

Synthesis, Structure, Dynamics, and Selective Methylation of Platinum and Palladium Diphosphametallacyclobutane Complexes

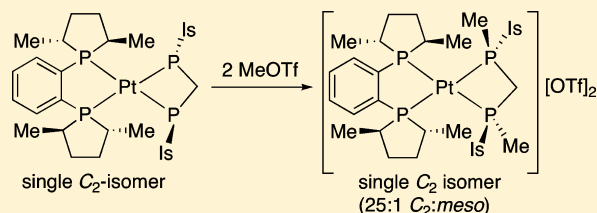
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S Supporting Information

ABSTRACT: Treatment of $M(\text{dppe})\text{Cl}_2$ ($M = \text{Pd}, \text{Pt}$) or $\text{Pt}((R,R)\text{-Me-DuPhos})\text{Cl}_2$ with $\text{IsHPCH}_2\text{P}(\text{H})\text{Is}$ (**1**; $\text{Is} = \text{isityl} = 2,4,6\text{-}(i\text{-Pr})_3\text{C}_6\text{H}_2$) and 2 equiv of NaOSiMe_3 gave the mononuclear diphosphametallacyclobutane complexes $M(\text{dppe})(\text{IsPCH}_2\text{P}(\text{H})\text{Is})$ ($M = \text{Pd}$ (**2**), Pt (**3**)), or $\text{Pt}((R,R)\text{-Me-DuPhos})(\text{IsPCH}_2\text{P}(\text{H})\text{Is})$ (**4**). Dynamic processes involving phosphorus inversion and rotation about the $\text{P}\text{--}\text{C}(\text{Is})$ bonds in **2**–**4** were characterized by variable-temperature NMR spectroscopy, which suggested that each existed as a single C_2 -symmetric diastereomer in solution, consistent with their solid-state structures determined by X-ray crystallography. The MiniPhos derivative $\text{IsMePCH}_2\text{P}(\text{H})\text{MeIs}$ (**5**) was prepared as a 5.5/1 *rac*/*meso* mixture by sequential arylation and methylation of $\text{Cl}_2\text{PCH}_2\text{P}(\text{H})\text{Cl}_2$. Alternatively, the catalyst precursor $\text{Pt}((R,R)\text{-Me-DuPhos})(\text{Ph})(\text{Cl})$ mediated alkylation of secondary phosphines in the presence of NaOSiMe_3 to yield selectively *meso*-**5** either from $\text{PHMe}(\text{Is})$ and CH_2I_2 or from **1** and MeI . Recrystallization and chromatography yielded diastereomerically enriched *rac*-**5** and *meso*-**5**. Treatment of $M(\text{dppe})(\text{OTf})_2$ ($M = \text{Pd}, \text{Pt}$) or $\text{Pt}((R,R)\text{-Me-DuPhos})(\text{OTf})_2$ with *meso*-**5** gave the dications *meso*- $[\text{M}(\text{diphos})(\text{IsMePCH}_2\text{P}(\text{H})\text{MeIs})][\text{OTf}]_2$ ($\text{M}(\text{diphos}) = \text{Pd}(\text{dppe})$ (**6**), $\text{Pt}(\text{dppe})$ (**8**), $\text{Pt}((R,R)\text{-Me-DuPhos})$ (**10**)). Similar reactions of *rac*-**5** yielded the dications *rac*- $[\text{M}(\text{diphos})(\text{IsMePCH}_2\text{P}(\text{H})\text{MeIs})][\text{OTf}]_2$ ($\text{M}(\text{diphos}) = \text{Pd}(\text{dppe})$ (**7**), $\text{Pt}(\text{dppe})$ (**9**)) and a 1/1 mixture of the C_2 -symmetric diastereomers $[\text{Pt}((R,R)\text{-Me-DuPhos})(\text{IsMePCH}_2\text{P}(\text{H})\text{MeIs})][\text{OTf}]_2$ (**11a,b**). Treatment of **2** and **3** with 2 equiv of methyl triflate gave the dications **6**–**9** as ca. 1/1 *meso*/*rac* mixtures, and methylation of **4** selectively gave one of the C_2 -symmetric diastereomers, **11a**. These alkylations proceeded via the observable monomethylated intermediates $[\text{M}(\text{diphos})(\text{IsMePCH}_2\text{P}(\text{H})\text{Is})][\text{OTf}]$ (**12**–**14**).



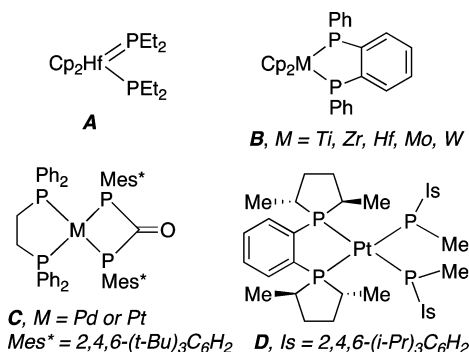
INTRODUCTION

Terminal metal phosphido complexes are important intermediates in catalytic reactions which form $\text{P}\text{--}\text{C}$ bonds, such as hydrophosphination of alkenes and phosphination of aryl or alkyl halides,¹ and in dehydrocoupling processes which lead to $\text{P}\text{--}\text{element}$ bond formation.² Structure, bonding, and reactivity in the $\text{M}\text{--}\text{PR}_2$ functional group has been studied in detail.³ Complexes with *two* terminal phosphido groups, some of which are stabilized by the chelate effect, are also known; some examples are shown in Chart 1.^{4–6}

However, mononuclear complexes of the simplest dianionic bis(phosphido) ligand, $(\text{R}(\text{PCH}_2\text{PR})_2)^{2-}$, have not been reported.⁷ Such diphosphametallacyclobutanes are of interest by analogy to the metallacyclobutanes shown to be intermediates in olefin metathesis.⁸ We hypothesized that large R groups would prevent the formation of μ -phosphido bridges⁹ and would make these complexes preferentially adopt the C_2 -symmetric conformation shown in Scheme 1, to avoid steric overcrowding in the *meso* form. The diastereomers *rac*-**E** and *meso*-**E** could interconvert by pyramidal inversion at the phosphido stereocenters, which typically occurs rapidly.¹⁰

Methylation of the nucleophilic phosphido groups^{1d} of **E** would give the chelating bis(tertiary phosphine) complex **F**

Chart 1. Selected Metal Bis(phosphido) Complexes



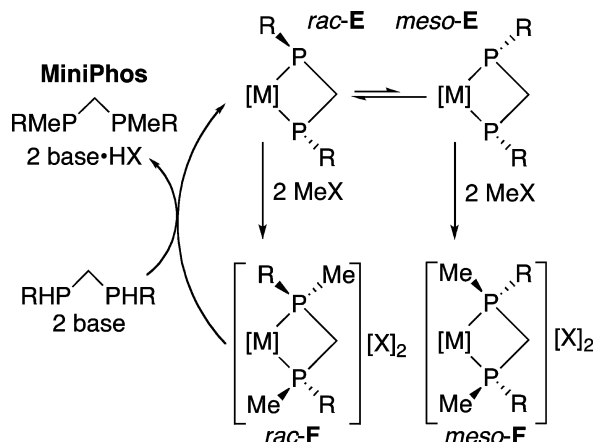
(Scheme 1). This is attractive, because Imamoto has shown that the P -stereogenic $\text{RMePCH}_2\text{P}(\text{H})\text{MeR}$ “MiniPhos” ligands are valuable in asymmetric catalysis.¹¹ If *rac*-**E** were present in greater concentration than *meso*-**E** and/or underwent alkylation more quickly, C_2 -symmetric *rac*-**F** might be the favored

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Scheme 1. Potential Synthesis of MiniPhos Ligands via Diphosphametallacyclobutanes



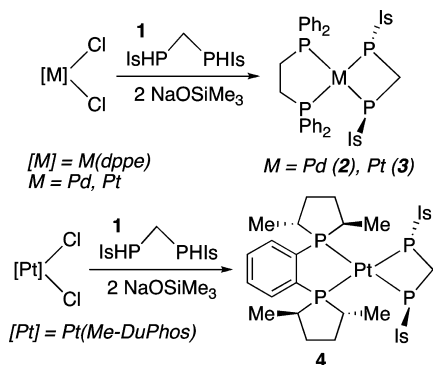
product. If a chiral ancillary ligand was used, this process could be enantioselective, favoring one enantiomer of complexed MiniPhos. Finally, steric crowding in the strained four-membered ring of F might enable dissociation of the chelate and, hence, catalytic turnover by conversion of F to E. To investigate these possibilities, we report here studies of platinum and palladium diphosphametallacyclobutane complexes.

RESULTS AND DISCUSSION

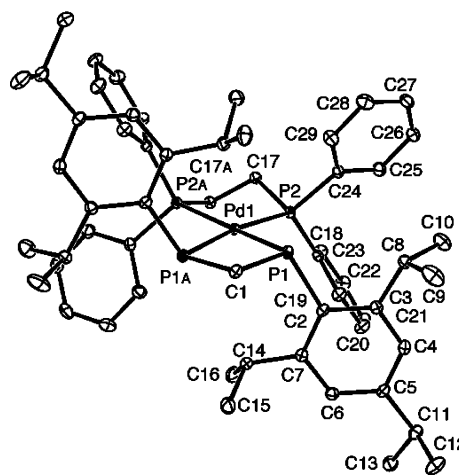
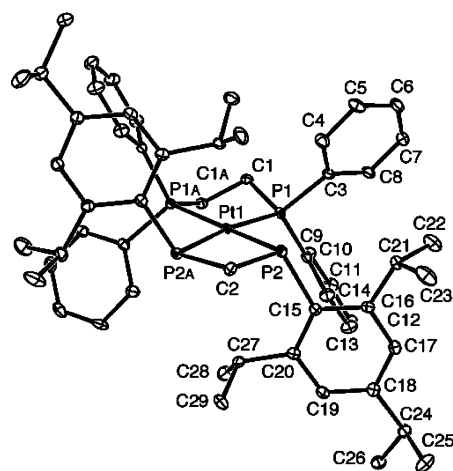
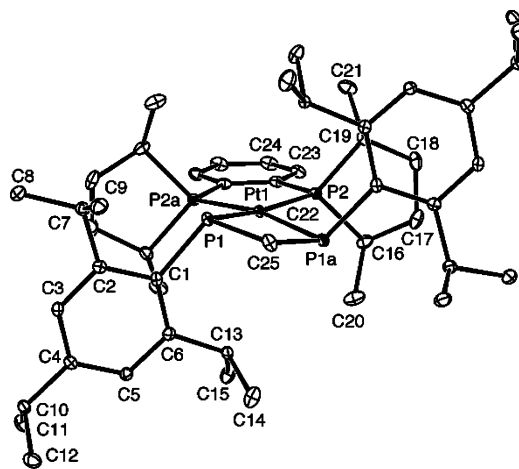
Synthesis and Solid-State Structures of Platinum and Palladium Diphosphametallacyclobutane Complexes.

Treatment of platinum and palladium dichloride precursors with the known bulky bis(secondary phosphine) IsHPCH₂PIs (**1**; Is = isityl = 2,4,6-(*i*-Pr)₃C₆H₂)¹² and 2 equiv of NaOSiMe₃ gave the target bis(phosphido) complexes M(dppe)(IsPCH₂PIs) (M = Pd (**2**), Pt (**3**)) and the sparingly soluble Pt((*R,R*)-Me-DuPhos)(IsPCH₂PIs) (**4**) as air-sensitive yellow crystalline solids (Scheme 2).

Scheme 2. Synthesis of Diphosphametallacyclobutane Complexes 2–4



The crystal structures of complexes **2–4** are shown in Figures 1–3; see Table 1 and the Supporting Information for details. In the solid state, the predicted sterically favored diastereomers were observed: *rac*-**2** and *rac*-**3** and a C₂-symmetric isomer of **4** (*S,S* configuration at the phosphido stereocenters), in which the bulky isityl groups avoided the quadrants occupied by the DuPhos phospholane methyl substituents.¹³

Figure 1. ORTEP diagram of Pd(dppe)(IsPCH₂PIs) (**2**).Figure 2. ORTEP diagram of Pt(dppe)(IsPCH₂PIs) (**3**).Figure 3. ORTEP diagram of Pt((*R,R*)-Me-DuPhos)((*S,S*)-IsPCH₂PIs) (**4**).

Complexes **2–4** adopted distorted-square-planar structures, constrained by the bite angles of the dppe and Me-DuPhos ligands and, more strikingly, by the 73° bite angle of the four-membered diphosphametallacyclobutane ring (Table 2). The phosphido P atoms were pyramidal, with angle sums of 314–

Table 1. Crystallographic Data for Pd(dppe)(IsPCH₂PIs) (**2**), Pt(dppe)(IsPCH₂PIs) (**3**), Pt((*R,R*)-Me-DuPhos)(IsPCH₂PIs) (**4**), *meso*-[Pd(dppe)(IsMePCH₂PMeIs)][OTf]₂·Et₂O (*meso*-6·Et₂O), *meso*-[Pt(dppe)(IsMePCH₂PMeIs)][OTf]₂·Et₂O (*meso*-8·Et₂O), and *rac*-[Pt(dppe)(IsMePCH₂PMeIs)][OTf]₂ (*rac*-9)

| | 2 | 3 | 4 | <i>meso</i> -6·Et ₂ O | <i>meso</i> -8·Et ₂ O | <i>rac</i> -9 |
|---|---|---|---|---|---|---|
| formula | C ₅₇ H ₇₂ P ₄ Pd | C ₅₇ H ₇₂ P ₄ Pt | C ₄₉ H ₇₆ P ₄ Pt | C ₆₅ H ₈₈ F ₆ O ₇ P ₄ PdS ₂ | C ₆₅ H ₈₈ F ₆ O ₇ P ₄ PtS ₂ | C ₆₁ H ₇₈ F ₆ O ₆ P ₄ PtS ₂ |
| formula wt | 987.43 | 1076.12 | 984.07 | 1389.75 | 1478.44 | 1404.32 |
| space group | C2/c | C2/c | C222 ₁ | P6 ₅ | P6 ₁ | PI |
| <i>a</i> , Å | 33.225(9) | 33.135(4) | 13.735(8) | 13.4460(10) | 13.4616(2) | 11.915(7) |
| <i>b</i> , Å | 9.898(3) | 9.8628(10) | 17.118(8) | 13.4460(10) | 13.4616(2) | 13.515(8) |
| <i>c</i> , Å | 18.448(4) | 18.4542(19) | 20.647(11) | 66.635(7) | 66.2129(15) | 21.619(13) |
| α, deg | 90 | 90 | 90 | 90 | 90 | 73.777(7) |
| β, deg | 121.377(3) | 121.312(2) | 90 | 90 | 90 | 77.495(8) |
| γ, deg | 90 | 90 | 90 | 120 | 120 | 68.875(9) |
| <i>V</i> , Å ³ | 5180(2) | 5152.5(9) | 4854(4) | 10433.2(15) | 10391.2(3) | 3092(3) |
| <i>Z</i> | 4 | 4 | 4 | 6 | 6 | 2 |
| <i>D</i> (calcd), g/cm ³ | 1.266 | 1.387 | 1.347 | 1.327 | 1.418 | 1.508 |
| μ(Mo Kα), mm ⁻¹ | 0.517 | 2.883 | 3.053 | 4.122 | 5.767 ^a | 2.507 |
| temp, K | 100(2) | 150(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| <i>R</i> (<i>F</i>), % ^b | 3.96 | 3.75 | 1.80 | 4.96 | 3.98 | 4.68 |
| <i>R</i> _w (<i>F</i> ²), % ^b | 11.89 | 10.02 | 3.72 | 13.17 | 9.83 | 11.18 |

^aCu Kα radiation was used. ^bQuantity minimized: $R_w(F^2) = \sum [w(F_o^2 - F_c^2)^2] / \sum [(wF_o^2)^{1/2}]$; $R = \sum \Delta / \sum (F_o)$, $\Delta = |F_o - F_c|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \text{Max}(F_o^2, 0)]/3$. A Bruker CCD diffractometer was used in all cases.

315° (compare to 328.5° for ideal tetrahedral coordination or 360° for trigonal-planar geometry).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Diphosphametallacyclobutane Complexes M(diphos)(IsPCH₂PIs) (**2–4**)

| | M(diphos) (compd no.) | | |
|--------------------------|-----------------------|-----------------------|----------------------------|
| | Pd(dppe) (2) | Pt(dppe) (3) | Pt(Me-DuPhos) (4) |
| M–P(diphos) | 2.3747(7) | 2.3238(12) | 2.2803(9) |
| M–P(Is) | 2.3554(8) | 2.3595(13) | 2.3464(10) |
| P–M–P(diphos) | 85.46(4) | 85.53(6) | 86.90(4) |
| P–M–P(Is) | 72.48(4) | 73.28(6) | 73.43(4) |
| P–M–P(trans) | 172.06(2) | 172.71(4) | 168.94(2) |
| P–M–P(cis) | 101.22(3) | 100.73(4) | 100.51(4) |
| P–C–P | 96.26(17) | 97.0(3) | 97.10(13) |
| M–P(Is)–CH ₂ | 95.63(9) | 94.84(17) | 94.74(7) |
| M–P–C(Is) | 112.15(8) | 113.59(16) | 113.84(8) |
| CH ₂ –P–C(Is) | 106.61(9) | 105.94(18) | 106.66(8) |
| sum of angles P(Is) | 314.39(9) | 314.37(18) | 315.24(8) |

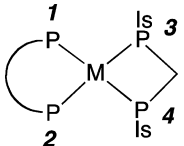
Solution Structures of the Diphosphametallacyclobutane Complexes. Dppe complexes **2** and **3** could exist as mixtures of *rac* and *meso* diastereomers, while the bis-(phosphido) ligand in **4** could have an *RR*, *RS*, or *SS*

configuration, giving rise to three diastereomers. However, ³¹P and ¹H NMR spectra at room temperature showed only one set of peaks for each complex. The ³¹P NMR spectra (AA'XX' patterns; Table 3) were consistent with the expected square-planar structures and chemical shifts and coupling constants observed for related Pt and Pd phosphido complexes.^{14,4d,9,3c}

The room-temperature ¹H NMR spectra of **2–4** included six *i*-Pr Me signals and three *i*-Pr CH signals, indicating that the two sides of the isityl groups were inequivalent (the Is aryl proton signals overlapped with other peaks). For complexes **2** and **3**, the dppe CH₂ signals gave rise to complicated ¹H NMR multiplets (AA'XX'MM'NN' spin systems); the ³¹P-decoupled AA'XX' patterns were successfully simulated using gNMR and the *J*_{PP} values were obtained from the ³¹P NMR spectra.¹⁵ The PCH₂P ¹H NMR signals of **2–4** were also complex multiplets.

In variable-temperature (VT) ¹H NMR studies, heating a toluene-*d*₈ solution of Pt complex **3** resulted in coalescence of the *i*-Pr signals to give spectra with three (instead of six) Me peaks and two (instead of three) CH resonances. Similarly, the dppe CH₂ multiplet coalesced to a singlet. Measurement of the coalescence temperatures and standard analysis provided approximate free energies of activation at the coalescence temperatures for the relevant dynamic process (Table 4).¹⁶ The good agreement between the data obtained for these five

Table 3. ³¹P NMR Data for Diphosphametallacyclobutane Complexes **2–4**^a

| complex (compd no.) |  | | <i>J</i> ₁₂ | <i>J</i> ₁₃ | <i>J</i> ₁₄ | <i>J</i> ₃₄ |
|--|---|---------------------------------------|------------------------|------------------------|------------------------|------------------------|
| | δ(P1/P2) (<i>J</i> _{Pt–P}) | δ(P3/P4) (<i>J</i> _{Pt–P}) | | | | |
| Pd(dppe)(IsPCH ₂ PIs) (2) ^b | 24.5 | –159.5 | 15 | –29 | 66 | 11 |
| Pt(dppe)(IsPCH ₂ PIs) (3) ^b | 39.1 (2101) | –154.3 (819) | 0 | –13 | 105 | 40 |
| Pt((<i>R,R</i>)-Me-DuPhos)(IsPCH ₂ PIs) (4) ^c | 58.4 (1993) | –156.3 (826) | 10 | –15 | 105 | 45 |

^aData were obtained at 21 °C. The chemical shift standard was 85% H₃PO₄. Coupling constants are given in Hz. ^bToluene-*d*₈. ^cC₆D₆.

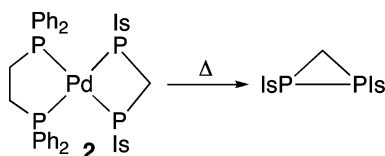
Table 4. Variable-Temperature ^1H NMR Data for Diphosphametallacyclobutane Complexes 2–4^a

| M(dipho) (compd no.) | resonance | δ (ppm) | $\Delta\nu$ (Hz) | T_c (K) | ΔG_c^\ddagger (kcal/mol) |
|--------------------------------|----------------------|----------------|------------------|-----------|----------------------------------|
| Pd(dppe) (2) | <i>i</i> -Pr CH | 5.06, 4.70 | 183 | 401 | 19 |
| | <i>p</i> -Me | 1.42, 1.41 | 4 | 338 | 18 |
| Pt(dppe) (3) | <i>i</i> -Pr CH | 5.04, 4.84 | 100 | 366 | 18 |
| | dppe CH ₂ | 1.89, 1.84 | 22 | 323 | 17 |
| | <i>o</i> -Me | 1.71, 1.49 | 107 | 366 | 18 |
| | <i>p</i> -Me | 1.375, 1.369 | 3 | 304 | 17 |
| | <i>o</i> -Me | 1.06, 0.96 | 49 | 356 | 18 |
| Pt(<i>R,R</i>)-Me-DuPhos (4) | <i>i</i> -Pr CH | 5.42, 5.29 | 65 | 401 | 20 |
| | <i>o</i> -Me | 1.69, 1.60 | 43 | 346 | 17 |
| | <i>o</i> -Me | 1.66, 1.49 | 88 | 401 | 20 |
| | | | | | |

^aThe solvent was toluene-*d*₈ for 3 and *p*-xylene-*d*₁₀ for 2 and 4. Chemical shifts, $\Delta\nu$ values, and coupling constants are from slow-exchange spectra at 21 °C. Estimated errors are different for each resonance; “typical” errors are 5 Hz in $\Delta\nu$, 10 °C in T_c , and 0.5 kcal/mol in ΔG_c^\ddagger .

different groups of signals suggested that the same process is responsible in each case, with a barrier of about 18 kcal/mol.

Analogous VT NMR studies of Pd(dppe) complex 2 were complicated by its partial decomposition on heating to yield the known diphosphirane¹⁷ IsPCH₂PIs in an apparent P–P reductive elimination process (Scheme 3).¹⁸

Scheme 3. Thermal Decomposition of 2

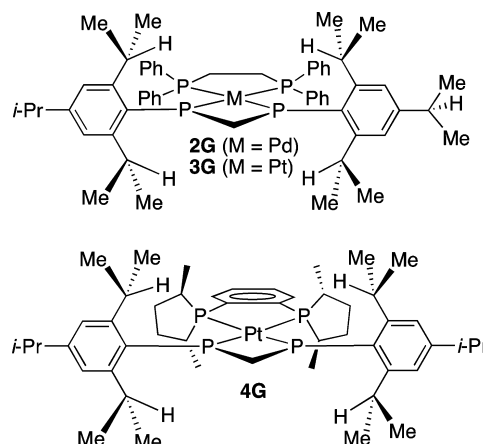
Nonetheless, coalescence phenomena similar to those for 3 were observed in 2 and 4, although for fewer groups of signals. Analysis of these data (Table 4) showed that the barriers to the dynamic processes involved (about 18 kcal/mol for 2 and 19 kcal/mol for 4) were very similar to that for 3.

Dynamic Processes in Diphosphametallacyclobutane Complexes 2–4. What are the solution structures of 2–4, and what dynamic process is responsible for these NMR observations? An answer to these questions should also explain why only one set of NMR signals was observed for each complex, despite the potential presence of diastereomers. The simplest explanation for the latter observations is that the solid-state structures are maintained in solution and the other possible isomers (*meso* for 2 and 3 or *meso* and *R,R* for DuPhos complex 4) are not present in NMR-detectable concentrations. For 4, this is consistent with the ^1H NMR AA'MM'NN' PCH₂P signals, because these hydrogens would be inequivalent in the *meso* isomer.

Likely dynamic processes include phosphido pyramidal inversion and rotation about the P–C(Is) bonds.^{14b,c} In dppe complexes 2 and 3, slow rotation about the P–C(Is) bonds on the NMR time scale would be consistent with the room-temperature observation of inequivalent *o*-*i*-Pr groups. Fast rotation on the NMR time scale at higher temperature would

make them equivalent and match the experimental observations.

Alternatively, if phosphido inversion was fast on the NMR time scale, then planar structure **G** would be accessible transiently (Chart 2). This analysis assumes that the puckered

Chart 2. Planar Structures **G** Accessible via Phosphido Inversion in dppe Complexes 2 and 3 (M = Pd, Pt) and DuPhos Complex 4

dppe chelate, as commonly observed, can access a conformation in which the square plane of the molecule is a plane of symmetry.¹⁹ Further, the P–Is groups must be able to reach the position perpendicular to this plane, as shown. Then, the molecular symmetry plane would make equivalent the *o*-*i*-Pr groups above and below it, as well as the *p*-*i*-Pr Me groups.^{14h} Finally, this plane, along with rotation about a C₂ axis, would make all the dppe CH₂ hydrogens equivalent, matching the experimental coalescence behavior. Thus, fast phosphido inversion on the NMR time scale, via **G**, would be consistent with all of the high-temperature NMR observations for Pt complex 3. In contrast, fast rotation about the P–C(Is) bonds would have no effect on the dppe CH₂ ^1H NMR signals. Therefore, we conclude that phosphorus inversion via a planar transition state is the dynamic process responsible for the VT NMR behavior of Pt complex 3.

At low temperature, the NMR observations require that both P inversion and rotation about the P–C(Is) bonds in 3 is slow. Inversion must be fast on the NMR time scale at high temperature, but we cannot determine from the data if the rotation process is fast or slow under these conditions. However, indirect evidence on this point was obtained from VT NMR analysis of DuPhos complex 4 (see below).

Slow inversion on the NMR time scale at room temperature means that the single set of ^{31}P and ^1H NMR signals observed for 3 at room temperature cannot be an average spectrum resulting from fast interconversion between *rac* and *meso* diastereomers. Instead, it is most simply explained by the dominant presence of one thermodynamically favored isomer, likely the C₂-symmetric one observed in the solid state. Although the VT NMR behavior of Pd complex 2 was less well-behaved, the similarity of the structures and spectra of 2 and 3 and their identical barriers for the dynamic processes suggest that the same conclusions apply for 2.

The reduced symmetry of DuPhos complex 4 has significant effects on related analyses. In particular, in planar structure **4G** (Chart 2), the presence of the chiral phospholane groups

means that the *i*-Pr groups above and below the square plane of the molecule are not equivalent, since, unlike the case for **2G** and **3G**, this is not a symmetry plane. Therefore, rapid phosphido inversion on the NMR time scale would not affect the number of *i*-Pr Me and CH ¹H NMR signals. In contrast, as for **2** and **3**, fast rotation about the P–C(Is) bonds in **4** at high temperature would be consistent with the observed coalescence behavior of the *i*-Pr signals. At room temperature, this process must be slow on the NMR time scale, but we cannot determine if P inversion is fast or slow under these conditions.

Thus, in Pt(dppe) complex **3**, the dynamic process responsible for the VT NMR observations is P inversion, while P–C(Is) rotation must be slow at room temperature, but we cannot evaluate its rate at high temperature. The conclusions are reversed for Pt(DuPhos) complex **4**, in which P–C(Is) rotation accounts for the coalescence behavior, but we cannot tell directly if P inversion is fast or slow. The structural similarity of these complexes and the near-identical barriers to their dynamic processes suggest that their fluxional behavior is the same. Thus, it is likely that both P inversion and P–C(Is) rotation are slow on the NMR time scale in both **3** and **4** at low temperature and fast at high temperature. In fact, these motions might be correlated, and the measured barriers may correspond to a composite process.

As for **3**, slow P inversion in **4** at room temperature suggests that a single set of NMR signals was observed for **4** because one of its three possible diastereomers is favored in solution. Although we did not investigate the absolute stereochemistry of **4**, steric considerations suggest the C₂-symmetric (*S,S*)-IsPCH₂PIs solid-state structure is maintained in solution.

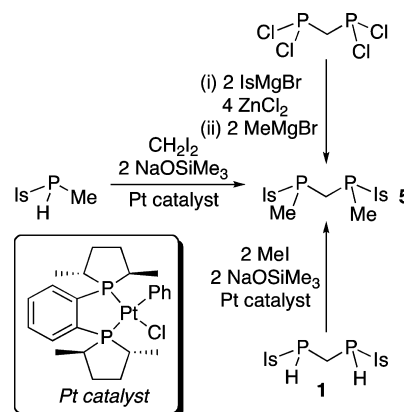
Methylation of Bis(phosphido) Complexes 2–4: Independent Synthesis and Structure of the Products. These conclusions substantiated the first hypothesis of Scheme 1, that the preferred geometry of diphosphametalacyclobutane complexes **2**–**4** would be C₂-symmetric, not *meso*. With the chiral ligand (*R,R*)-Me-DuPhos, one of the two possible C₂-symmetric diastereomers ((*S,S*)-IsPCH₂PIs) also appeared to be preferred strongly for **4**. Would these structural preferences lead to selective methylation (Scheme 1)?

To find out, we prepared the expected products of methylation, the dicationic [M(diphos)(IsMePCH₂PMeIs)]-[OTf]₂ (**6**–**11**). The bis(tertiary phosphine) IsMePCH₂PMeIs (**5**) was synthesized by three different methods (Scheme 4). Sequential treatment of commercially available Cl₂PCH₂PCl₂ with 2 equiv of IsMgBr/ZnCl₂ and 2 equiv of MeMgBr gave a 5.5/1 mixture of *rac*- and *meso*-**5**. Recrystallization from acetone gave highly enriched *rac*-**5**. A combination of recrystallization and chromatography on the mixture of borane adducts *rac*- and *meso*-IsMeP(BH₃)CH₂P(BH₃)MeIs (**5**-BH₃) enabled isolation of enriched *meso*-**5**.²⁰

Alternatively, alkylation of bis(secondary phosphine) **1** with MeI was catalyzed by Pt((*R,R*)-Me-DuPhos)(Ph)(Cl) in the presence of NaOSiMe₃. The same Pt catalyst and base mediated coupling of 2 equiv of PHMe(Is) with diiodomethane. Both reactions were *meso*-selective, with low diastereoselectivity and enantioselectivity (Scheme 4); they also led to the formation of byproducts (Experimental Section).

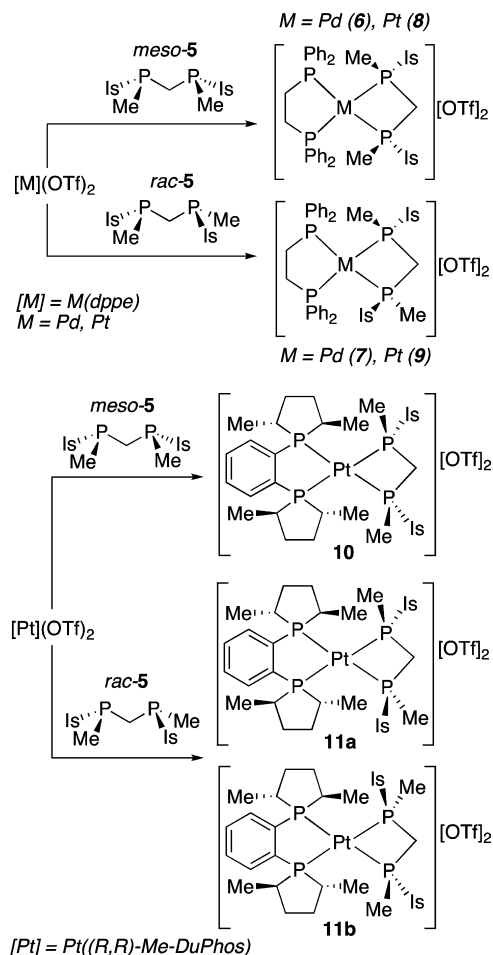
The dicationic complexes [M(diphos)(IsMePCH₂PMeIs)]-[OTf]₂ (**6**–**11**) were prepared selectively by separate reactions of *meso*-**5** or *rac*-**5** with the known triflate complexes M(dppe)(OTf)₂ (M = Pd, Pt)²¹ or Pt((*R,R*)-Me-DuPhos)-(OTf)₂ (Scheme 5).^{4d}

Scheme 4. Direct and Pt-Catalyzed Syntheses of MiniPhos Derivative **5**^a

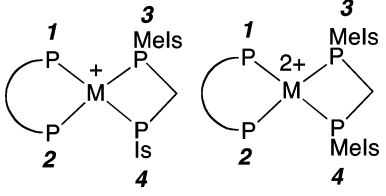


^aFor the synthesis of **5** from Cl₂PCH₂PCl₂, the *dr* (*rac*/*meso* ratio) was 5.5/1. The Pt-catalyzed formation of **5** was *meso*-selective. For the synthesis of **5** from **1**, *dr* = 1/2.2 and *er* (enantiomeric ratio) = 3.5. For the synthesis of **5** from PHMe(Is), *dr* = 1/3.2 and *er* = 1.1.

Scheme 5. Synthesis of *meso*- and *rac*-MiniPhos Complexes **6**–**11**



The stereochemistry of complexed IsMePCH₂PMeIs (**5**) in these dicationic complexes was identified by their characteristic AA'XX' (*rac*) or ABXY (*meso*) ³¹P NMR spectra (Table S). Methylation led to the expected increases in *J*_{P–P} and *J*_{Pt–P} coupling constants as the bis(phosphido) ligands in **2**–**4** were

Table 5. ^{31}P NMR Data for Intermediates 12–14 and Cationic MiniPhos Complexes 6–11^a


| complex (compd no.) | $\delta(\text{P1/P2})$ ($J_{\text{Pt-P}}$) | $\delta(\text{P3/P4})$ ($J_{\text{Pt-P}}$) | J_{12} | $J_{13}^{13}\text{C}^b$ | J_{14} [J_{23}^b] | J_{34} |
|---|--|--|----------------|-------------------------|-------------------------|----------|
| $[\text{Pd}(\text{dppe})(\text{IsMePCH}_2\text{Pis})][\text{OTf}]$ (12a) | 40.5, ^c 35.0 | −89.6, −94.8 | 42 | 22 [d] | 48 [342] | 12 |
| $[\text{Pd}(\text{dppe})(\text{IsMePCH}_2\text{Pis})][\text{OTf}]$ (12b) | 40.5, ^c 36.8–35.8 | −103.9 | d | d | [365] | d |
| $[\text{Pt}(\text{dppe})(\text{IsMePCH}_2\text{Pis})][\text{OTf}]$ (13) | 43.3 (1824), 40.1 (2644) | −87.4 (2246), −114.3 (764) | 8 ^e | d [25] ^e | 73 [348] | d |
| $[\text{Pt}((R,R)\text{-Me-DuPhos})(\text{IsMePCH}_2\text{Pis})][\text{OTf}]$ (14) | 68.0 (1710), 60.7 (2219) | −85.6 (2214), −113.6 (705) | 11 | 6 [d] | 64 [351] | 26 |
| <i>meso</i> - $[\text{Pd}(\text{dppe})(\text{IsMePCH}_2\text{PMeIs})][\text{OTf}]_2$ (6) | 55.4 | −86.0 | 22 | 7 | 375 | 79 |
| C_2 - $[\text{Pd}(\text{dppe})(\text{IsMePCH}_2\text{PMeIs})][\text{OTf}]_2$ (7) | 56.6 | −71.3 | 20 | 1 | 358 | 75 |
| <i>meso</i> - $[\text{Pt}(\text{dppe})(\text{IsMePCH}_2\text{PMeIs})][\text{OTf}]_2$ (8) | 44.4 (2333) | −83.4 (1973) | 7 | −6 | 333 | 54 |
| C_2 - $[\text{Pt}(\text{dppe})(\text{IsMePCH}_2\text{PMeIs})][\text{OTf}]_2$ (9) | 45.8 (2313) | −78.2 (1940) | 6 | −13 | 320 | 57 |
| <i>meso</i> - $[\text{Pt}((R,R)\text{-Me-DuPhos})(\text{IsMePCH}_2\text{PMeIs})][\text{OTf}]_2$ (10) | 69.7 (2268), 69.0 (2198) | −72.8 (1856), −76.4 (1997) | 5 | 9 [7] | 318 [324] | 53 |
| C_2 - $[\text{Pt}((R,R)\text{-Me-DuPhos})(\text{IsMePCH}_2\text{PMeIs})][\text{OTf}]_2$ (11a) | 71.4 (2253) | −58.8 (1932) | 5 | −13 | 307 | 49 |
| C_2 - $[\text{Pt}((R,R)\text{-Me-DuPhos})(\text{IsMePCH}_2\text{PMeIs})][\text{OTf}]_2$ (11b) | 69.9 (2138) | −76.9 (1969) | 5 | −14 | 303 | 65 |
| $[\text{Pt}(\text{dppe})(\text{dppm})][\text{BPh}_4]_2$ ^{23f} | 48.8 (2312) | −38.9 (1959) | ±5.7 | −11.1 | 309.8 | ±57.5 |

^aThe chemical shift standard was 85% H_3PO_4 . Coupling constants are given in Hz. Negative values of coupling constants were obtained from simulation of AA'XX' patterns; coupling constants in ABXY spin systems are absolute values. See ref 23 for comments on the signs of coupling constants in related compounds. The solvent was CH_2Cl_2 for **12–14**, CDCl_3 for $[\text{Pt}(\text{dppe})(\text{dppm})][\text{BPh}_4]_2$, and CD_2Cl_2 for all other compounds.

^bThe additional couplings J_{23} and J_{24} are included for ABXY spin systems (**10**, **12–14**). ^cOverlapping peaks from major and minor isomers **12a,b**.

^dNot observed (in some cases due to broad signals). ^eThe broadness of the signals precluded unambiguous assignment of these small couplings, which could be interchanged. ^fData for a related dicationic complex are included for comparison.

quaternized.⁹ The ^1H NMR spectra of the PCH_2P groups in **6–11** could also be used to characterize the *rac* and *meso* diastereomers. As in the free phosphines *rac*- and *meso*-**5**,²² these PCH_2P hydrogens were equivalent in the C_2 -symmetric *rac* isomers but showed significantly different chemical shifts in the *meso* complexes. For example, in the ^1H NMR spectrum of *meso*-Pd complex **6** (CD_2Cl_2), the CH_2 signals appeared at δ 6.27–6.17 and 3.93–3.85, respectively, with $J_{\text{HH}} = 16$ Hz.

The ^{31}P NMR spectra (AA'XX' patterns) of the two C_2 -symmetric diastereomeric DuPhos complexes **11a,b** were similar (Table 5), but their ^1H NMR spectra differed: restricted rotation about the P–C(Is) bonds in **11b** gave rise to two Is aryl signals, three *i*-Pr CH peaks, and six *i*-Pr Me signals. In contrast, several of the analogous signals for **11a** were broad, but only one Is-Ar, two CH, and three Me peaks were observed. Although we did not carry out NOESY studies to determine the absolute stereochemistry of **11a,b** or of their precursor **4**, we suppose that **11a** contains (S,S)-MiniPhos, in which the bulky Is substituents, as in **4**, are oriented to avoid the quadrants occupied by the DuPhos methyl groups. The expected greater steric hindrance for (R,R)-**11b** would then be consistent with the observed restricted rotation.

The crystal structures of the isomorphous Pd and Pt dppe complexes *meso*-**6**·Et₂O and *meso*-**8**·Et₂O and of the Pt(dppe) complex *rac*-**9** (Figures 4–6 and Tables 1 and 6) confirmed the stereochemical assignments. As anticipated by the presence of the two bulky isityl groups and their forced proximity in the *meso* isomers, the structures of **6** and **8** were distorted from planarity. While the metal and three of the P atoms occupied the square plane, P3 was more than 1 Å out of the plane in both

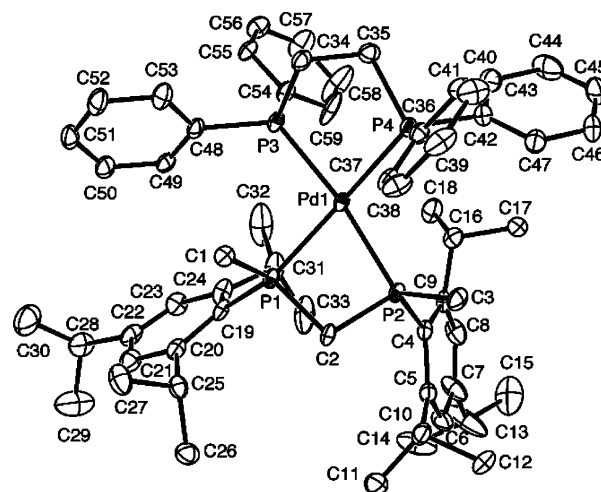


Figure 4. ORTEP diagram of *meso*- $[\text{Pd}(\text{dppe})(\text{IsMePCH}_2\text{PMeIs})][\text{OTf}]_2 \cdot \text{Et}_2\text{O}$ (*meso*-**6**·Et₂O). The anions and solvent are not shown.

cases. Note that these solid-state structures are not consistent with the solution ^{31}P NMR spectra (AA'XX' spin systems), which suggests more conformational flexibility in solution. In contrast, in *rac*-**9**, Pt and all four P atoms were essentially coplanar.

The structures of neutral precursors *rac*-**2** and *rac*-**3** and dications *meso*-**6** and *meso*-**8** were remarkably similar (compare the data in Tables 2 and 6), considering their differences in charge, stereochemistry, and chelate ligands. The bite angles of the dppe and four-membered-ring ligands showed little change

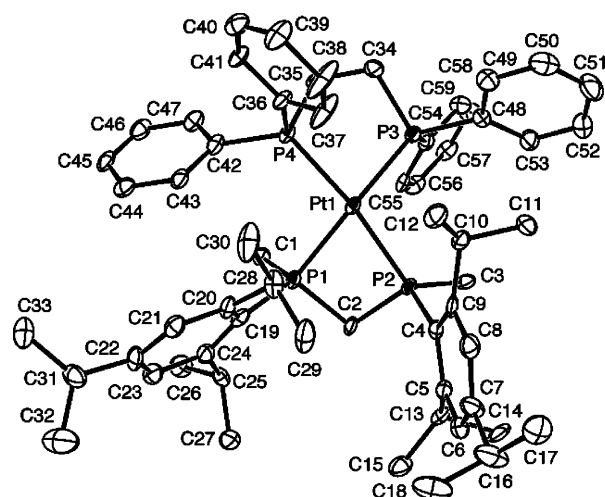


Figure 5. ORTEP diagram of *meso*-[Pt(dppe)(IsMePCH₂PMeIs)]·[OTf]₂·Et₂O (*meso*-8·Et₂O). The anions and disorder in an *i*-Pr group (C33) are not shown.

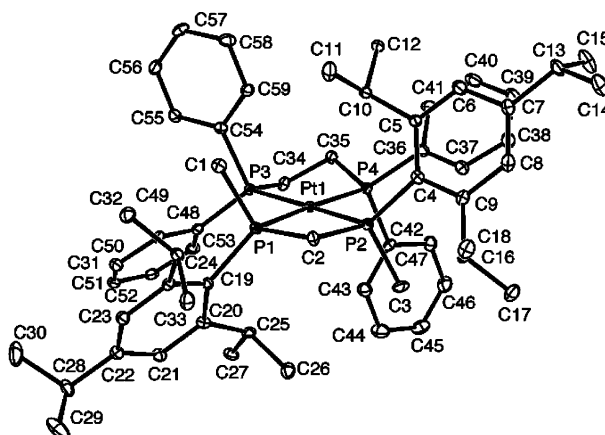
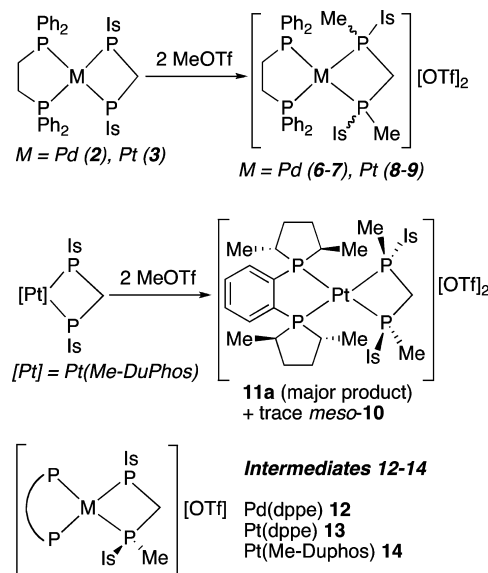


Figure 6. ORTEP diagram of *rac*-[Pt(dppe)(IsMePCH₂PMeIs)]·[OTf]₂ (*rac*-9). The disordered triflate anions are not shown.

on methylation, suggesting that these constraints control the geometries despite the expected effects of steric hindrance. Similarly, bond lengths and angles in the diastereomeric Pt complexes *meso*-8 and *rac*-9 were very similar, despite their large steric differences. However, in contrast to the distorted-square-planar solid-state structures of 6 and 8, Pt and all four P atoms in 9 were essentially coplanar.

Methylation of 2–4: Selectivity. On treatment of complexes 2–4 with 2 equiv of methyl triflate in CH₂Cl₂, monomethylation occurred in minutes to give the intermediates [M(diphos)(IsMePCH₂PIs)][OTf] (12–14), which were observed by ³¹P NMR spectroscopy (Scheme 6 and Table 5). These cations could exist as mixtures of diastereomers, but only one set of signals was observed at room temperature for Pt complexes 13 and 14 and a 9/1 mixture for Pd complex 12.

Scheme 6. Methylation of 2–4 with Methyl Triflate



These observations are most simply explained by diastereoselective methylation; we did not investigate potential dynamic processes in these intermediates further.

The second alkylation was much slower, forming ca. 1/1 *meso*/*rac* mixtures of the dications [M(dppe)(IsMePCH₂PMeIs)][OTf]₂ (M = Pd (6, 7), Pt (8, 9)) after several hours. Recrystallization of the 6/7 mixture gave a pure sample of *rac*-7. In contrast, methylation of the DuPhos complex 4 was more selective, yielding a ca. 25/1 mixture of *C*₂-symmetric [Pt((*R,R*)-Me-DuPhos)(IsMePCH₂PMeIs)][OTf]₂ (11a) and *meso*-[Pt((*R,R*)-Me-DuPhos)(IsMePCH₂PMeIs)][OTf]₂ (10), along with small amounts of other unidentified products. However, the other possible *C*₂-symmetric diastereomer 11b was not formed (Scheme 6).

CONCLUSION

The monomeric diphosphametallacyclobutane complexes reported here showed the structural features anticipated from their design; the *C*₂-symmetric conformation of the bis-(phosphido) ligand was favored over the *meso* form, resulting in formation of a single isomer for dppe complexes 2 and 3. Moreover, only one of the two possible *C*₂-symmetric diastereomers was observed for DuPhos complex 4. Although methylation of the dppe complexes 2 and 3 was not diastereoselective, that of DuPhos complex 4 led selectively to one enantiomer of complexed MiniPhos, as desired. To translate this stoichiometric reaction into an enantioselective catalytic process requires dissociation of the chelate diphosphine product, which might be promoted with Pd or Ni instead of Pt catalysts, and with bulkier chiral diphosphines, in order to destabilize dications such as 11 further. Further investigations of these ideas are in progress.

Table 6. Selected Bond Lengths (Å) and Angles (deg) in the Dicationic Complexes *meso*-[M(dppe)(IsMePCH₂PMeIs)][OTf]₂ (M = Pd (6·Et₂O), Pt (8·Et₂O)) and *rac*-[Pt(dppe)(IsMePCH₂PMeIs)][OTf]₂ (9)

| complex | M–P (dppe) | M–P (Is) | P–M–P (dppe) | P–M–P (Is) | P–M–P (trans) | P–M–P (cis) |
|---------------------|------------------------|------------------------|--------------|------------|----------------------|----------------------|
| 6·Et ₂ O | 2.3328(14), 2.3501(13) | 2.3203(13), 2.3706(13) | 83.56(5) | 73.43(5) | 153.08(4), 172.08(5) | 98.67(5), 103.22(5) |
| 8·Et ₂ O | 2.3316(15), 2.3197(14) | 2.3203(16), 2.3578(14) | 83.60(5) | 73.17(5) | 153.65(5), 172.36(6) | 99.19(5), 103.22(5) |
| 9 | 2.3352(17), 2.3239(16) | 2.3524(17), 2.3511(17) | 83.67(7) | 72.06(6) | 174.04(5), 174.08(5) | 102.02(7), 102.25(6) |

EXPERIMENTAL SECTION

General Experimental Details. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20 °C in a drybox or using standard Schlenk techniques. Petroleum ether (bp 38–53 °C), CH₂Cl₂, ether, THF, and toluene were dried over alumina columns similar to those described by Grubbs.²⁴ NMR spectra were recorded using Varian 300 or 500 MHz spectrometers. ¹H or ¹³C NMR chemical shifts are reported vs Me₄Si and were determined by reference to the residual ¹H or ¹³C solvent peaks. ³¹P NMR chemical shifts are reported vs H₃PO₄ (85%) used as an external reference. Coupling constants are reported in Hz, as absolute values unless noted otherwise. Unless indicated, peaks in NMR spectra are singlets. Instead of the expected quartet resonances²⁵ in the ³¹P NMR spectra of the phosphine–borane, a poorly resolved multiplet was observed. Elemental analyses were provided by Quantitative Technologies Inc. Mass spectra were recorded at the University of Illinois, Urbana–Champaign (<http://www.scs.uiuc.edu/~msweb>).

Reagents were from commercial suppliers, except for these compounds, which were made by the literature procedures: Pt((*R,R*)-Me-Duphos)(Ph)(Cl),²⁶ Pt(dppe)Cl₂ and Pd(dppe)Cl₂,²⁷ Pt((*R,R*)-Me-DuPhos)Cl₂,²⁸ Pt(dppe)(OTf)₂ and Pd(dppe)(OTf)₂,²¹ Pt((*R,R*)-Me-DuPhos)(OTf)₂^{4d} and PHMe(Is).²⁹

IsH(BH₃)P(CH₂)P(BH₃)HIs (1-BH₃). This synthesis of the diphosphine IsHP(CH₂)PHIs (1) was modified from a literature procedure; formation and isolation of the borane adduct is new.¹² Under nitrogen, a Schlenk flask was loaded with Mg powder (1.87 g, 76.8 mmol, 2 equiv, 50 mesh, Aldrich), which was then slurried in 5 mL of THF. A solution of 2-bromo-1,3,5-triisopropylbenzene (21.8 g, 76.8 mmol, 2 equiv) in 30 mL of THF was added dropwise via cannula with stirring. Two drops of 1,2-dibromoethane were added to initiate the reaction. The mixture was gently refluxed for 1 h and then stirred for 14 h. The resulting dark gray solution was transferred via cannula to a cooled (–40 °C) solution of Cl₂PCH₂PCl₂ (8.2 g, 38 mmol, 1 equiv) in 100 mL of THF. A solution of anhydrous ZnCl₂ (20.9 g, 153.6 mmol, 4 equiv) in 500 mL of THF was added via cannula; a white solid precipitated. The solution was stirred at –40 °C for 5 h. The mixture was transferred via wide-bore cannula to a filter frit with a Celite bed (3 cm high × 6 cm wide) and filtered under N₂. The solid was washed with two 100 mL portions of Et₂O, and the solvent was removed from the filtrate under reduced pressure.

The residue was redissolved in 200 mL of Et₂O (at this stage, the intermediate IsClPCH₂PClIs could be observed by ³¹P NMR (δ 71.0, 64.2)) and the solution with some white precipitate was transferred via filter cannula to a slurry of LiAlH₄ (1.46 g, 38.4 mmol, 1 equiv) in Et₂O (ca. 20 mL) at 0 °C. The resulting mixture was stirred for 1 h and then triethanolamine (5.6 mL, 42 mmol, 1 equiv) was injected via wide bore syringe at 0 °C, producing some effervescence. The solution was warmed to room temperature and was stirred vigorously overnight, causing the residual gray solid to become very finely divided. To this was added degassed H₂O (ca. 40 mL), generating minimal effervescence. The mixture was transferred via wide-bore cannula to a filter frit with a Celite bed (3 cm high × 6 cm wide) and filtered under N₂. The gray solid was washed with two 100 mL portions of Et₂O, and the organic layer was separated from the aqueous layer via cannula and dried over MgSO₄. After cannula filtration, the solvent was removed under reduced pressure to give 5.60 g (30% yield) of white solid.

The solid was redissolved in 100 mL of petroleum ether, the solution was cooled to 0 °C, and BH₃(SMe₂) (20 mL, 2.0 M in THF, 40 mmol, 2.66 equiv) was added via cannula with stirring. When the mixture was warmed to room temperature, a white solid precipitated, and the solvent was removed under reduced pressure. The solid was recrystallized from THF/petroleum ether at –28 °C to give 4.59 g of fine white solid (24% overall yield). Alternatively, we found that use of a slight excess of IsMgBr (2.4 equiv) ensured complete 1,2-diarylation of Cl₂PCH₂PCl₂, but subsequent formation of IsH during the workup hindered crystallization of 1-BH₃. See the Supporting Information for details.

Anal. Calcd for C₃₁H₅₆B₂P₂: C, 72.67; H, 11.02. Found: C, 72.78; H, 11.51. ³¹P{¹H} NMR (CDCl₃): δ –32.6, –34.9 (2/3 ratio). ¹H NMR (CDCl₃): δ 7.1 (d, *J* = 4, 4H, Ar, minor), 7.0 (d, *J* = 3, 4H, Ar, major), 6.3 (broad dm, *J*_{PH} = 393, 2H, P–H, minor), 5.9 (broad dm, *J*_{PH} = 393, 2H, P–H, major), 3.3 (m, 2H, Is CH, minor), 3.1 (br, 4H, Is CH), 2.88 (m, 4H, Is CH, major), 2.6 (m, 2H, CH₂, major), 2.4 (m, 2H, minor, CH₂), 1.33 (d, *J* = 7, 4H, Is CH₃ minor), 1.26 (d, *J* = 7, 4H, Is CH₃ minor), 1.243 (d, *J* = 7, 4H, Is CH₃ major), 1.24 (d, *J* = 7, 4H, Is CH₃ minor), 1.2 (br d, *J* = 7, 4H, Is CH₃ major), 1.08 (d, *J* = 7, 4H, Is CH₃ major). ¹³C{¹H} NMR (CDCl₃): δ 153.1 (quat, Ar, major), 153.0 (quat, Ar, minor), 122.74 (CH, Ar, minor), 122.68 (CH, Ar, major), 119.4 (d, *J* = 56, quat Ar), 118.2 (d, *J* = 53, quat Ar, major), 34.32 (Is CHMe₂, minor), 34.27 (Is CHMe₂, major), 32.5 (br, Is CHMe₂), 24.7 (m, Is CH₃), 24.0 (br, Is CH₃), 23.6 (m, Is CH₃), 20.1 (t, *J* = 20, CH₂, minor), 19.7 (t, *J* = 20, CH₂, major).

IsHPCH₂PHIs (1).¹² Piperazinomethyl polystyrene (1 g, 2.7 mmol/g, 2.7 mmol, 4 equiv)³⁰ and 1-BH₃ (327 mg, 0.64 mmol, 1 equiv) were slurried in toluene (ca. 20 mL) under N₂. The mixture was stirred at 50 °C for 72 h, after which ³¹P NMR spectroscopy showed complete deprotection to diphosphine 1 (δ –99.0, –99.2). The solvent was removed under reduced pressure, the resin–phosphine mixture was brought into the glovebox, and the phosphine was redissolved in toluene; then the resin was removed by filtration through a frit. The solvent was removed under reduced pressure to leave 291 mg (94% yield) of clear thick oil.

Pd(dppe)(IsPCH₂PIs) (2). To a slurry of Pd(dppe)Cl₂ (33 mg, 0.058 mmol) in 5 mL of THF was added IsHPCH₂PHIs (1; 29 mg, 0.059 mmol) in 5 mL of THF. The solution was cooled to –78 °C, and then a solution of NaOSiMe₃ (14 mg, 0.12 mmol, 2 equiv) in 5 mL of THF was added dropwise to the cooled solution over 10 min. The solution turned canary yellow with the first addition of NaOSiMe₃. The solution was stirred for 1 h at –78 °C and was then warmed to room temperature and stirred overnight; it became orange-yellow. The solvent was removed under reduced pressure, and the residue was brought into the glovebox and then dissolved in 2 mL of toluene to give an orange solution, which was filtered through a Celite pipet filter (0.5 cm wide × 2.0 cm high). The flask was rinsed with two more 2 mL portions of toluene, and these extracts were passed through the filter to give 6 mL of orange filtrate. The ³¹P NMR spectrum showed the desired product (δ 24.5, –159 (86%)), residual 1 (δ –98, –99 (5%)), the diphosphirane IsPCH₂PIs (δ –170 (3%)),¹⁷ and additional small quantities of unidentified impurities (δ 30, 28, 26, –14, and –16 (totaling 5%)). The solvent was removed under reduced pressure, and the orange residue was washed with three 1 mL portions of petroleum ether to give a pale orange-yellow solid. The solid was taken up in toluene and filtered a second time through a Celite pipet filter (0.5 cm wide × 2.0 cm high) to give 34 mg (60% yield) of the desired product containing the δ 30 impurity (3%) and a small quantity of the diphosphirane (<1%). Recrystallization from THF/petroleum ether at –30 °C gave 10 mg (18% yield) of yellow powder. Note: if an excess of IsHPCH₂PHIs was not used, the solution became a deep brown-red, which was also generated from the addition of NaOSiMe₃ to Pd(dppe)Cl₂. Once this colored solution was generated, the addition of IsHPCH₂PHIs to the solution did not result in the formation of the yellow color associated with product 2.

We could not obtain spectroscopically pure bulk samples of 2; therefore, elemental analysis was not possible. See the Supporting Information for NMR spectra. HRMS (ESI): *m/z* calcd for C₅₇H₇₃P₄Pd (MH⁺) 987.3718, found *m/z* 987.3712. ³¹P{¹H} NMR (C₇D₈): δ 24.5 (PPh₂, m), –159.5 (PIs, m). ¹H NMR (C₇D₈): δ 8.17 (m, 4H, Ar), 7.14 (m, 4H, Ar), 7.09 (m, 2H, Ar), 6.99 (2H, Ar), 6.88 (m, 4H, Ar), 6.80 (m, 4H, Ar), 6.75 (m, 4H, Ar), 5.00 (m, 2H, Is CH), 4.63 (m, 2H, Is CH), 3.25 (m, 2H, CH₂), 2.78 (septet, *J* = 7, 2H, Is CH), 1.90 (br m, 2H, CH₂), 1.74 (br m, 2H, CH₂), 1.58 (d, *J* = 7, 6H, Is CH₃), 1.45 (d, *J* = 7, 6H, Is CH₃), 1.29 (d, *J* = 7, 6H, Is CH₃), 1.28 (d, *J* = 7, 6H, Is CH₃), 1.02 (d, *J* = 7, 6H, Is CH₃), 0.89 (d, *J* = 7, 6H, Is CH₃). ¹³C{¹H} NMR (CDCl₃): δ 154.2 (br, quat, Ar), 153.9 (br, quat, Ar), 147.5 (quat, Ar), 140.8 (br d, *J* = 25, quat, Ar), 136.1 (br d, *J* = 26, quat, Ar), 135.3 (m, CH, Ar), 134.3 (br d, *J* = 28, quat, Ar), 131.4 (d, *J* = 12, CH, Ar), 130.5 (CH, Ar), 129.2 (CH, Ar), 128.5

(CH, Ar), 128.2 (d, $J = 6$, CH, Ar), 125.4 (CH, Ar), 122.3 (CH, Ar), 120.2 (CH, Ar), 34.7 (Is CHMe₂), 33.3 (br d, $J = 20$, Is CHMe₂), 32.3 (br d, $J = 43$, Is CHMe₂), 26.3 (CH₂), 26.2 (Is CH₃), 26.0 (m, CH₂), 25.7 (Is CH₃), 24.8 (Is CH₃), 24.6 (Is CH₃), 24.4 (Is CH₃), 23.5 (Is CH₃).

Pt(dppe)(IsPCH₂PIs) (3). A solution of IsHPCH₂PIIs (34 mg, 0.07 mmol) in 5 mL of THF was added to a slurry of Pt(dppe)Cl₂ (43 mg, 0.07 mmol) and NaOSiMe₃ (16 mg, 0.14 mmol, 2 equiv) in 5 mL of THF; the solution turned a cloudy yellow. The mixture was stirred for 1 h, at which point the ³¹P NMR spectrum showed mostly the desired product along with some unreacted **1**. The solvent was removed under reduced pressure and the residue was washed with two 1 mL portions of petroleum ether. To the residue was added 3 mL of toluene to give a yellow solution with a white precipitate. The solution was filtered through a Celite pipet filter 0.5 cm wide by 3.0 cm high. The solvent was removed from the filtrate to give 67 mg of yellow solid. Recrystallization from THF/petroleum ether by solvent layering at -28°C gave 24 mg (34% yield) of yellow needlelike crystals.

We could not obtain satisfactory elemental analysis data for the air-sensitive phosphido complexes **3** and **4**, even accounting for their potential oxidation. This problem has been encountered previously with electron-rich phosphido complexes by us and others; see ref 4d and ref 11 therein. See the Supporting Information for NMR spectra of **2–4**, which were also characterized as their methylated derivatives **6–11**. Anal. Calcd for C₅₇H₇₂P₄Pt: C, 63.62; H, 6.74. Calcd for C₅₇H₇₂O₂P₄Pt: C, 61.78; H, 6.55. Found: C, 59.94; H, 6.35. HRMS (FAB): m/z calcd for C₅₇H₇₃P₄Pt (MH⁺) 1076.4311, found m/z 1076.4340. ³¹P{¹H} NMR (C₇D₈): δ 39.1 (PPh₂, m, $J_{\text{Pt-P}} = 2101$), -154.3 (PIs, m, $J_{\text{Pt-P}} = 819$). ¹H NMR (C₇D₈): δ 8.17 (m, 4H, Ar), 7.17 (m, 4H, Ar), 7.09 (m, 2H, Ar), 6.98 (d, $J = 1.5$, 2H, Ar), 6.88 (m, 4H, Ar), 6.80 (m, 4H, Ar), 6.73 (m, 4H, Ar), 5.04 (m, 2H, Is CH), 4.84 (m, 2H, Is CH), 4.28 (m, 2H, CH₂), 2.80 (septet, $J = 7$, 2H, Is CH), 1.79 (br m, 4H, CH₂), 1.63 (d, $J = 7$, 6H, Is CH₃), 1.41 (d, $J = 7$, 6H, Is CH₃), 1.30 (d, $J = 7$, 6H, Is CH₃), 1.29 (d, $J = 7$, 6H, Is CH₃), 0.98 (d, $J = 7$, 6H, Is CH₃), 0.89 (d, $J = 7$, 6H, Is CH₃). ¹³C{¹H} NMR (C₇D₈): δ 154.6 (br, quat, Ar), 154.5 (br, quat, Ar), 137.2 (br, quat, Ar), 135.4 (m, CH, Ar), 131.3 (d, $J = 14$, CH, Ar), 130.7 (CH, Ar), 129.2 (CH, Ar), 128.8 (CH, Ar), 128.4 (d, $J = 10$, CH, Ar), 128.3 (CH, Ar), 128.2 (d, $J = 10$, CH, Ar), 125.4 (CH, Ar), 122.5 (CH, Ar), 120.2 (CH, Ar), 34.7 (Is CHMe₂), 32.4 (br m, Is CHMe₂), 30.9 (br, CH₂), 29.0 (dd, $J = 29$, 17, CH₂), 26.4 (Is CH₃), 26.1 (Is CH₃), 24.8 (Is CH₃), 24.7 (Is CH₃), 24.5 (Is CH₃), 23.3 (Is CH₃).

Pt((R,R)-Me-Duphos)(IsPCH₂PIs) (4). A solution of IsHPCH₂PIIs (**1**; 34 mg, 0.07 mmol) in 5 mL of toluene was added to a slurry of Pt((R,R)-Me-DuPhos)Cl₂ (40 mg, 0.07 mmol) in 5 mL of toluene. The mixture was cooled to -78°C , and a solution of NaOSiMe₃ (16 mg, 0.14 mmol, 2 equiv) in 5 mL of toluene was added via cannula; the mixture turned pale yellow. When it was warmed to room temperature, the solution turned darker yellow, but ³¹P NMR spectroscopy showed signals due to unreacted **1** and the desired product. The toluene was removed under reduced pressure, and the residue was redissolved in 10 mL of THF to give a clear yellow solution that was stirred overnight to produce a yellow solution with white precipitate. ³¹P NMR spectroscopy still showed a trace of unreacted IsHPCH₂PIIs, along with **4**. Two additional portions of Pt((R,R)-Me-DuPhos)Cl₂ (5 mg, 0.009 mmol, then 3 mg, 0.005 mmol) were added, stirring each time for 1 h, monitoring the progress of the reaction by ³¹P NMR spectroscopy, until **1** was consumed.

The solvent was removed under reduced pressure, and 7 mL of toluene was added to the residue to give a yellow solution with a white precipitate. The mixture was filtered through a Celite pipet filter (0.5 cm wide \times 2 cm high) and eluted with 9 mL of toluene. The solvent was removed from the filtrate under reduced pressure and the yellow solid was washed with three 1 mL portions of petroleum ether to give 35 mg of yellow solid. An additional 20 mL of toluene was passed through the Celite pipet filter until the eluting solution was pale yellow, giving an additional 17 mg of yellow solid for an overall 75% yield (52 mg total). This complex was only sparingly soluble at room temperature in benzene, toluene, THF, chloroform, and methylene

chloride. X-ray-quality crystals were obtained by slow evaporation of a toluene solution.

Anal. Calcd for C₄₉H₇₇P₄Pt: C, 59.80; H, 7.78. Found: C, 56.02; H, 6.73. HRMS (FAB): m/z calcd for C₄₉H₇₇P₄Pt (MH⁺) 983.4603, found m/z 983.4591. ³¹P{¹H} NMR (C₆D₆): δ 58.4 (P-DuPhos, m, $J_{\text{Pt-P}} = 1993$), -156.3 (P-Is, m, $J_{\text{Pt-P}} = 826$). ¹H NMR (C₆D₆): δ 7.18 (broad, 2H, Ar), 7.15–7.12 (m, 4H, Ar), 6.93–6.91 (m, 2H, Ar), 5.39–5.34 (m, 2H, *i*-Pr CH), 5.30–5.21 (m, 2H, *i*-Pr CH), 4.67–4.58 (m, 2H, P-CH₂), 2.81 (sep, $J = 7$, 2H, *i*-Pr CH), 2.24–2.19 (m, 2H, CH₂), 2.02–1.93 (m, 2H, CH₂), 1.81–1.71 (m, 2H, CH), 1.65 (dd, $J = 18$, 7, 6H, CH₃), 1.62 (d, $J = 7$, 6H, *i*-Pr CH₃), 1.54 (d, $J = 7$, 6H, *i*-Pr CH₃), 1.51 (d, $J = 7$, 6H, *i*-Pr CH₃), 1.50–1.42 (m, 4H, overlapping CH₂), 1.40 (d, $J = 7$, 6H, *i*-Pr CH₃), 1.23 (d, $J = 7$, 6H, *i*-Pr CH₃), 1.22 (d, $J = 7$, 6H, *i*-Pr CH₃), 1.06–0.97 (m, 2H, CH), 0.55 (dd, $J = 14$, 7, 6H, CH₃).

IsMePCH₂PMels (5). Under nitrogen, a Schlenk flask was loaded with Mg powder (802 mg, 33 mmol, 2 equiv, 50 mesh, Aldrich), which was then slurried in THF (5 mL). To this was added dropwise a solution of 2-bromo-1,3,5-triisopropylbenzene (9.354 g, 33 mmol, 2 equiv) in THF (30 mL) via cannula with stirring at 0°C . Two drops of 1,2-dibromoethane were added to initiate the reaction. The mixture was warmed to room temperature and then stirred for 14 h. The resulting dark gray solution was transferred via cannula to a cooled (-40°C) solution of Cl₂PCH₂PCl₂ (3.597 g, 16.5 mmol, 1 equiv) in THF (ca. 15 mL). A solution of anhydrous ZnCl₂ (8.990 g, 66 mmol, 4 equiv) in THF (75 mL) was then added via cannula; a white solid precipitated. The mixture was stirred at -40°C for 5 h and then warmed to room temperature and stirred for an additional 12 h. To this mixture was added MeMgBr (2.5 mL of a 3.0 M solution in Et₂O (7.5 mmol) plus 27 mL of a 1.0 M solution in THF (34.5 mmol)) at 0°C . The reaction mixture was warmed to room temperature and was stirred for 1 h. ³¹P NMR spectroscopy showed 40% conversion to **5** (δ -57.4 (major), -57.8 (minor)). After 2 h, little further conversion had occurred; therefore, additional MeMgBr (20 mL of a 1.0 M solution in THF (20 mmol)) was added. After 19 h, conversion was at 94%. After the reaction mixture was stirred for an additional 24 h, the reaction was complete by ³¹P NMR spectroscopy, giving **5** in a 5.5/1 ratio of diastereomers.

The mixture was transferred via wide-bore cannula to a filter frit with a Celite bed (3 cm high \times 6 cm wide) and filtered under N₂. The solid was washed with three 30 mL portions of THF, and the solvent was removed from the filtrate under reduced pressure to give a yellow oil. The residue was redissolved in 100 mL of Et₂O to give a cloudy yellow solution. To this was added 30 mL of a degassed saturated solution of aqueous NH₄Cl; additional white solid precipitated in the aqueous layer. An additional 30 mL of degassed distilled H₂O was added, and the two layers were stirred vigorously for 12 h. The yellow organic layer was passed through a plug of silica (6.0 cm wide \times 3.0 cm high) under N₂. The extraction–filtration process was repeated two additional times with 50 mL of Et₂O. The combined yellow extracts were dried over MgSO₄, and the solid was removed by filtration. The solvent was removed under reduced pressure to give 7.583 g (90% crude yield) of yellow oil.

A portion of the yellow oil (3.789 g) was recrystallized at -30°C from 10 mL of acetone to give an off-white solid. The yellow solution was removed by pipet, and an additional 7 mL of acetone was added to give a lighter yellow solution over a white solid. The mixture was cooled to -30°C for 30 min, and then the pale yellow solution was removed by pipet. This process was repeated two more times until the solution was colorless to give 1.191 g (31% yield) of white solid **5** almost exclusively as the *rac* diastereomer.

To the other portion of yellow oil (3.749 g) in 7 mL of pentane was added (BH₃)SMe₂ (8 mL of a 2.0 M solution in THF, 16 mmol). A white precipitate formed, and the mixture was stirred overnight and then filtered through an air-free frit. The white solid was washed with two 10 mL portions of Et₂O to give 1.71 g of the *rac*-enriched monoborane adduct IsMe(BH₃)PCH₂PMels (³¹P NMR (CDCl₃): δ 2.9 (broad), -58.2 (d, $J = 87$)). Deprotection of a small portion of this material with morpholine (procedure described below) to give the free

phosphine showed that the product was a 7.5/1 mixture of *rac* and *meso*-5.

The yellow filtrate was concentrated to give a yellow oil, whose ^{31}P NMR spectrum (CDCl_3) showed that it was $\text{IsMe}(\text{BH}_3)\text{PCH}_2\text{P}(\text{BH}_3)\text{MeIs}$ (**5-BH₃**, δ 2.4 (broad)). A portion of the oil (~300 mg) was passed through a column of silica (2.5 cm wide \times 14.0 cm high) with 5% ethyl acetate in petroleum ether, and 14 10 mL fractions were collected. The bulk of the material eluted in fractions 4–6 to give 20, 27, and 12 mg of product, respectively. The other fractions contained a combined total of 19 mg. A final elution of the column with neat EtOAc gave 43 mg of material. TLC analysis suggested that fraction 5 contained the most product; the ^{31}P NMR spectrum (CDCl_3) of this material showed that it was the *meso*-enriched monoborane adduct $\text{IsMe}(\text{BH}_3)\text{PCH}_2\text{PMeIs}$ (δ 2.4 (broad), -59.2 (d , $J = 139$)). This material (27 mg, 0.05 mmol) was dissolved in neat morpholine (ca. 0.75 mL) under N_2 and transferred to an NMR tube. The mixture was heated to 100 °C for 45 min, and then the morpholine was removed under reduced pressure. To the residue was added 7 mL of 5% Et_2O in pentane to give a cloudy solution. The mixture was eluted through a silica pipet column (0.5 cm wide \times 3.0 cm high) to give 17 mg (65% yield) of enriched *meso*-5 containing some *rac*-5 (11/1 ratio).

In attempts to optimize the synthesis and separation of *rac*- and *meso*-5 (see the Supporting Information for details), we found that selective precipitation of *rac*-enriched **5-BH₃** was reproducible on a large scale but was less efficient on a smaller scale. This precluded effective *rac*/*meso* separation when BH_3 -THF was added to small amounts of a 1/1 mixture of *rac*- and *meso*-5 obtained by thermal epimerization. Similarly, because attempts to separate *rac*- and *meso*-**5-BH₃** by chromatography were unsuccessful, *meso*-enriched **5** was best obtained after selective precipitation or recrystallization of *rac*-5 or its borane adduct.

Data for *rac*-5. Anal. Calcd for $\text{C}_{33}\text{H}_{54}\text{P}_2(\text{acetone})_{0.5}$: C, 76.48; H, 10.60. Found: C, 76.35; H, 10.50. The white solid obtained by recrystallization from acetone contained residual acetone, which was observed by ^1H NMR spectroscopy. Attempts to quantify the amount of cocrystallized solvent were unsuccessful, since acetone appeared to be lost on standing. HRMS (ES^+): m/z calcd for $\text{C}_{33}\text{H}_{55}\text{P}_2$ (MH^+) 513.3779, found m/z 513.3773. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ -52.1 (*meso*), -53.1 (*rac*) (81:1 *rac*/*meso*). ^1H NMR (CDCl_3): δ 7.03 (broad, 4H, Ar), 4.01–3.93 (m, 4H, *i*-Pr CH), 2.88 (sep, $J = 7$, 2H, *i*-Pr CH), 2.54 (2H, P-CH₂), 1.55 (t, $J = 3$, 6H, P-CH₃), 1.28–1.23 (m, 36H, *i*-Pr CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 155.2 (t, $J = 7$, quat, Ar), 150.1 (quat, Ar), 131.0 (t, $J = 2$, quat, Ar), 121.9 (t, $J = 2$, CH, Ar), 34.2 (*i*-Pr-CH), 31.2 (t, $J = 11$, *i*-Pr-CH), 29.9 (t, $J = 20$, P-CH₂), 24.9 (*i*-Pr CH₃), 24.81 (*i*-Pr CH₃), 23.8 (d , $J = 4$, *i*-Pr CH₃), 12.1 (t, $J = 7$, P-CH₃).

Data for *meso*-5. Anal. Calcd for $\text{C}_{33}\text{H}_{54}\text{P}_2$: C, 77.30; H, 10.62. Found: C, 76.87; H, 9.82. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ -52.1 (*meso*), -53.1 (*rac*) (11/1 ratio). ^1H NMR (CDCl_3): δ 6.94 (broad, 4H, Ar), 3.91–3.84 (m, 4H, *i*-Pr CH), 2.83 (sep, $J = 7$, 2H, *i*-Pr CH), 2.60–2.47 (m, 2H, P-CH₂), 1.59 (t, $J = 3$, 6H, P-CH₃), 1.22 (d , $J = 7$, 12H, *i*-Pr CH₃), 1.15 (d , $J = 7$, 12H, *i*-Pr CH₃), 1.12 (d , $J = 7$, 12H, *i*-Pr CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 155.0 (t, $J = 7$, quat, Ar), 149.9 (quat, Ar), 131.2 (d , $J = 6$, quat, Ar), 121.8 (CH, Ar), 34.1 (*i*-Pr CH), 31.2 (d , $J = 11$, *i*-Pr CH), 30.2–29.7 (m, P-CH₂), 24.8 (*i*-Pr CH₃), 24.6 (*i*-Pr CH₃), 23.8 (d , $J = 2$, *i*-Pr CH₃), 13.3 (t, $J = 5$, P-CH₃).

Pt-Catalyzed Synthesis of 5. *Method 1 (from PHMe(Is) and CH₂I₂).* A solution of PHMe(Is) (25 mg, 0.1 mmol) in 1 mL of toluene was added to Pt((*R,R*)-Me-DuPhos)(Ph)(Cl) (3 mg, 0.005 mmol, 5 mol %). The resulting solution was added to solid NaOSiMe₃ (11 mg, 0.1 mmol, 2 equiv). The solution, now yellow, was transferred to an NMR tube fitted with a septum, and CH_2I_2 (4 μL , 0.05 mmol, 2 equiv) was injected via microliter syringe. A white precipitate formed, and the reaction was monitored by ^{31}P NMR spectroscopy. After 71 h the reaction had stopped, giving **5** (δ -53.7 , -53.9 (combined 48%)) as well as a byproduct (δ 37.4, 36%) and unreacted PHMe(Is) (δ -109.2 (16%)). Additional NaOSiMe₃ (5 mg, 0.04 mmol) and CH_2I_2 (2 μL , 0.04 mmol) were added to the reaction mixture. The reaction was complete, as judged by ^{31}P NMR spectroscopy after an additional 24 h (95 h total), yielding a 2/3 mixture of **5** and the byproduct, identified

as $\text{PMe}_2\text{Is}(\text{O})$ (see below); Pt((*R,R*)-Me-DuPhos)(Ph)(I) was also observed.²⁵ The solvent was removed under reduced pressure, and the residue was extracted with 9/1 petroleum ether/THF (ca. 1 mL). The extract was eluted over a silica pipet column with four 1 mL portions of 9/1 petroleum ether/THF. The solvent was removed under reduced pressure to give 13 mg (50% yield) of **5** as an oily residue (3.2/1 *meso*/*rac* ratio) which contained unidentified impurities (^{31}P NMR: δ -42.5 (<1%), -61.1 (<0.5%)). For details on the scaleup of this reaction and characterization data for $\text{PMe}_2\text{Is}(\text{O})$, see the Supporting Information.

Method 2 (from IsHPCH₂PHIs (1) and MeI). A solution of IsHPCH₂PHIs (**1**; 27 mg, 0.06 mmol) in 1 mL of THF was added to Pt((*R,R*)-Me-DuPhos)(Ph)(Cl) (3 mg, 0.006 mmol, 10 mol %), and this solution was transferred to solid NaOSiMe₃ (13 mg, 0.12 mmol, 2 equiv) to give a yellow solution, which was transferred to an NMR tube. MeI (7 μL , 0.12 mmol, 2 equiv) was injected via microliter syringe through a rubber septum; the solution turned pale yellow. The ^{31}P NMR spectrum showed signals due to a mixture of **5** (δ -57.3 , -57.6 , 29%), monoalkylated IsHPCH₂PMeIs (δ -52.3 (d , $J = 121$), -102.7 (d , $J = 121$), 56%), starting material **1** (δ -102.9 , -103.9 , 7%), and another compound, perhaps overalkylated [$\text{IsMe}_2\text{PCH}_2\text{PMeIs}$][**1**] (δ 18.8 (d , $J = 128$), -65.9 (d , $J = 128$), 8%). The reaction was complete after 1.75 h. The solvent was removed under reduced pressure, and the residue was extracted with three 1 mL portions of 9/1 petroleum ether/THF. The collected extracts were passed through a silica pipet column (0.5 cm wide \times 3.0 cm high). The solvent was removed under reduced pressure to give 12 mg (43% yield) of **5** (2.2/1 *meso*/*rac* ratio) as a clear residue also containing an unidentified impurity (^{31}P NMR: δ -61.1 (10%)). For determination of the enantioselectivity of these Pt-catalyzed reactions, see the Supporting Information.

meso-[Pd(dppe)(IsMePCH₂PMeIs)][OTf]₂ (**6**). To a slurry of Pd(dppe)(OTf)₂ (34 mg, 0.04 mmol) in 7 mL of CH_2Cl_2 was added a solution of *meso*-IsMePCH₂PMeIs (22 mg, 0.04 mmol) in 5 mL of CH_2Cl_2 . The slurry turned homogeneous and pale yellow almost immediately. The solution was stirred for 20 min, and then the solvent was removed under reduced pressure. The residue was washed with petroleum ether and then recrystallized from CH_2Cl_2 and petroleum ether at 21 °C by solvent layering. A small quantity of orange residue precipitated, leaving a pale yellow solution, which was removed with a pipet. The solvent was removed under reduced pressure to leave 34 mg (84% yield) of pale yellow solid. Recrystallization from CH_2Cl_2 /Et₂O at 21 °C by vapor diffusion gave yellow needlelike crystals for X-ray analysis.

Anal. Calcd for $\text{C}_{61}\text{H}_{78}\text{F}_6\text{O}_6\text{P}_4\text{PdS}_2$: C, 55.69; H, 5.98. Found: C, 55.34; H, 6.36. HRMS (ES^+): m/z calcd for $\text{C}_{60}\text{H}_{78}\text{F}_3\text{O}_3\text{P}_4\text{PdS}$ ($\text{M} - \text{SO}_3\text{CF}_3$)⁺ 1165.3629, found m/z 1165.3721. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 55.4 (m, P-dppe), -86.0 (m, P-MeIs). ^1H NMR (CD_2Cl_2): δ 7.82–7.77 (m, 2H, Ar), 7.72–7.65 (m, 10H, Ar), 7.64–7.58 (m, 4H, Ar), 7.49 (td, $J = 8$, 2, 4H, Ar), 7.01 (d , $J = 2$, 4H, Ar), 6.27–6.17 (dm, $J = 16$, 1H, PCH₂P), 3.93–3.85 (dm, $J = 16$, 1H, PCH₂P), 3.27–3.21 (m, 4H, *i*-Pr CH), 2.83 (sep, $J = 7$, 2H, *i*-Pr CH), 2.70–2.46 (broad m, 4H, dppe CH₂), 1.88 (dd, $J = 9$, 2, 6H, P-CH₃), 1.17 (dd, $J = 7$, 1, 12H, *i*-Pr CH₃), 0.98 (d , $J = 7$, 12H, *i*-Pr CH₃), 0.73 (d , $J = 7$, 12H, *i*-Pr CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 155.4 (quat, Ar), 154.9–154.7 (broad m, quat, Ar), 134.6 (broad, CH, Ar), 134.4 (broad, CH, Ar), 133.9–133.8 (broad m, CH, Ar), 133.6–133.5 (broad m, CH, Ar), 131.3–131.2 (broad m, CH, Ar), 131.1–131.0 (broad m, CH, Ar), 127.9 (d , $J = 50$, quat, Ar), 125.8 (d , $J = 49$, quat, Ar), 124.1–124.0 (m, CH, Ar), 121.0–120.6 (m, quat, Ar), 120.0 (q, $J_{\text{C-F}} = 321$, CF₃), 47.2–46.7 (m, PCH₂P), 34.6 (*i*-Pr CH), 34.1–34.0 (m, *i*-Pr CH), 26.2–25.8 (m, PCH₂CH₂P), 25.6 (*i*-Pr CH₃), 24.4 (*i*-Pr CH₃), 23.5 (d , $J = 12$, *i*-Pr CH₃), 18.2–17.8 (m, PCH₃).

rac-[Pd(dppe)(IsMePCH₂PMeIs)][OTf]₂ (**7**). To a slurry of Pd(dppe)(OTf)₂ (34 mg, 0.04 mmol) in 4 mL of CH_2Cl_2 was added a solution of *rac*-IsMePCH₂PMeIs (*rac*-5; 22 mg, 0.04 mmol) in 5 mL of CH_2Cl_2 . The slurry turned homogeneous and pale yellow almost immediately. The solution was stirred for 20 min, at which time ^{31}P NMR spectroscopy showed that the reaction was complete.

Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at 21 °C by vapor diffusion gave 41 mg (95% yield) of a pale yellow solid.

Anal. Calcd for $\text{C}_{61}\text{H}_{78}\text{F}_6\text{O}_6\text{P}_4\text{PdS}_2$: C, 55.69; H, 5.98. Found: C, 55.26; H, 5.98. HRMS (ES^+): m/z calcd for $\text{C}_{60}\text{H}_{78}\text{F}_3\text{O}_3\text{P}_4\text{PdS}$ ($\text{M} - \text{CF}_3\text{SO}_3$) $^+$ 1165.3609, Found m/z 1165.3623. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 56.6 (m, P-dppe), -72.1 (m, P-MeIs). ^1H NMR (CD_2Cl_2): δ 7.76–7.72 (m, 2H, Ar), 7.68–7.63 (m, 8H, Ar), 7.49 (t, $J = 8$, 2H, Ar), 7.38–7.33 (m, 4H, Ar), 7.23 (td, $J = 8$, 3, 4H, Ar), 7.04 (broad, 4H, Ar), 4.71 (t, $J = 11$, 2H, PCH_2P), 3.32 (broad, 4H, i -Pr CH), 3.07–2.93 (m, 2H, CH_2), 2.90 (sep, $J = 7$, 2H, i -Pr CH), 2.77–2.65 (m, 2H, CH_2), 2.20–2.17 (br m, 6H, P-Me), 1.25 (d, $J = 7$, 12H, i -Pr CH_3), 1.24 (d, $J = 7$, 12H, i -Pr CH_3), 1.02–0.96 (broad m, 12H, i -Pr CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 155.5 (quat, Ar), 154.1 (broad m, quat, Ar), 134.4 (CH, Ar), 133.8–133.7 (m, CH, Ar), 133.6 (CH, Ar), 133.0–132.9 (m, CH, Ar), 131.0–130.9 (m, CH, Ar), 130.3–130.2 (m, CH, Ar), 128.3 (d, $J = 47$, quat, Ar), 126.0 (d, $J = 49$, quat, Ar), 124.9 (broad, CH, Is), 121.2 (q, $J = 321$, quat, CF_3), 119.3 (broad d, $J = 62$, quat, Ar), 48.6–48.2 (m, PCH_2P), 34.5 (overlapping, i -Pr CH), 34.5 (broad, overlapping, i -Pr CH), 27.9–27.6 (m, $\text{PCH}_2\text{CH}_2\text{P}$), 26.4 (broad, i -Pr CH_3), 24.8 (broad, i -Pr CH_3), 23.5 (d, $J = 20$, i -Pr CH_3), 20.3–19.8 (m, P- CH_3).

meso-[Pt(dppe)(IsMePCH₂PMels)](OTf)₂ (8). To a solution of $\text{Pt}(\text{dppe})(\text{OTf})_2$ (82 mg, 0.09 mmol) in 7 mL of CH_2Cl_2 was added a solution of *meso*-IsMePCH₂PMels (*meso*-5; 46 mg, 0.09 mmol) in 5 mL of CH_2Cl_2 . The solution was stirred for 5 min and then concentrated under reduced pressure to ca. 2 mL. Addition of 7 mL of Et_2O resulted in the formation of a white precipitate. The solution was allowed to stand until the solid settled and the solvent was removed with a pipet. The white solid was washed with three 0.5 mL portions of Et_2O to give 99 mg of white solid (79% yield). Recrystallization at -45 °C from minimal CH_2Cl_2 and Et_2O by solvent layering gave white crystals suitable for X-ray crystallography and elemental analysis.

Anal. Calcd for $\text{C}_{61}\text{H}_{78}\text{F}_6\text{O}_6\text{P}_4\text{PtS}_2$: C, 52.17; H, 5.60. Found: C, 51.87; H, 5.78. HRMS (ES^+): m/z calcd for $\text{C}_{60}\text{H}_{78}\text{F}_3\text{O}_3\text{P}_4\text{PtS}$ ($\text{M} - \text{SO}_3\text{CF}_3$) $^+$ 1254.4216, found m/z 1254.4227. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 44.4 (m, P-dppe, $J_{\text{Pt-P}} = 2333$), -83.4 (m, P-Mels, $J_{\text{Pt-P}} = 1973$). ^1H NMR (CD_2Cl_2): δ 7.80–7.76 (m, 2H, Ar), 7.73–7.69 (m, 8H, Ar), 7.68–7.62 (m, 6H, Ar), 7.47 (td, $J = 8$, 3, 4H, Ar), 7.03 (d, $J = 4$, 4H, Ar), 6.64–6.55 (dm, $J = 16$, 1H, PCH_2P), 4.18–4.10 (dm, $J = 16$, 1H, PCH_2P), 3.29–3.23 (m, 4H, i -Pr CH), 2.85 (sep, $J = 7$, 2H, i -Pr CH), 2.57–2.42 (m, 4H, dppe CH_2), 1.95–1.92 (broad m, 6H, P- CH_3), 1.17 (dd, $J = 7$, 2, 12H, i -Pr CH_3), 0.97 (d, $J = 7$, 12H, i -Pr CH_3), 0.73 (d, $J = 7$, 12H, i -Pr CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 155.4 (quat, Ar), 154.9–154.7 (broad m, quat, Ar), 134.5 (broad, 2 CH, Ar), 133.9 (d, $J = 11$, CH, Ar), 133.7 (d, $J = 11$, CH, Ar), 131.1 (d, $J = 11$, CH, Ar), 130.8 (d, $J = 11$, CH, Ar), 127.6 (d, $J = 50$, quat, Ar), 125.3 (d, $J = 59$, quat, Ar), 124.09–124.01 (m, CH, Ar), 121.3 (q, $J_{\text{C-F}} = 321$, CF_3), 120.0–119.6 (m, quat, Ar), 49.7–49.1 (m, PCH_2P), 34.5 (i -Pr CH), 34.1 (filled-in d, $J = 5$, i -Pr CH), 25.9 (dd, $J = 36$, 8, $\text{PCH}_2\text{CH}_2\text{P}$), 25.6 (i -Pr CH_3), 24.4 (i -Pr CH_3), 23.5 (d, $J = 13$, i -Pr CH_3), 18.9–18.6 (m, PCH_3).

rac-[Pt(dppe)(IsMePCH₂PMels)](OTf)₂ (9). To a solution of $\text{Pt}(\text{dppe})(\text{OTf})_2$ (86 mg, 0.1 mmol) in 5 mL of CH_2Cl_2 was added a solution of *rac*-IsMePCH₂PMels (*rac*-5; 49 mg, 0.1 mmol) in 2 mL of CH_2Cl_2 . The solution was stirred for 5 min and then concentrated under reduced pressure to ca. 3 mL. Recrystallization by vapor diffusion with $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at 21 °C resulted in the formation of a white crystalline solid. The solvent was removed with a pipet, and the solid was washed with three 1 mL portions of Et_2O . The solid was dried under vacuum to give 124 mg (92% yield) of the product.

Anal. Calcd for $\text{C}_{61}\text{H}_{78}\text{F}_6\text{O}_6\text{P}_4\text{PtS}_2$: C, 52.17; H, 5.60. Found: C, 51.87; H, 5.58. HRMS (ES^+): m/z calcd for $\text{C}_{60}\text{H}_{78}\text{F}_3\text{O}_3\text{P}_4\text{PtS}$ ($\text{M} - \text{SO}_3\text{CF}_3$) $^+$ 1254.4222, found m/z 1254.4231. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 45.8 (m, $J_{\text{Pt-P}} = 2312$, P-dppe), -79.0 (m, $J_{\text{Pt-P}} = 1934$, P-Mels). ^1H NMR (CD_2Cl_2): δ 7.73–7.68 (m, 2H, Ar), 7.64–7.58 (m, 8H, Ar), 7.53–7.49 (m, 2H, Ar), 7.36–7.32 (m, 4H, Ar), 7.23 (td, $J = 8$, 3, 4H, Ar), 7.11–7.01 (broad, 4H, Ar), 5.11 (broad t, $J = 12$, 2H, PCH_2P), 2.93 (sep, $J = 7$, 4H, i -Pr CH), 2.87–2.80 (m, 2H, i -Pr CH), 2.76–2.63 (m, 4H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.45–2.35 (br m, 6H, P-Me), 1.27 (d, $J = 7$, 12H, i -Pr CH_3), 1.26 (d, $J = 7$, 12H, i -Pr CH_3), 1.08–

0.82 (broad m, 12H, i -Pr CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 155.6 (quat, Ar), 154.3 (broad m, quat, Ar), 134.3 (CH, Ar), 133.8 (CH, Ar), 133.5–133.4 (m, CH, Ar), 133.0–132.9 (m, CH, Ar), 130.8–130.7 (m, CH, Ar), 130.3–130.2 (m, CH, Ar), 128.3 (d, $J = 54$, quat, Ar), 126.0–124.8 (broad m, CH, Is), 124.8 (d, $J = 58$, quat, Ar), 121.1 (q, $J_{\text{C-F}} = 321$, CF_3), 118.6–118.2 (m, quat, Ar), 52.1–51.6 (m, PCH_2P), 35.4–34.2 (broad m, i -Pr CH), 34.4 (i -Pr CH), 27.3–26.9 (m, CH_2 , $\text{PCH}_2\text{CH}_2\text{P}$), 25.8–24.0 (broad, i -Pr CH_3), 23.6 (i -Pr CH_3), 23.4 (i -Pr CH_3), 21.9–21.7 (m, P- CH_3).

meso-[Pt((R,R)-Me-DuPhos)(IsMePCH₂PMels)](OTf)₂ (10). To a solution of $\text{Pt}((R,R)\text{-Me-DuPhos})(\text{OTf})_2$ (75 mg, 0.09 mmol) in 7 mL of CH_2Cl_2 was added *meso*-IsMePCH₂PMels (*meso*-5; 46 mg, 0.09 mmol) in 5 mL of CH_2Cl_2 . The solution was stirred for 20 min and then concentrated under reduced pressure to ca. 2 mL to give a pale yellow solution. An off-white solid was precipitated by the addition of 5–7 mL of petroleum ether. The solvent was removed by pipet, and the solid was washed with three 0.5 mL portions of petroleum ether. The solid was redissolved in 2 mL of CH_2Cl_2 ; 7 mL of petroleum ether was layered on top, and cooling overnight at -45 °C resulted in the formation of an off-white precipitate. ^{31}P NMR spectroscopy revealed a residual impurity (δ 61.3, 0.5%). Addition of 2 mg more of IsMePCH₂PMels in 2 mL of CH_2Cl_2 did not remove the impurity to give the desired product. Removal of the solvent under reduced pressure and washing with three 0.5 mL portions of petroleum ether removed any residual phosphine. The solid was recrystallized again from CH_2Cl_2 (3 mL) and petroleum ether (15 mL) by solvent layering at -45 °C to give pale yellow needlelike crystals (103 mg, 86% yield) suitable for elemental analysis.

Anal. Calcd for $\text{C}_{53}\text{H}_{82}\text{F}_6\text{O}_6\text{P}_4\text{PtS}_2$: C, 48.51; H, 6.30. Found: C, 48.39; H, 6.21. ESI-MS: m/z calcd for $\text{C}_{52}\text{H}_{82}\text{F}_3\text{O}_3\text{P}_4\text{PtS}$ ($\text{M} - \text{SO}_3\text{CF}_3$) $^+$ 1161.4514, found m/z 1161.4545. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 69.7 (dm, $J = 325$, $J_{\text{Pt-P}} = 2268$), 69.0 (broad dm, $J = 318$, $J_{\text{Pt-P}} = 2198$), -72.8 (ddd, $J = 7$, 53, 324, $J_{\text{Pt-P}} = 1856$), -76.4 (ddd, $J = 9$, 53, 318, $J_{\text{Pt-P}} = 1997$). ^1H NMR (CD_2Cl_2): δ 8.00–7.88 (m, 4H, Ar), 7.29 (broad, 3H, Ar), 7.09 (broad, 1H, Ar), 6.49 (dm, $J = 16$, 1H, PCH_2P), 4.35 (dm, $J = 16$, 1H, PCH_2P), 3.22–2.98 (broad overlapping m, 3H, DuPhos CH), 3.00 (sep, $J = 7$, 4H, i -Pr CH), 2.93 (sep, $J = 7$, 2H, i -Pr CH), 2.82–2.70 (broad m, 1H, DuPhos CH), 2.77 (dd, $J = 4$, 10, 3H, P- CH_3), 2.68 (broad d, $J = 9$, 3H, P- CH_3), 2.65–2.50 (m, 3H, DuPhos CH_2), 2.28–2.15 (m, 3H, DuPhos CH_2), 1.99–1.83 (m, 2H, DuPhos CH_2), 1.61 (dd, $J = 8$, 20, 3H, DuPhos CH_3), 1.40–1.22 (broad overlapping m, 18H, i -Pr CH_3 and 6H, DuPhos CH_3), 1.29 (d, $J = 7$, 6H, i -Pr CH_3), 1.24 (d, $J = 7$, 6H, i -Pr CH_3), 1.10 (broad, 3H, i -Pr CH_3), 1.00 (dd, $J = 8$, 18, 3H, DuPhos CH_3), 0.57 (broad, 3H, i -Pr CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 155.8 (quat, Ar), 155.2 (quat, Ar), 155.0 (broad, quat, Ar), 154.1 (broad, quat, Ar), 138.8 (dd, $J = 29$, 47, quat DuPhos P-C), 136.3 (dd, $J = 28$, 50, quat DuPhos P-C), 135.1–135.0 (broad m, Ar, CH), 134.6–134.5 (broad m, Ar, CH), 134.4–134.2 (broad m, CH, Ar), 133.9–133.7 (broad m, CH, Ar), 125.6 (broad, CH, Ar), 124.7 (broad, CH, Ar), 122.3 (broad dm, $J = 49$, quat, P-C), 121.2 (q, $J_{\text{C-F}} = 321$, CF_3), 118.5 (broad dm, $J = 138$, quat P-C), 53.3–52.7 (m, P- CH_2), 48.6 (d, $J = 33$, CH), 43.3 (d, $J = 36$, CH), 40.6 (d, $J = 28$, CH), 39.7 (d, $J = 34$, CH), 37.9 (CH_2), 36.4 (d, $J = 6$, CH_2), 36.3 (CH_2), 35.5 (d, $J = 5$, CH_2), 34.6 (i -Pr CH), 34.4 (i -Pr CH), 32.5 (broad, i -Pr CH), 26.9 (broad dm, $J = 40$, i -Pr CH_3), 26.4 (broad, i -Pr CH_3), 24.9 (broad dm, $J = 87$, i -Pr CH_3), 23.5 (d, $J = 6$, i -Pr CH_3), 23.4 (d, $J = 5$, i -Pr CH_3), 21.6 (d, $J = 35$, P- CH_3), 21.0 (d, $J = 25$, P- CH_3), 18.9 (DuPhos CH_3), 17.4 (d, $J = 5$, DuPhos CH_3), 15.8 (d, $J = 3$, DuPhos CH_3), 14.5 (d, $J = 2$, DuPhos CH_3).

rac-[Pt((R,R)-Me-DuPhos)(IsMePCH₂PMels)](OTf)₂ (11a,b). To a solution of $\text{Pt}((R,R)\text{-Me-DuPhos})(\text{OTf})_2$ (91 mg, 0.11 mmol) in 5 mL of CH_2Cl_2 was added a solution of *rac*-IsMePCH₂PMels (*rac*-5; 58 mg, 0.11 mmol) in 2 mL of CH_2Cl_2 . The solution was stirred for 20 min. ^{31}P NMR spectroscopy showed formation of a 1/1 mixture of 11a,b and a small quantity of residual $\text{Pt}((R,R)\text{-Me-DuPhos})(\text{OTf})_2$. Additional *rac*-IsMePCH₂PMels (5 mg, 0.01 mmol) was added, the solution was concentrated to ca. 1 mL, and the product was precipitated by the addition of 5 mL of Et_2O . The solvent was removed by pipet, and the solid was washed with three 0.5 mL portions of Et_2O and dried under vacuum to give 138 mg (96% yield)

of white solid. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ by solvent layering at -30°C gave 100 mg (70% yield) of analytically pure white solid as a mixture of diastereomers.

Anal. Calcd for $\text{C}_{53}\text{H}_{82}\text{F}_6\text{O}_6\text{P}_4\text{PtS}_2$: C, 48.51; H, 6.30. Found: C, 48.20; H, 6.37. ESI-MS: m/z calcd for $\text{C}_{52}\text{H}_{82}\text{F}_3\text{O}_3\text{P}_4\text{PtS}$ ($\text{M} - \text{SO}_3\text{CF}_3$)⁺ 1162.4535, found m/z 1162.4536. The following NMR data are for **11b**, observed in the mixture with **11a** (see below for data for **11a**, prepared independently). $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2): δ 69.9 (P-DuPhos, m, $J_{\text{Pt-P}} = 2138$), -76.9 (P-Is, m, $J_{\text{Pt-P}} = 1969$). ^1H NMR (CD_2Cl_2): δ 7.95–7.92 (m, 2H, Ar), 7.92–7.87 (m, 2H, Ar, overlapping **11a** signal), 7.27 (broad, 2H, Ar, overlapping **11a** signal), 7.23 (broad d, $J = 3$, 2H, Ar), 4.82 (apparent t, $J = 11$, 2H, PCH_2P), 4.16 (broad sep, $J = 6$, 2H, i -Pr CH), 3.30–3.27 (broad m, 2H, CH), 3.08–3.02 (m, 2H, CH), 3.04 (sep, $J = 7$, 2H, i -Pr CH, overlapping previous signal), 2.97 (sep, $J = 7$, 2H, i -Pr CH, overlapping **11a** signal), 2.78 (broad, 2H, CH), 2.77–2.75 (m, 6H, P-Me), 2.61–2.51 (m, 4H, CH_2 , overlapping **11a** signal), 1.80–1.66 (m, 4H, CH_2 , overlapping **11a** signal), 1.51 (d, $J = 7$, 6H, i -Pr CH_3), 1.42 (d, $J = 6$, 6H, i -Pr CH_3), 1.33 (d, $J = 7$, 6H, i -Pr CH_3), 1.32 (d, $J = 7$, 6H, i -Pr CH_3), 1.26 (d, $J = 7$, 6H, i -Pr CH_3), 1.25 (d, $J = 7$, 6H, i -Pr CH_3), 0.96 (dd, $J = 20$, 8, 6H, CH_3), 0.73 (dd, $J = 17$, 7, 6H, CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2): δ 155.7 (quat, Ar), 154.7 (broad, quat, Ar), 153.4 (broad, quat, Ar), 135.7 (m, quat, Ar), 134.5 (m, CH, Ar), 133.5–133.3 (m, CH, Ar), 126.2–126.1 (m, CH, Ar), 125.4–125.3 (m, CH, Ar), 121.3 (q, $J = 321$, quat CF_3), 120.8–120.0 (m, quat, Ar), 53.1 (apparent t, $J = 31$, PCH_2P), 40.7 (d, $J = 32$, CH), 39.0 (d, $J = 29$, CH), 36.9 (m, CH_2), 36.6 (d, $J = 6$, CH_2), 34.9 (i -Pr CH), 34.4 (i -Pr CH), 32.6 (i -Pr CH), 28.0 (i -Pr CH_3), 25.3 (i -Pr CH_3), 24.3 (i -Pr CH_3), 23.47 (i -Pr CH_3), 23.43 (i -Pr CH_3), 23.4–23.2 (m, P- CH_3), 18.3 (d, $J = 4$, DuPhos CH_3), 15.7 (DuPhos CH_3).

Methylation of 2. Synthesis of *rac*-/*meso*-[Pd(dppe)-(IsMePCH₂PMels)][OTf]₂ (6**, **7**).** To an orange-red solution of Pd(dppe)(IsPCH₂PIs) (**2**; 47 mg, 0.048 mmol) in 1.5 mL of CH_2Cl_2 in an NMR tube was added MeOTf (11 μL , 0.1 mmol, 2 equiv). The solution remained orange-red. The monomethylated product [Pd(dppe)(IsMePCH₂PIs)][OTf] (**12a**, δ 40.5 (apparent dt, $J = 342$, 42), 35.0 (ddd, $J = 48$, 42, 22), -89.6 (m), -94.8 (ddd, $J = 12$, 22, 342)) was observed by ^{31}P NMR spectroscopy within minutes after the injection of MeOTf. Some additional peaks in the ^{31}P NMR spectrum were tentatively assigned to minor diastereomer **12b** (δ 40.5 (dm, $J = 365$), 36.8–35.8 (m), -103.9 (dm, $J = 365$)). The ratio **12a**/**12b** was about 9/1. Formation of dications **6** and **7** was slower. The reaction was incomplete after standing overnight. After addition of more MeOTf (2 μL , 0.02 mmol), and standing overnight, the reaction was complete, according to ^{31}P NMR spectroscopy, which showed a 1.1/1 mixture of *meso*-**6** and *rac*-**7**. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ by solvent layering at 21°C gave 14 mg (29% yield) of an off-white solid that was almost exclusively the *rac* diastereomer **7** (63/1 *rac*/*meso* from integration of the ^{31}P NMR dppe signals). NMR data for this material matched that obtained for independently prepared **7** (see above).

Methylation of 3. Synthesis of *rac*-/*meso*-[Pt(dppe)-(IsMePCH₂PMels)][OTf]₂ (8**, **9**).** To a yellow solution of Pt(dppe)-(IsPCH₂PIs) (**3**; 30 mg, 0.027 mmol) in 1.5 mL of CH_2Cl_2 in an NMR tube was added MeOTf (6 μL , 0.054 mmol, 2 equiv). The solution remained yellow. The monomethylated product [Pt(dppe)-(IsMePCH₂PIs)][OTf] (**13**, δ 43.3 (broad d, $J = 73$, $J_{\text{Pt-P}} = 1824$), 40.1 (ddd, $J = 9$, 25, 348, $J_{\text{Pt-P}} = 2644$), -87.4 (apparent d, $J = 350$, $J_{\text{Pt-P}} = 2246$), -114.3 (broad, $J_{\text{Pt-P}} = 764$)) was observed by ^{31}P NMR spectroscopy within minutes. Formation of dications **8** and **9** was slower. The reaction mixture was allowed to stand overnight, at which time the reaction was complete, according to ^{31}P NMR spectroscopy, which showed a mixture of *rac*-**9** and *meso*-**8** that was slightly enriched in the *rac* diastereomer (1.2/1 on the basis of integration of the ^1H NMR PCH_2P signals). The solvent was removed under reduced pressure, and the residue was washed with three 1 mL portions of petroleum ether. The residue was recrystallized twice at 21°C , once from CH_2Cl_2 (1 mL)/ Et_2O (5 mL) and once from THF (2 mL)/petroleum ether (5 mL), to give 26 mg (68% yield) of pale yellow

solid. NMR and mass spectral data for this mixture of **8** and **9** matched results from independently prepared samples (see above).

Methylation of 4. Synthesis of *C*₂-[Pt(*RR*)-Me-DuPhos)-(IsMePCH₂PMels)][OTf]₂ (11a**).** To a yellow slurry of Pt(*RR*)-Me-DuPhos(IsPCH₂PIs) (**4**; 10 mg, 0.01 mmol) in 1 mL of CH_2Cl_2 was added MeOTf (3 μL , 0.02 mmol, 2 equiv) via microliter syringe. The yellow slurry became homogeneous and then pale yellow within 5 min of adding the MeOTf. The ^{31}P NMR spectrum of the crude reaction mixture suggested the presence of monomethylated [Pt-((*RR*)-Me-DuPhos)(MeIsPCH₂PIs)][OTf] (**14**; δ 68.0 (ddd, $J = 6$, 11, 64, $J_{\text{Pt-P}} = 1710$), 60.7 (ddd, $J = 11$, 26, 351, $J_{\text{Pt-P}} = 2219$), -85.6 (apparent dd, $J = 6$, 351, $J_{\text{Pt-P}} = 2214$), -113.6 (broad d, $J = 64$, $J_{\text{Pt-P}} = 705$)). The mixture was allowed to stand overnight, and then the solvent was removed under reduced pressure and the pale yellow residue was washed with three 1 mL portions of petroleum ether. Recrystallization from CH_2Cl_2 /pentane at -30°C gave 10 mg (77% yield) of white crystalline solid. The same procedure was repeated on a slightly larger scale (34 mg, 0.035 mmol of **4**) to give 36 mg (80% yield) of product after recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at -30°C . In four such experiments, a 25/1 mixture of *C*₂-symmetric **11a** (major product) and *meso*-**10** (minor) and two additional unidentified minor products was formed. One of the unidentified products (δ 73.6 (dm, $J = 315$), 71.8 (dm, $J = 304$), -59.8 (dm, $J = 305$), -60.1 (dm, $J = 316$), $\sim 9\%$) was retained while the other (δ 56.2 (dd, $J = 374$, 12), 55.9 (dd, $J = 385$, 10)) appeared and then dissipated over the course of the reaction.

ESI-HRMS: m/z calcd for $\text{C}_{51}\text{H}_{83}\text{P}_4\text{Pt}$ ($\text{MH} - 2\text{SO}_3\text{CF}_3$)⁺ 1014.5098, found m/z 1014.4767. NMR data for **11a** are as follows. (see above for data for **11b**, observed in a mixture with **11a**). $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2): δ 71.4 (P-DuPhos, m, $J_{\text{Pt-P}} = 2253$), -58.8 (P-Is, m, $J_{\text{Pt-P}} = 1932$). ^1H NMR (CD_2Cl_2): δ 8.01–7.97 (m, 2H, Ar), 7.93–7.89 (m, 2H, Ar), 7.27 (broad, 4H, Ar), 4.47 (apparent t, $J = 11$, 2H, PCH_2P), 3.63 (broad, 2H, i -Pr CH), 3.30–3.16 (m, 2H, CH), 2.97 (sep, $J = 7$, 4H, i -Pr CH), 2.78 (broad, 2H, CH), 2.65–2.57 (m, 2H, CH_2), 2.56–2.53 (m, 6H, P-Me), 2.44–2.33 (m, 2H, CH_2), 2.08–2.00 (m, 2H, CH_2), 1.74–1.69 (m, 2H, CH_2), 1.58 (dd, $J = 20$, 7, 6H, CH_3), 1.45–1.36 (broad m, 6H, i -Pr CH_3), 1.33–1.29 (broad m, 6H, i -Pr CH_3), 1.27 (d, $J = 7$, 24H, i -Pr CH_3), 1.01 (dd, $J = 17$, 7, 6H, CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2): δ 156.0 (quat, Ar), 155.1 (broad, quat, Ar), 153.6 (broad, quat, Ar), 137.1 (broad m, quat, Ar), 134.8 (m, CH, Ar), 134.4 (m, CH, Ar), 127.2 (broad, CH, Ar), 125.1 (broad, CH, Ar), 122.6 (q, $J = 322$, CF_3), 118.8–118.3 (m, quat, Ar), 49.7 (apparent t, $J = 35$, PCH_2P), 46.6 (d, $J = 33$, CH), 38.7 (d, $J = 31$, CH), 37.8 (CH_2), 36.3 (d, $J = 7$, CH_2), 34.5 (i -Pr CH), 32.4 (broad, i -Pr CH), 28.0 (broad, i -Pr CH), 26.7 (i -Pr CH_3), 26.6 (broad, i -Pr CH_3), 25.9 (broad, i -Pr CH_3), 25.4 (broad, i -Pr CH_3), 23.4 (i -Pr CH_3), 21.7–21.3 (m, P- CH_3), 17.7 (d, $J = 5$, DuPhos CH_3), 16.3 (DuPhos CH_3).

■ ASSOCIATED CONTENT

● Supporting Information

Text, tables, figures, and CIF files giving additional experimental and crystallographic details and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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