Influence of the Reaction Temperature on the Enantioselection of Styrene Hydroformylation Catalyzed by $PtCl(SnCl_3)$ Complexes of *p*-Aryl-Substituted Chiral Ligands

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The asymmetric hydroformylation of styrene catalyzed by $PtCl(SnCl_3)$ complexes of (-)-(2*S*,4*S*)-2,4-bis[bis(*p*-(dimethylamino)phenyl)phosphino]pentane (1), (-)(2*S*,3*S*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis[bis(*p*-(dimethylamino)phenyl)phosphino]butane (2), and (-)-(2*S*,3*S*)-2,3-bis[bis(*p*-(dimethylamino)phenyl)phosphino]butane (3) is strongly temperature dependent. With 1 and 2 as the catalysts a reversal in the prevailing product configuration occurs at relatively low temperatures (53 and 72 °C, respectively). 1 provides good enantioselectivities in both directions, 56.7% ee in the *R* product at 100 °C and 60.6% ee in the *S* product at 30 °C. The variation of enantioselectivity with temperature is consistent with competing reaction pathways via diastereomeric intermediates of a single chelate conformation.

At the present time commercial hydroformylation processes use either rhodium or cobalt complexes as catalysts.[1] Ruthenium and platinum complexes are also active for hydroformylation, but their commercial use is precluded for reasons of cost, selectivity, and activity.[1] For asymmetric hydroformylation, however, platinum complexes hold promise for future applications since modified platinum–tin catalysts have provided the highest degree of enantioselection to date for asymmetric hydroformylation.[2-4]

Although the major steps in the proposed mechanism[5] for platinum–tin-catalyzed hydroformylation are generally accepted[6,7] and recent studies with $Pt(PPh_3)_2Cl_2{\cdot}SnCl_2$ have revealed many important details,[8-11] much remains to be discovered. For asymmetric hydroformylation it has been suggested that initial coordination of the olefin controls the ultimate enantioselectivity.[12] It has been shown that the alkyl groups in Pt–alkyl complexes generated from prochiral olefins are chiral,[6,13] but it is not certain if the optical purity of the product is determined at this point. The observed enantioselectivity in platinum asymmetric hydroformylation may be due to kinetic control between competing diastereomeric pathways as observed in asymmetric hydrogenation.[14]

The hydroformylation of styrene with $PtCl(SnCl_3)$-[(*S*,*S*)-BDPP] (BDPP = 2,4-bis(diphenylphosphino)-pentane) leads to the enantioselective formation of 2-phenylpropanal.[3,15] The optical yields in this case are strongly influenced by the reaction temperature. At 40 °C the *S* product enantiomer predominates in up to 75% ee, while at 120 °C the *R* product dominates with up to 19% ee obtained. The prevalance of the opposite product enantiomer at higher temperatures was suggested to be due either to a change in the Pt–BDPP chelate ring conformation or to kinetic effects.[15] A change in ring conformation of δ-skew to the less stable λ-skew could, in principle, lead to the predominance of the opposite product configuration.[16]

A similar reversal of product configuration as a function of reaction temperature was reported earlier for the hydroformylation of 1-butene with $PtCl(SnCl_3)$DIOP (DIOP = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane)[13] and more recently for the hydroformylation of styrene with $PtCl(SnCl_3)$BINAP (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl).[17] In the former case, the isomerization of the α-olefin and decomposition of the catalyst and, in the latter case, hindered rotation of the axial phenyl rings was considered to be responsible for the switch in product enantiomer. A slight but definite reversal has also been observed by the use of a bis(dibenzophosphole) ligand in the rhodium-catalyzed hydroformylation of styrene.[18] Most asymmetric hydroformylation catalysts do not show a switch in product selectivity with temperature; the typical behavior is for

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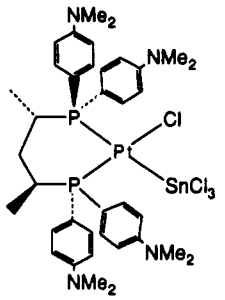
Chart I

$PtCl(SnCl_3)[(S,S)\text{-BDPP-}(pNMe_2)_4]$

1



$PtCl(SnCl_3)[(S,S)\text{-DIOP-}(pNMe_2)_4]$

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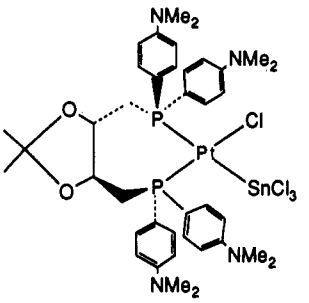

$PtCl(SnCl_3)[(S,S)\text{-Chiraphos-}(pNMe_2)_4]$

3

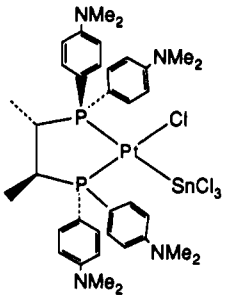

Table I. Asymmetric Hydroformylation of Styrene by $PtCl(SnCl_3)[(S,S)\text{-BDPP-}(pNMe_2)_4]$ (1)[a]

reacn temp (°C)	$1/T$ ($1/K \times 10^3$)	reacn time (h)	conversn to aldehydes (%)	regioselectivity (n/b)[b]	conversn to ethylbenzene (%)	enantioselectivity (% ee)	ln ([*R*]/[*S*])
30	3.30	550	17.1	1.52	0	60.6 (*S*)	−1.4
40	3.19	120	45.2	1.65	0	39.1 (*S*)	−0.83
50	3.09	48	18.2	1.71	0	7.3 (*S*)	−0.15
60	3.00	48	34.0	1.80	0	9.4 (*R*)	0.19
70	2.91	40	67.2	2.17	0.8	17.2 (*R*)	0.35
80	2.83	14	71.3	3.00	1.1	26.4 (*R*)	0.54
100	2.68	3	32.1	3.32	4.0	41.4 (*R*)	0.88
100[c]	2.68	0.3	23.6	3.60	2.1	56.7 (*R*)	1.3
120	2.54	3	57.2	3.62	8.8	22.1 (*R*)	0.45
140	2.42	2	53.1	3.80	12.7	12.7 (*R*)	0.26

[a] Reaction conditions: subst/Pt = 1000/1, Sn/Pt = 3/1, 0.015 mmol of Pt in 10 mL of solvent, 70 bar of H_2/CO (1/1). [b] Ratio of linear to branched products. [c] subst/Pt = 100/1.

enantioselectivities to improve at low temperature.[2,4,15,19-21] For example, the enantiomeric excess of (*S*)-hydratropaldehyde increases from 68.1% to 86.3% upon decreasing the reaction temperature from 80 to 40 °C in the asymmetric hydroformylation of styrene with $PtCl(SnCl_3)$-[(*R*,*R*)-Bco-dbp] (Bco-dbp = [bicyclo[2.2.2]octane-3,4-diylbis(methylene)]bis(5*H*-benzo[*b*]phosphindole)).[4]

The synthesis and use of platinum complexes of tetra-*p*-amino-functionalized BDPP, DIOP, and Chiraphos as shown in Chart I was rationalized by the success of the analogous nonfunctionalized ligands in homogeneous enantioselective hydroformylation[3,11,21] and by the ease of catalyst handling provided by the amino groups in Rh complexes for asymmetric hydrogenation.[22,23]

All of the new complexes 1–3 (Chart I) show a strong temperature dependence on the optical yields for the hydroformylation of styrene. Furthermore, compounds 1 and 2 give a reversal in product configuration at relatively low temperatures (53 and 72 °C, respectively). The results with 1 are particularly interesting, since the ligand (*S*,*S*)-BDPP-$(pNMe_2)_4$ appears, by NMR spectroscopy, to be conformationally stable.[24]

Results

Hydroformylation with 1. Data for the hydroformylation of styrene with 1 + excess $SnCl_2$ as the catalyst are summarized in Table I. As expected, the optical yield of 2-phenylpropanal is strongly temperature dependent. However, the change in configuration of the dominant product enantiomer occurs about 40 °C lower in temperature than with the nonfunctionalized analog $PtCl(SnCl_3)$-BDPP (Figure 1).[15] The enantioselectivity for the opposite configuration continues to increase with increasing temperature. An ee of 41.4% for the product of *R* configuration is observed at 100 °C with 1 + excess $SnCl_2$ as the catalyst at a substrate/catalyst ratio of 1000/1. At temperatures above 100 °C the enantioselectivity drops, as observed with the nonsubstituted system.[15] The performance of 1 is not significantly improved by the addition of excess $SnCl_2$; essentially the same enantioselectivities were obtained with 1 + $SnCl_2$ as with 1 alone. Both the necessary reaction times and the selectivity to 2-phenylpropanal (branched product) decrease with increasing temperature. The observed selectivity to the branched product is slightly lower with 1 compared to that with the

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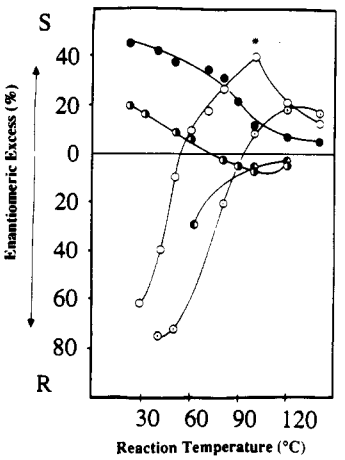

Figure 1. Platinum hydroformylation enantioselectivity as a function of reaction temperature: (○) 1; (◑) 2; (●) 3; (◎) $PtCl(SnCl_3)[(S,S)$-BDPP];[15] (◐) $PtCl(SnCl_3)[(R,R)$-DIOP];[3,21] (*) $PtCl(SnCl_3)[(S,S)$-Chiraphos].[21]

unsubstituted analog.[15] Unlike the nonsubstituted analog, no hydrogenation activity is observed with 1 at reaction temperatures less than 70 °C.

The conversion to styrene was intentionally kep low in order to minimize the racemization of the product.[2,13] The racemization of 2-phenylpropanal increases with increasing temperature; for example, a sample of aldehyde with an optical purity of 52% in hydratropaldehyde was completely racemized in 24 h at 120 °C in the presence of 0.001 equiv of 1. Further evidence for increasing racemization rates with increasing temperature is the fact that the optical yields are significantly improved when the overall reaction time is decreased. Thus, an ee of 56.7% (*R*) is observed when the reaction time is reduced to 20 min at 100 °C (Table I).

Racemization may be avoided in asymmetric hydroformylation by the in situ trapping of products.[25] The use of triethyl orthoformate as solvent and reagent is known to have such an effect, as the formed acetals are not susceptible to racemization.[2,26] It has been reported, for example, that this technique yields optically pure aldehydes from the asymmetric hydroformylation of styrene derivatives with $PtCl(SnCl_3)[(S,S)$-Bppm][2] (Bppm = 1-(*tert*-butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine) as the catalyst. We find that with triethyl orthoformate as solvent the hydroformylation of styrene with 1 is extremely slow. The results with triethyl orthoformate, as well as with several other solvents of different polarity, are summarized in Table II. Consistent with the literature,[12] the best results are achieved in solvents of medium polarity such as toluene and chlorobenzene. The enantioselectivity is the lowest in triethyl orthoformate, and the low enantioselectivity obtained is not due to a strong temperature dependence. Furthermore, the conversion of aldehydes to acetals is not quantitative in triethyl orthoformate with 1. Although the latter problem could be eliminated by adding 10% EtOH in triethyl orthoformate, the presence of EtOH lowered the enantioselectivity further.

Several attempts were made to characterize the possible intermediates present in catalytically active triethyl orthoformate or toluene solutions of 1 by ^{31}P NMR spectroscopy. However, aliquots taken under 1 atm of CO from the operating catalysts showed only $PtCl_2[BDPP-(pNMe_2)_4]$ in both solvent systems.

Table II. Influence of Solvents on the Asymmetric Hydroformylation of Styrene Catalyzed by 1[a]

solvent	reacn time (h)	conversn to aldehydes (%)	regioselectivity (n/b)[b]	conversn to ethylbenzene (%)	enantioselectivity (% ee)	turnover frequency[c] (h^{-1})
hexane	20	31.7	3.4	4.6	23.6 (*S*)	23.2
benzene	5	43.3	4.1	2.6	27.1 (*S*)	91.2
toluene	3	28.6	3.2	4.0	37.4 (*S*)	108.6
C_6H_5Cl	6	22.5	3.7	3.5	36.4 (*S*)	43.3
MEK	28	7.9	3.4	0.5	27.2 (*S*)	3.0
THF	22	22.7	4.3	5.9	32.9 (*S*)	13
TOF[d]	21	37.6	3.3	0	2.9 (*S*)	17.9
TOF[d]	60	7.8	1.9	0	4.0 (*R*)	1.6

[a] Reaction conditions: subst/Pt = 1000/1, Sn/Pt = 3/1, 0.015 mmol of Pt in 10 mL of solvent, 70 bar of H_2/CO (1/1). [b] Linear/branched product. [c] (mol of product/mol of catalyst)/h. [d] TOF = triethyl orthoformate.

Hydroformylation with 2 and 3. The results obtained in the hydroformylation of styrene with 2 and 3 are summarized in Tables III and IV, respectively. As seen in Table III and figure 1, a reversal in product configuration occurs with 2, as a function of temperature. The enantioselectivities with the nonsubstituted analogue $PtCl(SnCl_3)[(R,R)$-DIOP] are not reversed, although the enantioselectivity approaches zero with increasing temperature (Figure 1).[3,21] Similarly, the enantioselectivity is strongly influenced, but not reversed, with 3 as the catalyst. The regioselectivity to the branched product is somewhat higher with 2 and somewhat lower with 3 compound to that of their nonsubstituted analogs.[21]

The temperature dependence of the enantioselectivity of compounds 1–3 as the catalysts are shifted compared to their nonsubstituted analogs (Figure 1). The rate of hydroformylation decreases in the order **2 > 1 > 3**. This is consistent with previously observed trends in hydrogenation,[27] hydroformylation,[21] and carbonylation,[28] which show that catalytic activity increases with larger chelate ring size. The compounds 1–3 are somewhat less active in Pt–Sn hydroformylation than the analogous nonsubstituted derivatives. The opposite effect was observed with the same ligands in rhodium-catalyzed hydrogenation.[29b]

Discussion

Temperature Effects in Asymmetric Hydroformylation. In asymmetric hydroformylation the discriminative coordination of the olefin has been considered as the critical step which determines product antipode.[12,21] However, the hydroformylation of α-deuteriostyrene catalyzed by Rh-DIOP[30] yields the same product antipode for both the linear and branched products, while in the deuterioformylation of styrene catalyzed by $PtCl(SnCl_3)$-DIOP[12] the linear and branched products have the opposite configuration.

The results obtained in the hydroformylation of styrene with compounds 1–3 and $PtCl(SnCl_3)[(S,S)$-BDPP][15] are

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Table III. Asymmetric Hydroformylation of Styrene by PtCl(SnCl$_3$)[(*S,S*)-DIOP-(pNMe$_2$)$_4$][a]

reacn temp (°C)	$1/T$ ($1/K \times 10^3$)	reacn time (h)	conversn to aldehydes (%)	regioselectivity (n/b)[b]	conversn to ethylbenzene (%)	enantioselectivity (% ee)	ln ([*R*]/[*S*])
25	3.35	480	20.2	1.30	0	20.0 (*R*)	0.41
35	3.24	17	28.6	1.40	0	16.6 (*R*)	0.34
50	3.09	46	34.5	1.38	0	8.3 (*R*)	0.17
60	3.00	20	18.0	1.37	0	5.6 (*R*)	0.11
80	2.83	6	39.0	1.38	0	3.6 (*S*)	–0.072
90	2.75	4	37.2	1.78	3.2	4.7 (*S*)	–0.094
100	2.68	2	17.6	1.84	5.1	6.4 (*S*)	–0.13
120	2.54	1	22.6	2.18	10.0	4.2 (*S*)	–0.084

[a] Reaction conditions: subst/Pt = 1000/1, Sn/Pt = 3/1, 0.015 mmol of Pt in 10 mL of solvent, 70 bar of H_2/CO (1/1). [b] Ratio of linear to branched products.

Table IV. Asymmetric Hydroformylation of Styrene by PtCl(SnCl$_3$)[(*S,S*)-Chiraphos-(pNMe$_2$)$_4$] (3)[a]

reacn temp (°C)	$1/T$ ($1/K \times 10^3$)	reacn time (h)	conversn to aldehydes (%)	regioselectivity (n/b)[b]	conversn to ethylbenzene (%)	enantioselectivity (% ee)	ln ([*R*]/[*S*])
25	3.35	300	12.4	0.62	0.1	46.0 (*R*)	0.99
40	3.19	186	14.2	0.64	0.1	42.0 (*R*)	0.89
50	3.09	96	12.6	0.64	0.2	37.0 (*R*)	0.77
70	2.91	70	18.2	0.71	0.6	32.9 (*R*)	0.68
80	2.83	30	16.3	0.79	0.8	30.4 (*R*)	0.62
90	2.75	19	23.3	1.19	1.3	22.1 (*R*)	0.45
100	2.68	12	19.6	1.46	2.4	12.4 (*R*)	0.25
120	2.54	6	13.1	1.35	3.0	7.4 (*R*)	0.15
140	2.42	2	10.5	1.94	3.5	6.0 (*R*)	0.12

[a] Reaction conditions: subst/Pt = 1000/1, Sn/Pt = 3/1, 0.015 mmol of Pt in 10 mL of solvent, 70 bar of H_2/CO (1/1). [b] Ratio of linear to branched products.

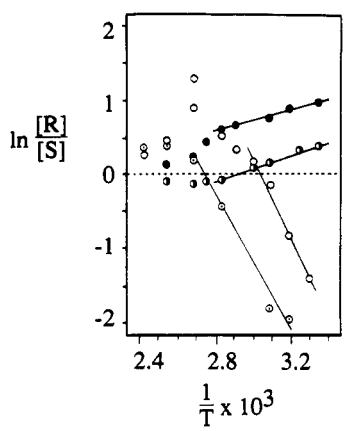

Figure 2. Plot of ln ([*R*]/[*S*]) vs $1/T$ for asymmetric hydroformylation catalysts: (○) **1**; (◑) **2**; (●) **3**; (◎) PtCl(SnCl$_3$)[(*S,S*)-BDPP].[15]

summarized in Figure 2, in a ln ([*R*]/[*S*]) vs $1/T$ diagram. These Eyring plots are linear at low temperatures. At higher temperatures (>80 °C for **1–3** and >100 °C for PtCl(SnCl$_3$)BDPP) the plots curve. This is attributed to product racemization, which becomes increasingly significant at elevated temperatures.

A reversal in product antipode as a function of temperature could be due to reaction via different chelate conformations of the complex. However, NMR spectroscopy is consistent with a stable chelate ring conformation in PtCl(SnCl$_3$)[(*S,S*)-BDPP-(pNMe$_2$)$_4$].[24] The prevalence of the opposite antipode occurs at relatively low temperature (53 °C). Under these circumstances, it is unlikely that the thermodynamically unstable λ-skew conformation plays a significant role in the catalysis.[16,31]

Conversely, the chelate ring in Pt-DIOP-(pNMe$_2$)$_4$ is conformationally labile[24] and a reversal of product configuration is still observed. A good linear correlation (R > 0.98) is obtained in the plot of ln ([*R*]/[*S*]) vs $1/T$ (Figure 2). Again, this can be explained either by competing reaction paths via the diastereomeric intermediates of a single catalytically active chelate conformation or by reaction via different chelate conformations. Because of the similarity in the Eyring plots of **1–3** at low temperatures, we prefer the explanation of reactivity via a single chelate conformation for each catalyst.

The observation of dramatic temperature effects on reaction selectivity in catalysis has recently been reviewed by Scharf et al. They argue that such effects are consistent with reactions that may proceed via competing paths of different activation energies.[32]

Conclusion

In asymmetric hydroformylation the discriminative coordination of the olefin has been considered as the source of asymmetric induction. However, it is likely that this is important in a kinetic rather than a thermodynamic sense; that is, the diastereomeric Pt–olefin complexes may have different activation energies in the subsequent reaction steps which ultimately lead to products. The final outcome of optical purity is determined only by the actual rates in the two competing reaction paths. Significantly, the same complex can provide either enantiomer as the dominant product with relatively good optical purity simply by controlling the reaction temperature. The work presented here provides additional examples that the characterization of a chiral catalyst is incomplete without determination of the temperature dependence on reaction selectivity.

Experimental Section

Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA. ^{1}H and ^{31}P NMR spectra were run on a Bruker WP-200 instrument. Integrated ratios on ^{1}H NMR were con-

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sistent with the given formulas. ^{31}P NMR chemical shifts are referenced to external 85% H_3PO_4; downfield shifts are positive. The optical purity of 2-phenylpropanol samples were determined by polarimetry on a Perkin-Elmer 241 polarimeter by comparison with the literature values[19] or by using the NMR shift reagent Eu(dmc)$_3$.[19] A loan of H_2PtCl_6 was provided by Johnson-Matthey. $PtCl_2$,[33] $Pt(PhCN)_2Cl_2$,[34] and the ligands[29a] were prepared by literature methods. Styrene and toluene were freshly distilled before use. All preparations and operations were carried out under an atmosphere of dry, deoxygenated argon.

$PtCl_2$[(*S,S*)-BDPP-(pNMe$_2$)$_4$]. This complex was prepared by the reaction of $Pt(PhCN)_2Cl_2$ with the ligand in the manner described in ref 15. The reaction is quantitative; the *p*-dimethylamino groups do not affect complexation. The reaction is selective for chelating ligands, as only the formation of the chelate complex was observed in the presence of excess tris[*p*-(dimethylamino)phenyl]phosphine. The product is obtained as a yellowish white crystalline solid. Anal. Calcd for $C_{37}H_{50}N_4P_2Cl_2Pt$: C, 50.57; H, 5.69; N, 6.38. Found: C, 52.60; H, 5.77; N, 6.12. ^1H NMR (δ; 200.1 MHz, $CDCl_3$): 7.79, 7.75 dd, dd ($^3J_{HH}$ = 8.9 Hz, $^3J_{PCCH}$ = 10.5 Hz); 6.67 d ($^3J_{HH}$ = 8.7 Hz); 3.01, 2.98 s, s; 2.68 m ($^3J_{HH}$ = $^3J_{PCCH}$ = 7.5 Hz, $^4J_{PCCCH} \approx$ 3 Hz); 1.91 t of t's ($^3J_{HH}$ = 7.6 Hz, $^3J_{PCCH}$ = 19.3 Hz); 0.98 dd ($^3J_{HH}$ = 6.9 Hz, $^3J_{PCCH}$ = 13.8 Hz). ^{31}P NMR (δ; 80.01 MHz, $CDCl_3$): 4.93 s ($^1J_{PtP}$ = 3479 Hz, satellites).

$PtCl(SnCl_3)$[(*S,S*)-BDPP-(pNMe$_2$)$_4$] (1). The complex was prepared by the reaction of the dichloride complex with 1 equiv of anhydrous $SnCl_2$ in dichloromethane by the literature methods.[2,13,15] The coordination of $SnCl_2$ is in equilibrium, as about 10% each of the dichloride and the bis complex $Pt(SnCl_3)_2$[(*S,S*)-BDPP-(pNMe$_2$)$_4$] are present in the dichloromethane solution, as determined by NMR. In other solvents such as MeOH, $CHCl_3$, and triethyl orthoformate $SnCl_2$ dissociates from 1 to greater extents. 1 was fractionally crystallized from a mixture of CH_2Cl_2–pentane, to give a yellow crystalline solid. Anal. Calcd for $C_{37}H_{50}Cl_4N_4P_2SnPt$: C, 41.58; H, 4.68; N, 5.24. Found: C, 39.66; H, 4.60; N, 5.07. ^1H NMR (δ; 200.1 MHz, CD_2Cl_2): 7.74 dd ($^3J_{HH}$ = 8.8 Hz, $^3J_{PCCH}$ = 11.7 Hz); 7.71 dd ($^3J_{HH}$ = 8.0 Hz, $^3J_{PCCH}$ = 10.9 Hz); 7.48 dd ($^3J_{HH}$ = 8.8 Hz, $^3J_{PCCH}$ = 10.8 Hz); 7.37 dd ($^3J_{HH}$ = 8.8 Hz, $^3J_{PCCH}$ = 11.2 Hz), 6.77, 6.75, 6.74 d, dd, d ($^3J_{HH}$ = 8.8 Hz); 3.04, 3.03, 3.01 (2× int.) s, s, s; 2.75, 2.69 m, m; 1.88 eight-line m ($^3J_{HH}$ = 7.0 Hz, $^3J_{P_1CCH}$ = $^3J_{P_2CCH}$ = 15.5 Hz, $^2J_{HH} \approx$ 7 Hz); 1.01 (2× int.), 0.95, 0.93 d, d, d ($^3J_{HH}$ = 7.0 Hz, $^3J_{P_1CCH}$ = 15.5 Hz, $^3J_{P_2CCH}$ = 13.1 Hz). ^{31}P NMR (δ; 80.01 MHz; CD_2Cl_2): 12.7, 3.5 d, d ($^1J_{PtP_1}$ = 2922 Hz, $^1J_{PtP_2}$ = 3341 Hz (P trans to Cl), satellites, $^2J_{PP}$ = 24.3 Hz).

$PtCl_2$[(*S,S*)-DIOP-(pNMe$_2$)$_4$]. ^1H NMR (δ; 200.1 MHz, $CDCl_3$): 7.55 dd ($^3J_{HH}$ = 8.9 Hz, $^3J_{PCCH}$ = 11.0 Hz); 6.64 dd ($^3J_{HH}$ = 8.8 Hz); 3.96 br s, 2.99 s, 2.88, 2.59 m, m (not res); 1.14 s. ^{31}P NMR (δ; 81.01 MHz, 293 K, $CDCl_3$): −5.5 s ($^1J_{PtP}$ = 3550 Hz, satellites).

$PtCl(SnCl_3)$[(*S,S*)-DIOP-(pNMe$_2$)$_4$] (2): prepared in situ for catalysis by the addition of anhydrous $SnCl_2$ (1–3 equiv) to $PtCl_2$[(*S,S*)-DIOP-(pNMe$_2$)$_4$] in the catalytic reaction mixtures.

$PtCl_2$[(*S,S*)-Chiraphos-(pNMe$_2$)$_4$]. ^1H NMR (δ; 200.1 MHz, $CDCl_3$): 7.8 dd ($^3J_{HH}$ = 8.9 Hz, $^3J_{PCCH}$ = 10.9 Hz); 7.55 dd ($^3J_{HH}$ = 8.9 Hz, $^3J_{PCCH}$ = 10.5 Hz); 6.73 dd ($^3J_{HH}$ = 8.6 Hz); 3.02 s, 2.16 br s, 0.97 br dd (not res). ^{31}P NMR (δ; 81.01 MHz, $CDCl_3$): 37.7 s ($^1J_{PtP}$ = 3597 Hz, satellites).

$PtCl(SnCl_3)$[(*S,S*)-Chiraphos-(pNMe$_2$)$_4$] (3): prepared in situ for catalysis by the addition of anhydrous $SnCl_2$ (1–3 equiv) to $PtCl_2$[(*S,S*)-Chiraphos-(pNMe$_2$)$_4$] in the catalytic reaction mixtures.

Hydroformylation Experiments. In a typical experiment 0.015 mmol of 1–3 and 0.03 mmol of anhydrous $SnCl_2$ (when used) were transferred to a 30-mL stainless steel autoclave. A 15-mmol amount of styrene in 10 mL of solvent (toluene) was added, and the reactor was pressurized to 70 bar by a mixture of CO/H_2 = 1/1. The autoclave was placed into a thermostated oil bath and stirred magnetically. After cooling and venting, the yellow solution was removed and quickly analyzed by GC. Fractional distillation to remove styrene and ethylbenzene was done prior to the determination of optical purity of 2-phenylpropanal.

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