Platinum Complexes of Rigid Bidentate Phosphine Ligands in the Hydroformylation of 1-Octene

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The synthesis of the two novel diphosphine compounds 1,2-bis(3-(diphenylphosphino)-4-methoxyphenyl)benzene (**1**; Terphos), and 1,2-bis(2-diphenylphosphino)benzene (**2**), both derived from a terphenyl backbone structure, are described. Straightforward synthetic routes have been employed to obtain these ligands in good yields from cheap starting materials. The coordination of ligands **1** and **2** with $PtCl_2$(cod) has been studied by NMR spectroscopy, and the X-ray crystal structures of the resulting complexes **4** and **5** were determined. The ^{31}P NMR spectra of the mononuclear products demonstrate solely cis coordination for both bidentate ligands, with corresponding coupling constants J_{Pt-P} of 3810 Hz (*cis*-[$PtCl_2$(**1**)], complex **4**) and 3712 Hz (*cis*-[$PtCl_2$(**2**)], **5**). The bite angles P_1-Pt-P_2 were 98.74 and 105.89°, respectively, in the distorted square-planar complexes. The new diphosphines have been applied in the platinum/tin-catalyzed hydroformylation of 1-octene, and both ligands give active and selective platinum catalysts.

Introduction

Homogeneous catalysis has proven to be a very powerful tool for the synthesis of intermediates and fine chemicals.[1] One especially significant application on an industrial scale is the hydroformylation of alkenes.[2] Most often cobalt and rhodium catalysts are applied, but also Pt−Sn systems with phosphorus ligands have been known since the pioneering work of Orchin.[3] In this system, the role of the $SnCl_2$ "cocatalyst" actually remains unclear,[4] and even tin-free systems have been reported.[5] Especially in the asymmetric hydroformylation of styrene, platinum-based catalysts have been extensively studied,[6] with generally high enantioselectivities but with lower chemo- and regioselectivities compared to those for the rhodium-based systems. For the platinum-catalyzed hydroformylation of (terminal) alkenes, most often (di)phosphine ligands are employed.[7] Rigid xanthene-based diphosphines (Figure 1) have been shown to give active and selective platinum catalysts for the hydroformylation of 1-octene.[8] We previously also reported the highly selective platinum-catalyzed hydroformylation of the industrially relevant internal alkene methyl *trans*-3-pentenoate.[9]

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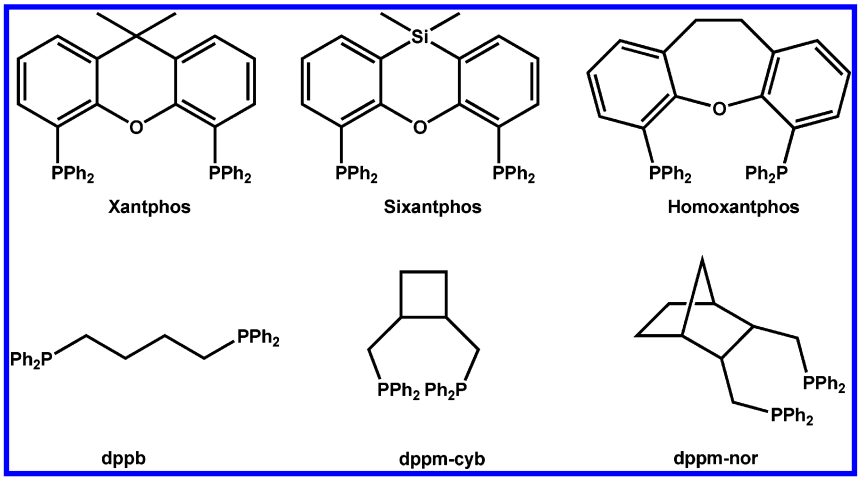
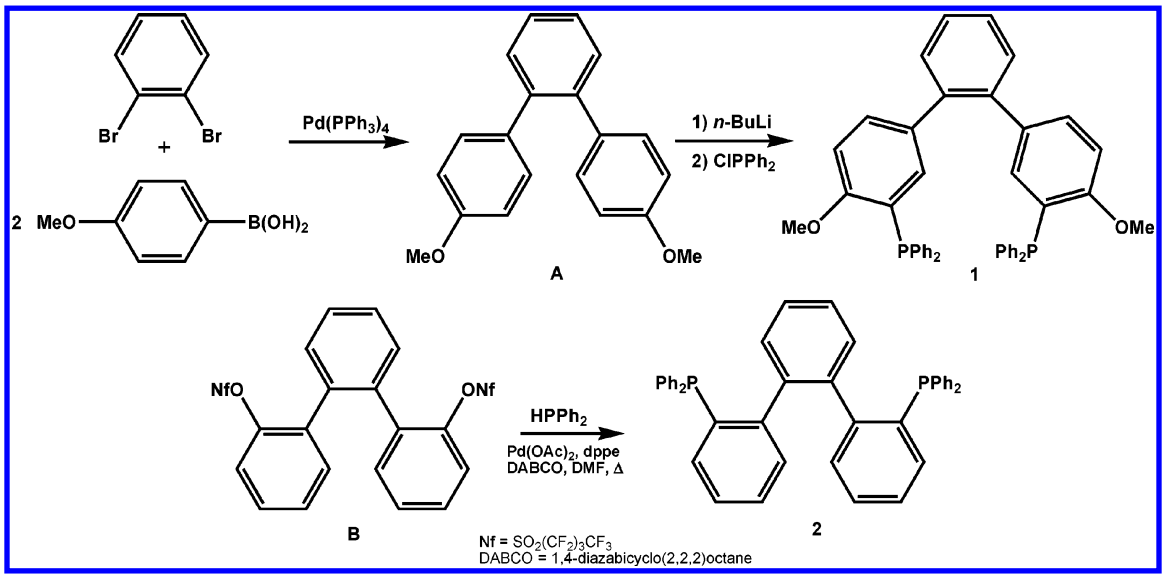


Figure 1.

Scheme 1. Synthetic Routes to Compounds 1 and 2



An early study by Hayashi et al., aimed at quantifying the effect of the diphosphine chelate ring size on catalytic performance, described that in the case of diphosphine ligands steric rather than electronic factors govern the reaction rate and regioselectivity.[10] In comparison to the benchmark system $PtCl_2(PPh_3)_2/SnCl_2$, the addition of 1,2-bis(diphenylphosphino)ethane (dppe) led to a considerably slower reaction rate.[11] The catalytic activity increased dramatically when a four-carbon-bridged diphosphine such as dppb was employed (Figure 1). The trans-substituted norbornane-derived ligand dppm-nor gave the fastest catalyst, but also with various other ligands containing a cyclic four-carbon bridge (e.g. dppm-cyb) increased rates were observed. The calculated natural bite angles of these particular ligands are all around 98°.[12]

We herein report the synthesis of the novel diphosphines **1** and **2** and their Pt complexes. To obtain information on the applicability of this type of diphosphine ligand in homogeneous catalysis, the Pt/Sn-catalyzed hydroformylation of 1-octene was chosen as a model reaction.

Results and Discussion

Synthesis of Diphosphines 1 and 2 and Selenide 3. The diphosphine compound **1** (named Terphos) was successfully synthesized in good yield from commercially available starting materials (Scheme 1). The palladium-catalyzed Suzuki coupling of 1,2-dibromobenzene with 4-methoxyphenylboronic acid, in the presence of Na_2CO_3 as a base, gave compound **A** in 73% yield. This is a significant improvement of the procedure reported by Blake et al., who used $Ba(OH)_2$ as a base in order to obtain the same compound.[13] Subsequent ortho lithiation and reaction with $ClPPh_2$, a strategy recently applied to obtain Bisphenol A derived diphosphine ligands,[14] yielded the desired diphosphine compound **1**, which was fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy as well as by elemental analysis. The structurally related compound **2** was obtained by reaction of the bis-nonaflate **B**[15] with $HPPh_2$ to yield

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compound **2**, which was fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy as well as by FAB-MS spectrometry.

The σ-donor ability and hence the basicity of a phosphine moiety is related to the coupling constant $^{1}J_{Se-P}$ in the ^{31}P NMR spectrum of the ^{77}Se isotopomer of the corresponding diphenylphosphine selenide.[16] We synthesized the corresponding chalcogen compound **3** by reaction of **1** with elemental selenium. The reaction proceeded smoothly at 60 °C in toluene within 15 min. The ^{31}P NMR spectrum showed a singlet at δ 32.1 ppm with concomitant ^{77}Se satellites. The coupling constant $^{1}J_{Se-P}$ of 724 Hz was in the range expected for diphenylphosphine-derived selenides.[16] For the selenide of PPh_3 a $^{1}J_{Se-P}$ value of 732 Hz is reported,[17] while the more electron-donating tris(4-methoxyphenyl)phosphine selenide gives a $^{1}J_{Se-P}$ value of 708 Hz.[18]

Preparation of Dichloroplatinum(II) Complexes 4 and 5. The reaction of $PtCl_2$(cod) with either ligand **1** or **2** led to the quantitative formation of the corresponding cis complexes, as indicated by the observed coupling constants J_{Pt-P} from ^{31}P NMR spectroscopy.[19] For complex **4**, *cis*-[$PtCl_2$(**1**)], the $^{31}P\{^{1}H\}$ NMR spectrum showed a singlet at δ 9.9 ppm, flanked by ^{195}Pt satellites with a J_{Pt-P} value of 3810 Hz, while the related complex **5**, *cis*-[$PtCl_2$(**2**)], appeared as a singlet at δ 8.2 ppm together with its ^{195}Pt satellites (J_{Pt-P} = 3712 Hz). The molecular structures were unequivocally determined by X-ray crystallography and were in full agreement with the spectroscopic data. Figure 2 depicts the molecular structure with values for important bond lengths and bond angles for complex **4**, which crystallized in the monoclinic space group $P2_1/n$ as the $CDCl_3$ adduct.

The geometry around the platinum atom is clearly distorted square planar, as evident from the observed bite angle P_1-Pt-P_2 of 98.74(2)°. The angles $P_1-Pt-Cl_2$ and $P_2-Pt-Cl_1$ are 170.90 and 172.80°, respectively. Consequently, the $Cl_1-Pt-Cl_2$ angle is small at only 84.93°. The Pt−P and Pt−Cl bond lengths are in their expected ranges, at 2.26−2.28 and 2.34−2.36 Å, respectively.[20] The aromatic rings of the terphenyl backbone

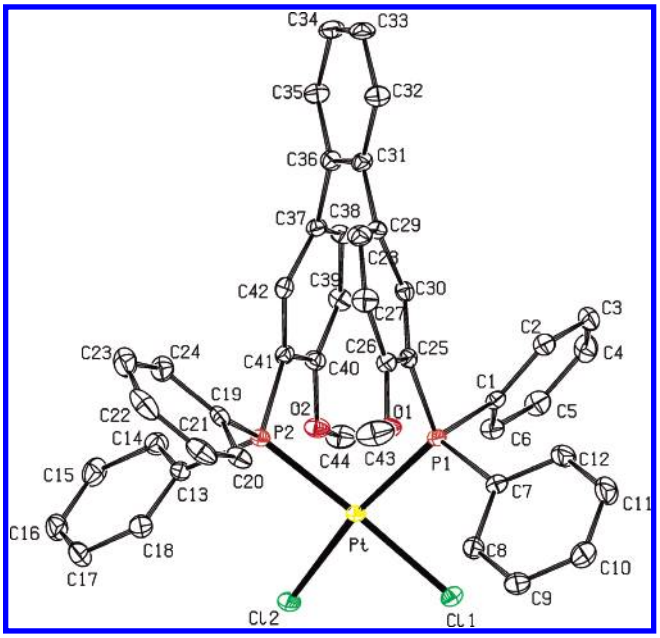

Figure 2. Ortep representation of complex **4**, *cis*-[$PtCl_2$(**1**)]. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pt−P_1, 2.2847(7); Pt−P_2, 2.2635(7); Pt−Cl_1, 2.3565(6); Pt−Cl_2, 2.3358(7); O_1-C_{26}, 1.352(3); O_2-C_{40}, 1.356(3); P_1-C_{25}, 1.832(3); P_2-C_{41}, 1.818(3); P_1-P_2, 3.4517(9); P_1-Pt-P_2, 98.74(2); $Cl_1-Pt-Cl_2$, 84.93(2); $P_1-Pt-Cl_1$, 86.34(2); $P_1-Pt-Cl_2$, 170.90(2); $P_2-Pt-Cl_1$, 172.80(3); $P_2-Pt-Cl_2$, 89.73(2); $Pt-P_1-C_{25}$, 122.03(9); $Pt-P_2-C_{41}$, 110.75(9).

have torsion angles $C_{28}-C_{29}-C_{31}-C_{36}$ of −135.7° and $C_{31}-C_{36}-C_{37}-C_{38}$ of −128.2°, showing that there is slight distortion from the local C_2 symmetry of the backbone. The intramolecular P_1-P_2 distance is only 3.4517 Å, whereas the corresponding Pt complex of the ligand Sixantphos showed a P_1-P_2 distance of 3.4295 Å.[21] Interestingly, the latter value is significantly smaller than reported for various other non-platinum complexes of the strongly related Xantphos.[22,23] The molecular structure obtained for the related complex **5**, *cis*-[$PtCl_2$(**2**)], is depicted in Figure 3, together with data for selected bond lengths and bond angles.

Again, the geometry around the platinum atom is distorted square planar. The observed bite angle P_1-Pt-P_2 is 105.83°. The angles $P_1-Pt-Cl_1$ and $P_2-Pt-Cl_1$ are 169.17 and 83.33°, respectively. The intramolecular P_1-P_2 distance is found to be 3.604 Å, somewhat longer than in complex **4**. The most notable structural difference between the two Pt compounds is the orientation of the middle phenyl ring in the backbone of the ligands. In complex **4**, this phenyl is directed away from the metal center, while in complex **5** the central phenyl ring of the backbone shields one face of the platinum center, acting as a "roof".

Platinum-Catalyzed Hydroformylation of 1-Octene. In the original work by Hayashi, the remarkable catalytic rate enhancement observed with diphosphines

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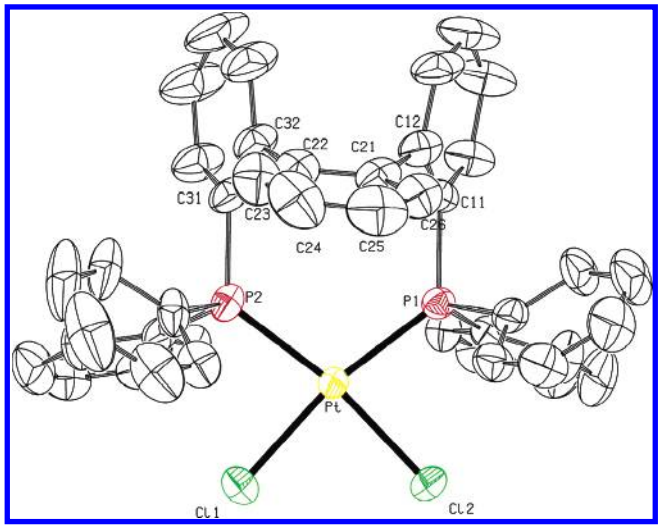
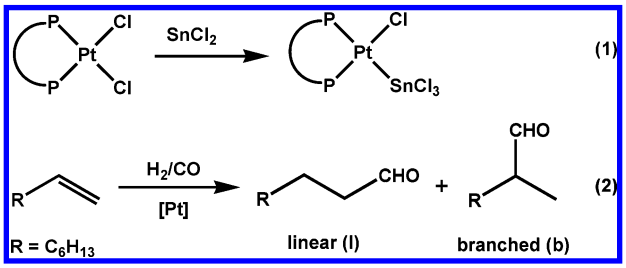


Figure 3. Ortep representation of complex **5**, *cis*-[$PtCl_2$(**2**)]. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pt−P_1, 2.2525; Pt−P_2, 2.2631; Pt−Cl_1, 2.3581; Pt−Cl_2, 2.3556; P_1−C_{11}, 1.830(4); P_2−C_{31}, 1.843(4); P_1−P_2, 3.604(2); P_1−Pt−P_2, 105.89; Cl_1−Pt−Cl_2, 86.07; P_1−Pt−Cl_1, 169.17; P_1−Pt−Cl_2, 83.33; P_2−Pt−Cl_1, 84.70; P_2−Pt−Cl_2, 170.76; Pt−P_1−C_{11}, 128.03; Pt−P_2−C_{31}, 125.54.

that form large chelate rings upon complexation was explained by the existence of a catalytic species wherein these ligands acted as monodentates instead of bidentates. Although strained cyclic phosphines can undergo dissociation of one phosphine arm, leading to more active catalysts, this is more likely to occur in Pt complexes with true monodentate ligands such as PPh_3. Therefore, the lower reaction rate of PPh_3 in comparison to these bidentate "large bite angle" ligands is not explained by this theory. It is well-known that the bite angle has a considerable influence on the rate in the platinum-catalyzed hydroformylation.[10,21] To get insight into the catalytic behavior of the structurally related platinum complexes **4** and **5**, the Pt−Sn-catalyzed hydroformylation of 1-octene was chosen as a test reaction. By using an equimolar amount of the cocatalyst $SnCl_2$, high chemo- and regioselectivity to the desired linear aldehyde have been reported.[24] We therefore carried out an initial preformation ex situ to form the [$PtCl_2$(P∩P)−$SnCl_3$] adduct (eq 1), which was then in situ activated with synthesis gas to obtain the precatalyst used in the hydroformylation of 1-octene (eq 2).



We have performed several catalytic runs under various reaction conditions, to examine the influences on both activity and selectivity. The formation of the desired linear product 1-nonanal, the unwanted branched aldehyde 2-methyloctanal, and the hydrogenated product octane was monitored by gas chromatography. The

Table 1. Hydroformylation of 1-Octene Catalyzed by $PtCl_2$/$SnCl_2$/1 or 2[a]

entry	ligand	time (h)	*T* (°C)	*p* (bar)	conversn (%)[b]	sel_{ald} (%)[b,c]	isom (%)[b,d]	l:b[b]	TOF[e] (h^{-1})
1	**1**	18	60	40	20.9	96.1	6.9	34.0	12
2	**1**	16.5	60	80	42.1	94.9	11.3	32.2	27
3	**1**	21	60	80[f]	77.6	93.3	75.3	18.1	39
4	**2**	64	60	40	51.3	98.6	5.0	8.5	8
5	**2**	18	60	80	13.4	>99		29.5	7
6	**2**	18	60	80[f]	48.1	98.9	1.6	45.3	25
7	**2**	5.5	100	40	39.4	94.5	26.7	2.1	70

[a] Reaction conditions: 1-octene (31.0 mmol), [$PtCl_2$(P∩P)/$SnCl_2$] = 0.39 mM, decane (12.5 mmol), CH_2Cl_2, 1-octene:Pt = 1050:1. [b] Determined by GC. [c] The only side product is hydrogenation. [d] Defined as fraction of remaining 1-octene. [e] Turnover frequency, defined as (mol of substrate converted) (mol of platinum)$^{-1}$ h^{-1}, determined at the end of the run. [f] 40 bar of CO/H_2 and 40 bar of H_2.

isomerization of 1-octene to internal isomers is expressed relative to non-converted 1-octene. Both ligands **1** and **2** gave active platinum catalysts, as can be seen from the results listed in Table 1. Activities were slightly lower than those obtained with the ligand Xantphos (tof of 240 at 80 °C), which has a natural bite angle β_n of 112°, but comparable to those found with Homoxantphos (natural bite angle β_n of 102°).[8] The chemoselectivity to aldehydes as well as the regioselectivity are high with ligand **1**. A direct comparison with the ligands applied by Hayashi is less straightforward, due to the varying reaction conditions, but the chemoselectivity is better than found with the ligand dppb, although the dppm−cyb-based system appears to be superior.[10] Increasing the total syngas pressure to 80 bar had no effect on these high levels with this catalyst system. When the ratio of H_2 to CO was altered to 3:1 at an overall pressure of 80 bar, i.e. 40 bar of H_2 and 40 bar of syngas, the catalytic activity was raised by about 50% (entry 3). There was significant isomerization of 1-octene, however, a known drawback of Pt/Sn catalysts.

On application of ligand **2**, which is expected to induce more steric hindrance around the metal center, lower activities and regioselectivities (l:b ratio of 8.5) were observed, compared to ligand **1**, at the standard reaction conditions of 60 °C and 40 bar of synthesis gas (entry 4). Increasing the total syngas pressure had a positive effect on the regioselectivity (l:b ratio of 29.5), while isomerization of 1-octene was virtually absent. As the hydrogenolysis of an acyl-complex intermediate, to form the aldehyde product, is usually rate limiting for Pt/Sn systems,[25] a higher hydrogen partial pressure proved advantageous for the overall performance of the catalyst system (entry 6). At a reaction temperature of 100 °C, the regioselectivity dropped dramatically (l:b ratio of 2.1), with over 20% isomerized product (entry 7). Although the bite angle difference between either ligand **1** or **2** and Homoxantphos appears relatively small, a marked effect is noted on the catalytic results, which implies that other factors in addition to the sterics of the ligand and its bite angle effect the activity and regioselectivity of Pt−Sn catalysts. Similar findings have been reported for the Rh-catalyzed hydroformylation.[26]

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(25) As reported for several systems.[9−11]

Conclusions

The novel diphosphine compounds **1** and **2** could be synthesized via straightforward procedures in good yields. Both ligands coordinated to platinum in a strictly chelating cis fashion, as demonstrated by NMR spectroscopy. The molecular structures for the complexes *cis*-[$PtCl_2$(**1**)] (**4**) and *cis*-[$PtCl_2$(**2**)] (**5**) were determined by X-ray crystallography. The bite angles P_1-Pt-P_2 were comparable for both complexes at around 100°, but subtle conformational differences could be noted, which led to varying steric constraints on the metal center. The ligands have been applied in the platinum/tin-catalyzed hydroformylation of 1-octene. Moderate activities and fairly high regioselectivities were found for both catalytic systems under appropriate but nonoptimized reaction conditions.

Experimental Section

Chemicals were purchased from Aldrich, Acros, or Merck and used as received. All preparations were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone (THF, diethyl ether, toluene, and hexanes) or calcium hydride (CH_2Cl_2 and $CDCl_3$) prior to use. All glassware was dried by heating under vacuum. $PtCl_2$(cod)[27] was synthesized according to a literature procedure. NMR spectra were recorded on Inova 500, Varian Mercury 300, and Varian Mercury 400 spectrometers, and chemical shifts are given in ppm referenced to solvent. GC analyses were performed on a Shimadzu 17A chromatograph equipped with a 50 m PONA column. Elemental analysis was performed by Kolbe Mikroanalytisches Laboratorium, Mulheim an der Ruhr, Germany.

Autoclaves were manufactured in-house from stainless steel 1.4571. For good heating capacity the autoclaves were fitted with a shrunk copper mantle. The autoclaves with a volume of 75 mL closed on a stainless steel ring in order to have line closure. To add substrates at elevated temperature and pressure, the autoclave was equipped with a dripping funnel, which could be cooled or heated. The autoclave was fitted with a tube manometer with a pressure range from 0 to 160 bar (Econosto), ball valves for the dripping funnel (VSM GmbH, KH 4M 4F HT X), needle valves (Swagelock, SS-4PDF4), a relief valve set at a pressure of 105 bar (Swagelock, SS-4R3A5-C), various high-pressure connections (Swagelock), and high-pressure tubing (Dockweiler, Finetron). The autoclave was heated with an electric heating mantle, and the temperature was measured internally with a PT-100 thermocouple. The autoclave was also safeguarded to overheating. The contents were stirred with an X-type stirring bar.

1,2-Bis(4-methoxyphenyl)benzene (A). This is a modification of a literature procedure:[13] 4-methoxyphenylboronic acid (1.60 g, 10.53 mmol) and 1,2-dibromobenzene (0.83 g, 5.26 mmol) were added to 30 mL of a degassed 2 M solution of Na_2CO_3 and 90 mL of dimethoxyethane, together with a catalytic amount (~10 mol %) of $Pd(PPh_3)_4$. The reaction mixture was refluxed overnight. The mixture was brought to pH 7 by addition of a 4 M HCl solution. The solution was concentrated to approximately 40 mL and the product extracted with CH_2Cl_2 (3 × 25 mL). The combined organic phases were dried over $MgSO_4$ and filtered by cannula, and the solvent was removed in vacuo to leave a yellow oil. Upon addition of 10 mL of MeOH a white precipitate was obtained that was separated, washed twice with 10 mL of acetonitrile, and dried to give 0.72 g (73%) of a white crystalline powder.

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^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (d, 4H, ^1J = 2.4 Hz), 7.07 (dt, 4H, ^1J = 8.3 Hz, ^2J = 1.2 Hz), 6.77 (dt, 4H, ^1J = 8.4 Hz, ^2J = 1.2 Hz) 3.79 (s, 6H, OCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 158.2, 140.0, 134.1, 130.9, 130.5, 127.1, 113.5, 55.2 ($-OCH_3$).

1,2-Bis(3-(diphenylphosphino)-4-methoxyphenyl)benzene (1; Terphos). To a solution of **A** (2.20 g, 7.57 mmol) and TMEDA (2.5 mL, 16.7 mmol) in 75 mL of ether, cooled to −40 °C, was added *n*-BuLi (6.7 mL, 16.7 mmol) as a 2.5 M solution in hexanes in a dropwise fashion. The reaction mixture was stirred overnight at room temperature. $ClPPh_2$ (3.68 g, 16.7 mmol) in 15 mL of hexanes was added dropwise at 0 °C, after which the solution was stirred overnight at room temperature. Volatiles were then removed in vacuo, 50 mL of THF and 75 mL of a 25% brine solution were added, and the organic phase was washed twice with 30 mL of water. After drying with $MgSO_4$, the solvent was removed and the precipitate washed with three 25 mL portions of methanol to give a white powder. Yield: 60% (2.11 g, 4.54 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.32 (m, 16H, PPh_2), 7.27 (dd, 2H, ^1J = 5.6 Hz, ^2J = 3.2 Hz), 7.19 (dd, 2H, ^1J = 5.6 Hz, ^2J = 3.2 Hz), 7.16 (m, 4H), 7.06 (dd, 2H, ^1J = 8.4 Hz, ^2J = 2.0 Hz), 6.82 (dd, 2H, ^1J = 8.4 Hz, ^2J = 4.8 Hz), 6.41 (dd, 2H, ^1J = 4.8 Hz, ^2J = 2.0 Hz), 3.72 (s, 6H, OCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ 159.6, 145.5, 140.2, 136.5 (d J_{P-C} = 9.8 Hz), 135.1, 134.3, 134.0 (d, J_{P-C} = 20.4 Hz), 131.4, 130.4, 128.5, 128.4 (d, J_{P-C} = 6.8 Hz), 128.4, 126.9, 110.0, 55.8 ($-OCH_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, ppm) δ −16.5 (s). Anal. Calcd for $C_{44}H_{36}O_2P_2$: C, 80.23; H, 5.51; P, 9.40. Found: C, 80.16; H, 5.43: P, 9.55.

1,2-Bis(2-(diphenylphosphino)phenyl)benzene (2). Compound **B**[15] (2.0 g, 2.42 mmol), dppe (21.2 mg, 53.2 μmol), $Pd(OAc)_2$ (10.87 mg, 48.4 μmol), and DABCO (1.1 g, 9.68 mmol) were dissolved in 35 mL of DMF (35 mL), and the mixture was stirred for 1 h at room temperature. $HPPh_2$ (0.93 mL, 5.32 mmol) was then added dropwise and the reaction mixture was heated to reflux. After 3 days the reaction was complete, as indicated by TLC (eluent 1/1 CH_2Cl_2/petroleum ether). Solvent was evaporated in vacuo, and the residue was dissolved in 75 mL of Et_2O and washed with 50 mL of degassed water. The organic layer was dried with $MgSO_4$ and filtered over neutral alumina. The light yellow filtrate was evaporated to dryness in vacuo to yield 1.25 g of crude residue. This was dissolved in a small amount of CH_2Cl_2 and recrystallized by slow diffusion of hexanes, to yield **2** (0.95 g, 65%). In the ^{31}P NMR spectrum a small amount of byproduct was observed, which could not be removed by silica gel column chromatography.

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.35 (m, 16H), 7.16 (m, 8H), 7.08 (m, 6H), 6.91 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): 140.1 (d, J_{C-P} = 7.2 Hz), 138.8 (d, J_{C-P} = 12.2 Hz), 137.7 (d, J_{C-P} = 11.4 Hz.), 136.3 (d J_{C-P} = 11.0 Hz), 134.3 (d, J_{C-P} = 19.8 Hz), 133.5 (d, J_{C-P} = 18.6 Hz), 131.4 (d, CH, J_{C-P} = 4.2 Hz), 131.0 (t, J_{C-P} = 6.1 Hz), 128.9, 128.7 (d, J_{C-P} = 6.8 Hz), 128.5 (d, J_{C-P} = 5.9 Hz), 128.3 (d, J_{C-P} = 11.0 Hz) 127.4, 126.7. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, ppm): δ −12.7 (s, ~5%, monophosphine), −14.3 (s). MS (FAB$^+$) (*m*/*z*) for $C_{42}H_{33}P_2$: calcd 599.2057, found 599.2044 [M + H].

1,2-Bis(3-(diphenylphosphino)-4-methoxyphenyl)benzene Diselenide (3). Compound **1** (57.8 mg, 8.75 mmol) and an excess of selenium black were suspended in 5 mL of toluene and stirred for 15 min at room temperature. Subsequently, the solution was filtered off to remove insolubles and the solvent was evaporated in vacuo to leave a yellow oil. Upon addition of 5 mL of hexanes, a white precipitate was formed that was isolated by filtration and then redissolved in 5 mL of dichloromethane. Removal of the solvent left **3** as a pure white solid. Yield: 93% (66.8 mg, 8.16 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.81 (ddd, 8H, ^1J = 14.4 Hz, ^2J = 7.2 Hz, ^3J = 2.0 Hz), 7.78 (d, 2H, ^1J = 2.8 Hz), 7.74 (d, 2H, ^1J = 2.8 Hz), 7.39 (m, 12H), 7.21 (dd, 4H, ^1J = 8.0 Hz, ^2J = 2.4 Hz), 6.81 (dd, 2H, ^1J = 8.4 Hz, ^2J = 1.6 Hz), 3.51

(s, 6H, O*C*H$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 159.2, 139.2, 138.0 (d, J_{P-C} = 11.4 Hz), 135.6 (d, J_{P-C} = 2.2 Hz), 132.3 (d, J_{P-C} = 11.3 Hz), 130.9 (d, J_{P-C} = 3.1 Hz), 130.6, 129.1, 128.1 (d, J_{P-C} = 12.9 Hz), 127.7, 111.8, 55.4 (−O*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, ppm) δ 32.1 (s, J_{Se-P} = 724 Hz). Anal. Calcd for $C_{44}H_{36}O_2P_2Se_2$: C, 64.71; H, 4.44. Found: C, 64.75; H, 4.70.

***cis*-[PtCl$_2$(1)] (4).** $PtCl_2$(cod) (35.9 mg, 95.9 μmol) was dissolved in 15 mL of CH_2Cl_2, and to this solution was slowly added ligand **1** (65.1 mg, 95.5 μmol), dissolved in 15 mL of CH_2Cl_2. The solution was stirred overnight. After evaporation of the solvent in vacuo, **4** was obtained as a white powder. Single crystals, suitable for X-ray analysis, could be obtained by slow evaporation of $CDCl_3$ from an NMR tube.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.83 (br s, 8H, PPh_2), 7.51 (dd, 2H, ^1J = 5.2 Hz, ^2J = 2.8 Hz), 7.44 (dd, 2H, ^1J = 5.2 Hz, ^2J = 2.8 Hz), 7.23 (dd, 12H, PPh_2, ^1J = 8.8 Hz, ^1J = 2.4 Hz), 6.57 (dd, 2H, Ph, ^1J = 8.4 Hz, ^2J = 4.8 Hz), 6.35 (d, 2H, Ph, ^1J = 9.2 Hz), 5.64 (d, 2H, Ph), 3.61 (s, 6H, OCH_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, ppm) δ 9.9 (s, J_{Pt-P} = 3810 Hz). Anal. Calcd for $C_{44}H_{36}Cl_2O_2PtP_2$: C, 57.15; H, 3.92. Found: C, 57.25; H, 4.06.

***cis*-[PtCl$_2$(2)] (5).** $PtCl_2$(cod) (5.0 mg, 13.5 μmol) together with ligand **2** (8.5 mg, 13.5 μmol) were dissolved in 1 mL of CH_2Cl_2, and the solution was stirred for 1 h at room temperature. After evaporation of the solvent in vacuo, **5** was obtained as a white powder. Single crystals, suitable for X-ray analysis, could be obtained by slow diffusion of Et_2O into a $CDCl_3$ solution in an NMR tube.

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.59 (tq, 4H, ^2J = 7.5 Hz, ^3J = 1.5 Hz), 7.44 (tq, 4H, ^2J = 7.5 Hz, ^3J = 1.5 Hz), 7.38 (dt, 4H, ^2J = 7.5 Hz, ^3J = 2.5 Hz), 7.28 (dd, 2H, ^2J = 5.5 Hz, ^3J = 3.5 Hz), 7.21 (m, 12H), 7.08 (dt, 4H, ^2J = 7.5 Hz, ^3J = 1.5 Hz), 6.87 (dd, 2H, ^2J = 5.5 Hz, ^3J = 3.5 Hz). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, ppm) δ 8.2 (s, J_{Pt-P} = 3712 Hz). Anal. Calcd for $C_{42}H_{32}Cl_2PtP_2$: C, 58.34; H, 3.73. Found: C, 58.37; H, 3.64.

Hydroformylation of 1-Octene. The appropriate *cis*-[$PtCl_2$L] complex (13.7 μmol) was dissolved in 10 mL of dichloromethane and then added to an equimolar amount of $SnCl_2$ (2.6 mg, 13.7 μmol). After 2 h a yellow solution containing the platinum/tin complex was obtained. The autoclave was pretreated with three consecutive vacuum−argon cycles prior to use. The CH_2Cl_2 solution containing the preformed platinum/tin complex was transferred to the autoclave by syringe. An additional 10 mL of dichloromethane was added to the autoclave to get a total volume of 20 mL. The autoclave was pressurized to 40 bar and heated to 60 °C. After 1 h of preformation a mixture of the octene (3.0 mL, 19.0 mmol) and *n*-decane (1.0 mL, 5.1 mmol), dissolved in 6.0 mL of dichloromethane, was added at the desired pressure and temperature. The pressure was kept constant by using a gas line with a pressure regulator. After the reaction the autoclave was cooled to room temperature with an ice bath. After the autoclave was vented, a sample was taken from it and analyzed by GC to determine conversion, chemoselectivity, and regioselectivity.

Crystal Structure Determination. The data for **4** were collected on a Bruker SMART APEX CCD instrument. Data integration and global cell refinement were performed with the program SAINT. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[28] The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. The unit cell contains one molecule of $CDCl_3$, which is disordered over two positions. Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $R_w(F^2)$ = 0.0673 for 10 560 reflections and $R(F)$ = 0.0275 for 9320 reflections with $F_o \geq 4.0\ \sigma(F_o)$ and 677 parameters.

For **5**, a crystal with approximate dimensions 0.30 × 0.40 × 0.50 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation and $\omega-2\theta$ scan. Corrections for Lorentz and polarization effects were applied. Absorption correction was performed with the program PLATON,[29] following the method of North et al.[30] The structure was solved by the PATTY option of the DIRDIF99 program system.[28] The hydrogen atoms were calculated, and a riding model was used during refinement. Full-matrix least-squares refinement on F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, was used. A final difference Fourier map revealed a residual electron density between −1.56 and 2.04 e Å^{-3} in the vicinity of the Pt. Scattering factors were taken from Cromer and Mann and from the International Tables of Crystallography.[31] The anomalous scattering of Pt, P, and Cl was taken into account.[32] All calculations were performed with XTAL3.7,[33] unless stated otherwise.

The CCDC files 270182 and 275889 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033 and email deposit@ccdc.cam.uk).

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Supporting Information Available: X-ray crystallographic files (in CIF format) for Pt complexes **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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