−Pt−C(20) = 155.9(4), (P−Pt−P) − (C−Pt−C) = 3.9.

bons. In a more complicated case (Scheme 3), racemic secondary phosphines PH(R)(R′) would give a mixture of diastereomeric phosphido hydride complexes which are expected to interconvert readily by phosphorus inversion.[6] Depending on the relative rates of P inversion and olefin insertion, this scheme could lead to P-chiral phosphines with controlled stereochemistry at phosphorus.

Successful asymmetric hydrophosphination requires a tightly binding chiral ligand which will not be displaced by the substrates or products.[5] In comparison to related Pt(0) stilbene complexes of chiral diphosphines, Pt(Me-Duphos)(*trans*-stilbene) (**1**, Figure 1) has shorter Pt−P bond distances, consistent with tight binding, and the rigid structure of Me-Duphos should help prevent its displacement by monodentate phosphines.[7] Treatment of **1** with the secondary phosphine PH(Ph)(Is) (Is = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$)[8] gave the phosphido hydride Pt(Me-Duphos)[P(Ph)(Is)](H) (**2**, Scheme 4).[9] As expected from previous studies of diastereomeric phosphido complexes Pt(chiral diphosphine)(Me)[P(R)(R′)], the NMR spectra of **2** show only a single set of resonances even at low

Scheme 4



temperature, consistent with rapid P inversion on the NMR time scale.[6] A crystal of **2** whose structure was solved by X-ray crystallography was found to be a single diastereomer (Figure 2).[10]

Treatment of **2** with acrylonitrile, observed by NMR at −20 °C, led to diastereoselective insertion into the Pt−P bond and formation of four alkyl hydrides Pt(Me-Duphos)[CH(CN)CH$_2$P(Ph)(Is)](H) (**3a**−**d**, Scheme 4, see Table 1 for selected NMR data) whose relative abundance in solution depended on temperature and reaction time. For example, after 30 min at −20 °C, the ratio of these isomers was 1:7:9:20.[11] On warming to room temperature, complexes **3a**−**d** formed the P-chiral tertiary phosphine PPh(Is)(CH$_2$CH$_2$CN) (**4**, 63−71% ee)[12] and the acrylonitrile complex Pt(Me-Duphos)(CH$_2$-CHCN) (**5**);[13] some PH(Ph)(Is) was also produced.[14]

(6) (a) Wicht, D. K.; Glueck, D. S.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5130−5140. (b) Wicht, D. K.; Kovacik, I.; Glueck, D. S.; Liable-Sands, L. M.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5141−5151.

(7) (a) Me-Duphos = (*R*,*R*)-Me-Duphos as shown in Figures 1 and 2 and Scheme 4; see: Wicht, D. K.; Zhuravel, M. A.; Gregush, R. V.; Glueck, D. S.; Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1998**, *17*, 1412−1419, for this and other stilbene complexes. (b) Crystal data for **1**: $P2_1$, orange block, a = 10.4240(4) Å, b = 13.6432(5) Å, c = 11.3386(4) Å, β = 114.682(2)°, V = 1465.22(9) Å^3, Z = 2, μ(Mo Kα) = 49.16 cm^{-1}, temp = 173(2) K, R(F) = 3.93%, $R(wF^2)$ = 9.28%. (c) Pt−P distances (Å) for other chiral Pt(diphos)(*trans*-stilbene) complexes: for Tol-Binap, 2.2806(9), 2.2840(8); for Chiraphos, 2.272(2), 2.277(2), 2.271(2), 2.274(2); for Diop, 2.284(2), 2.290(2).

(8) Brauer, D. J.; Bitterer, F.; Dorrenbach, F.; Hessler, G.; Stelzer, O.; Kruger, C.; Lutz, F. *Z. Naturforsch. B* **1996**, *51*, 1183−1196.

(9) **Pt(*R*,*R*-Me-Duphos)[P(Ph)(Is)](H) (2)**. To Pt(R,R-Me-Duphos)(*trans*-stilbene) (**1**, 95 mg, 0.14 mmol) in THF (5 mL) was added PH(Ph)(Is) (50 mg, 0.15 mmol) in THF (5 mL). The reaction mixture immediately turned bright orange and was allowed to stir at room temperature for 10 min. The solvent was removed under vacuum, and the orange residue was dissolved in petroleum ether (10 mL) and filtered. The orange solution was concentrated slightly under vacuum and cooled to −25 °C to give 106 mg (94%) of orange-yellow solid in three crops. Recrystallization from petroleum ether at room temperature gave crystals suitable for X-ray diffraction. This material was spectroscopically pure, but we were unable to get satisfactory elemental analyses for it. ^{1}H NMR (C_6D_6): δ 7.84−7.80 (m, 2H, Ar), 7.17−6.70 (m, 9H, Ar), 4.78−4.67 (m, 2H, *o*-C*H*Me$_2$), 2.75 (septet, $^3J_{HH}$ = 7, 1H, *p*-C*H*Me$_2$), 2.70−2.60 (m, 1H, CH), 2.13−2.02 (m, 2H, CH), 1.94−1.85 (m, 1H, CH), 1.67−1.54 (m, 4H, CH$_2$), 1.42−1.28 (m, 2H, CH$_2$), 1.29 (d, $^3J_{HH}$ = 7, 6H, CH*Me*$_2$), 1.23 (d, $^3J_{HH}$ = 7, 6H, CH*Me*$_2$), 1.15 (d, $^3J_{HH}$ = 7, CH*Me*$_2$), 1.13 (dd, $^3J_{HH}$ = 7, $^3J_{PH}$ = 14, 3H, Me), 1.07 (dd, $^3J_{HH}$ = 7, $^3J_{PH}$ = 14, 3H, Me), 1.10−0.95 (m, 2H, CH$_2$), 0.45 (dd, $^3J_{HH}$ = 7, $^3J_{PH}$ = 14, 3H, Me), 0.35 (dd, $^3J_{HH}$ = 7, $^3J_{PH}$ = 14, 3H, Me), −1.58 (ddd, $^2J_{PH}$ = 178, 11, 10, $^1J_{Pt-H}$ = 1048, 1H, Pt−H). ^{31}P{^{1}H} NMR (C_6D_6): δ 75.9 (dd, $^2J_{PP}$ = 154, 10, $^1J_{Pt-P}$ = 1852), 68.6 (d, $^2J_{PP}$ = 10, $^1J_{Pt-P}$ = 1903), −28.0 (d, $^2J_{PP}$ = 154, $^1J_{Pt-P}$ = 1153). IR: 2952, 2868, 1991 (Pt−H), 1447, 1381, 1243, 1160, 1118, 1052, 1016, 753. Anal. Calcd for $C_{39}H_{57}P_3Pt$: C, 57.54; H, 7.07. Found: C, 65.62; H, 7.75; an additional sample also gave poor results: C, 51.65; H, 7.00.

(10) Crystal data for **2**: $P2_12_12_1$, orange block, a = 14.071(14) (Å), b = 14.841(3) Å, c = 19.0769(4) Å, V = 3775(3) Å^3, Z = 4, μ(Mo Kα) = 38.69 cm^{-1}, temp = 238(2) K, $R(F)$ = 4.24%, $R(wF^2)$ = 12.05%.

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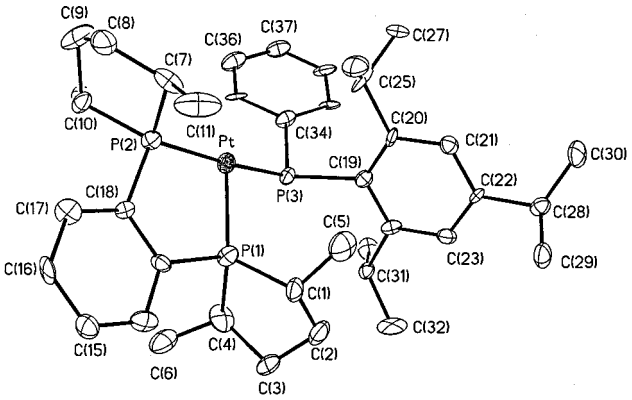


Figure 2. ORTEP diagram of Pt(Me-Duphos)[P(Ph)(Is)]-(H) (**2**) with 30% thermal ellipsoids, and hydrogen atoms omitted for clarity. The Pt hydride could not be located. Selected bond lengths (Å) and angles (deg): Pt−P(1) = 2.298(5), Pt−P(2) = 2.226(4), Pt−P(3) = 2.335(5), P(3)−C(34) = 1.853(9), P(3)−C(19) = 1.899(9), P(2)−Pt−P(1) = 86.83(18), P(1)−Pt−P(3) = 100.89(16), C(34)−P(3)−Pt = 112.5(4), C(19)−P(3)−Pt = 111.9(4), C(34)−P(3)−C(19) = 102.2(5).

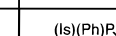
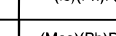
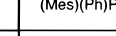
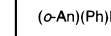
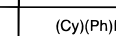
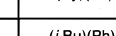
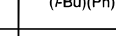
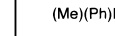
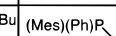
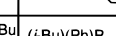
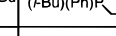
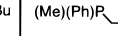
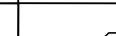
Table 1. Selected NMR Data for Pt(Me-Duphos)[CH(CN)CH$_2$P(Ph)(Is)](H) (3a−d) (toluene-d_8, −20 °C)[a]

complex	δ (^{31}P)[b]	$^4J_{PP}$	$^3J_{Pt-P}$	δ (^{1}H)[c]	$^2J_{PH}$	$^1J_{Pt-H}$
3a	−20.8	20, 4	257	−0.60	195, 17	1153
3b	−22.0	8	169	−0.33	195, 16	1150
3c	−23.4	21	259	−0.53	200, 16	1172
3d	−25.7	24	255	−0.13	199, 17	1172

[a] ^{31}P NMR chemical shift reference 85% H_3PO_4, coupling constants in Hz. [b] CH(CN)CH$_2$*P*(Ph)(Is). [c] Pt−*H*.

These steps comprise a catalytic cycle, if **5** can undergo P−H oxidative addition. Indeed, complex **1** is a catalyst precursor for addition of PH(Ph)(Is) to acrylonitrile at room temperature. However, the catalytic reaction is very slow, and at this temperature, the ee of phosphine **4** produced is lower than in the stoichiometric system (Table 2, entry 1). Related catalytic reactions with less bulky secondary phosphines are faster, but proceed with even lower ee's and with the formation of several byproducts (Table 2, entries 2−6).[15] In contrast, the very bulky phosphines PH(Me)(Mes*)[16] (Mes* = 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$) and PH(Ph)(Mes-F$_9$) (Mes-F$_9$ = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$)[6a] did not form hydrophosphination products under these conditions.

Table 2. Pt(Me-Duphos)-Catalyzed Asymmetric Hydrophosphination[a]

entry	phosphine[b]	alkene	product	TOF[c]	selectivity[d]	ee[e]
1	PH(Ph)(Is)			<1 d^{-1}	>90%	17%
2	PH(Ph)(Mes)			1 d^{-1}	80%	13%
3	PH(Ph)(*o*-An)			7 d^{-1}	80%	5%
4	PH(Ph)(Cy)			10 d^{-1}	60%	f
5	PH(Ph)(*i*-Bu)			10 d^{-1}	60%	5%
6	PH(Ph)(Me)			10 d^{-1}	70%	5%
7	PH(Ph)(Mes)			5 d^{-1}	100%	0%
8	PH(Ph)(*i*-Bu)			1 min^{-1}	95%	20%
9	PH(Ph)(Me)			1 min^{-1}	95%	22%
10	PHPh$_2$			2.5 h^{-1}	95%	27%
11	PHEt$_2$			1 min^{-1}	80%	0%
12	PHPh$_2$			14 d^{-1}	95%	4%
13	PHEt$_2$			14 h^{-1}	100%	18%

[a] General procedure for catalytic hydrophosphination: Complex **1** (8.2 mg, 0.012 mmol) was used as the catalyst precursor (5 mol %), and the amounts of phosphine and alkene varied accordingly. An NMR tube fitted with a rubber septum was charged with a solution of **1** and the phosphine (0.24 mmol) in THF (0.5 mL). The olefin (0.25 mmol) was added via microliter syringe, and the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy at room temperature. (In some cases when acrylonitrile was used, the formation of byproducts required addition of extra acrylonitrile for complete conversion of the starting phosphine.) After completion of the reaction, the mixture was treated with an excess (80 mg, 0.14 mmol) of (*R*)-{Pd[Me$_2$NCH(Me)C$_6$H$_4$](*μ*-Cl)}$_2$ to determine the ee of the generated tertiary phosphine (see ref 12 in the text). [b] Abbreviations: Is = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$, Mes = 2,4,6-(Me)$_3$C$_6$H$_2$, *o*-An = *o*-MeOC$_6$H$_4$, Cy = cyclo-C$_6$H$_{11}$. [c] TOF = turnover frequency = equiv of secondary phosphine converted per equiv of catalyst per unit time (from ^{31}P{^{1}H} NMR integration). For some substrates, reactions were also carried out with 2.5 or 1.25 mol % catalyst (Supporting Information). Hydrophosphination also occurs (more slowly, or, in some cases, not at all) in the absence of catalyst (Supporting Information). [d] Selectivity = percentage of the illustrated phosphine product in the mixture of P-containing organic products (from ^{31}P{^{1}H} NMR integration). [e] ee of the product phosphine, from ^{31}P{^{1}H} NMR integration of the signals of the chiral Pd−L complexes (see ref 12). The error in ee values depends on the table entry and is estimated to range from ca. 5 to 10%; thus only entries 1, 2, 8, 9, 10, and 13 reflect a significant ee. [f] Not determined due to overlap of ^{31}P{^{1}H} NMR signals for the two Pd−L diastereomers.

The results of the stoichiometric reactions suggested that the slow step in catalysis was P−H oxidative addition, since acrylonitrile binds Pt more tightly than does *trans*-stilbene. The formation of PH(Ph)(Is) from **2** also suggests that this step can be reversible. To promote oxidative addition, we used olefins bulkier than acrylonitrile, which resulted in faster rates, higher selectivity, and somewhat higher, but still modest, enantioselectivity at phosphorus (Table 2, entries 7−9). Achiral phosphines and disubstituted olefins (entries

(11) **Reaction of Pt(Me-Duphos)[P(Ph)(Is)](H) (2) with Acrylonitrile. Formation of Pt(Me-Duphos)[CH(CN)CH$_2$PPhIs](H) (3a−d)**. A solution of **2** (30 mg, 0.037 mmol) in toluene-d_8 (0.5 mL) was transferred to an NMR tube, which was fitted with a rubber septum. The solution was cooled to −78 °C in a dry ice/acetone bath, and acrylonitrile (10 μL, 0.15 mmol) was injected by microsyringe. The tube was immediately placed in the probe of the 500 MHz NMR spectrometer, which had been precooled to −20 °C, and the reaction was monitored by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. The composition of the mixture depended on temperature and reaction time. In addition to starting material **2**, four diastereomers (**3a−d**) of the product, phosphine **4**, PH(Ph)(Is), acrylonitrile complex **5**, and a minor, unidentified byproduct (^{31}P{^{1}H} NMR: δ −31.6 at room temperature) were observed. Their relative amounts were quantified by integration of the ^{31}P NMR signals due to the PPhIs groups and by integration of the ^{1}H NMR hydride signals.

(12) The ee of **4** (which depended on reaction temperature and time) and of the other chiral phosphines (see below) was determined by integration of ^{31}P{^{1}H} NMR spectra after complexation to the chiral Pd(II) dimer derived from nonracemic α-methylbenzylamine, [Pd(Me$_2$NCH(Me)C$_6$H$_4$)(*μ*-Cl)]$_2$, to give monomeric phosphine complexes [Pd(Me$_2$NCH(Me)C$_6$H$_4$)(Cl)(L)]. See: (a) Otsuka, S.; Nakamura, A.; Kano, T.; Tani, K. *J. Am. Chem. Soc.* **1971**, *93*, 4301−4303. (b) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254−6260. (c) For a review, see: Wild, S. B. *Coord. Chem. Rev.* **1997**, *166*, 291−311.

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10−13) gave tertiary phosphines with similarly poor stereocontrol at carbon.

The data of Table 2 show that smaller and more nucleophilic phosphines give faster reactions, but usually give more byproducts. More highly substituted olefins give reduced rates, and 1-cyanocyclopentene and 1-cyanocyclohexene did not react with $PHPh_2$ under these conditions. The relationship between the nature and substitution pattern of the olefin, the bulk of the P substituents, and the enantioselectivity is not yet clear. However, we anticipate that phosphines PH(R)(R′) having R and R′ groups with large differences in size will lead to increased enantioselectivity at P, while variations in the acrylate and acrylonitrile substrates may enable better control of stereochemistry at C. These ideas and additional mechanistic information, including studies of possible catalyst decomposition, should be useful in further development of Pt-catalyzed asymmetric hydrophosphination and analogous reactions.

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Supporting Information Available: Experimental details and characterization data for all new compounds, and details of the crystal structure determinations for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) **Pt(*R*,*R*-Me-Duphos)(CH_2CHCN) (5).** A white suspension of 300 mg (0.52 mmol) of Pt(*R*,*R*-Me-Duphos)Cl_2 in 10 mL of THF was treated with a solution of 300 mg (2.34 mmol) of $NaBH(OMe)_3$ in 5 mL of THF. The resulting orange suspension was stirred at room temperature for 3 h, then treated with acrylonitrile (700 μL, 10.6 mmol), which caused a color change to pale yellow and evolution of gas. The suspension was stirred for 2 h at room temperature. Removal of the solvent in vacuo gave a pale yellow solid, which was extracted with ca. 20 mL of toluene. The toluene extract was filtered through Celite, and the filtrate was passed down a column of silica gel (ca. 0.5 cm diameter, 1 cm height). More toluene (10 mL) was used to elute the product from the column. Evaporation of toluene from the resulting solution gave a viscous residue, which became sticky after addition of petroleum ether. The solvent was removed under vacuum, and the residue was redissolved in ether. Removal of this solvent under vacuum gave a white powder (as a mixture of diastereomers **a** and **b** in ratio 1.3:1), which was then dried in vacuo (yield: 180 mg (62%)). For elemental analysis, the solid was recrystallized from petroleum ether. Anal. Calcd for $C_{21}H_{31}NP_2Pt$: C, 45.48; H, 5.65; N, 2.53. Found: C, 45.75; H, 5.61; N, 2.45. $^{31}P\{^1H\}$ NMR (C_6D_6, **a**): δ 76.8 (d, $^2J_{PP} = 40$, $^1J_{Pt-P} = 3390$), 75.6 (d, $^2J_{PP} = 40$, $^1J_{Pt-P} = 2851$).$^{31}P\{^1H\}$ NMR (C_6D_6, **b**): δ 76.7 (d, $^2J_{PP} = 40$, $^1J_{Pt-P} = 3342$), 72.9 (d, $^2J_{PP} = 40$, $^1J_{Pt-P} = 2889$). For more spectroscopic data, see the Supporting Information.

(14) The relative amounts of these products depended on temperature and reaction time; phosphine **4** was the major organic product, and more PH(Ph)(Is) was formed at higher temperature. See the Supporting Information for additional details.

(15) Some of the tertiary phosphine products in Table 2 were reported previously. For entry 2, see ref 5b; for entries 4−6, see: Wolfsberger, W. *Chem. Ztg.* **1990**, *114*, 353−354. For entry 10, see: Habib, M.; Trujillo, H.; Alexander, C. A.; Storhoff, B. N. *Inorg. Chem.* **1985**, *24*, 2344−2349. For the other phosphines, see the Supporting Information.

(16) Yoshifuji, M.; Shibayama, K.; Inamoto, N. *Chem. Lett.* **1984**, 115−118.

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