The *gem*-Dialkyl Effect as a Test for Preliminary Diphosphine Chelate Opening in a Reductive Elimination Reaction[†]

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A significant kinetic effect of the placement of *gem*-dialkyl substituents in the carbon backbone of a bidentate phosphine ligand on a reductive elimination reaction involving chelate opening as a preliminary step has been documented. This observation confirms the viability of the *gem*-dialkyl effect as a mechanistic probe for preliminary phosphine dissociation in reactions of complexes containing chelating diphosphine ligands.

Introduction

Ancillary ligands are critical components in homogeneous transition metal catalyzed reactions. The steric, electronic, and chiral properties of these ligands are often the key to the effectiveness of the metal catalyst.[1] Bidentate phosphine ligands, whose properties can be easily modified by changing the groups attached to the phosphorus atoms and by changing the number or identity of the atoms in the backbone chain connecting the phosphorus groups, have proven particularly profitable in catalytic processes.[2] However, it is often challenging to predict which ligand modifications (steric and electronic) will lead to the desired increases in rate or selectivity. In some cases, the dissociation of an ancillary ligand is required during the reaction, and this adds a new element to the challenge of ligand design, particularly when chelating ligands are used.

Ligand dissociation to open a coordination site at the metal can be necessary to allow access to a low-energy pathway for reaction steps such as oxidative addition, reductive elimination, β-hydride elimination, and olefin insertion.[1] In complexes with chelating ancillary ligands, dissociation of one end of the chelate (i.e., opening of the chelate) may then be required to generate the open site. Yet, it is notoriously difficult to confirm the involvement of such preliminary chelate opening.[3] The traditional method to detect preliminary ligand dissociation, useful with monodentate ligands, involves the demonstration of rate inhibition by added ligand. This test is not valid for bidentate ligands, as the concentration of added ligand can never approach the intrinsic high *effective* concentration of the partially coordinated ligand.

Numerous examples of reductive elimination, often the product-forming and rate-determining step in a catalytic cycle, have been shown to involve ancillary ligand dissociation as a preliminary reaction step.[3] Primarily, such reactions to form C−H and C−C bonds have involved monodentate ligands, and obtaining evidence for a preequilibrium ligand dissociation mechanism in these model systems via kinetic studies (rate inhibition by added ligand) has been straightforward.

Recently, the use of the *gem*-dialkyl effect[4] was proposed as a test for detecting preliminary ligand dissociation involving chelating ligands.[5] Marcone and Moloy studied the rates of C−CN reductive elimination from the Pd(II) complexes $L_2Pd(CN)(CH_2SiMe_3)$ (L_2 = dppp, Et_2dppp, cbdppp, Scheme 1).[5] The geminal substitution of alkyl groups for hydrogen atoms on the aliphatic backbone of the phosphine chelate dppp was expected to hinder opening of the chelate ring via the *gem*-dialkyl effect. This proposal was based on the very large rate differences (as much as 10^{10})[6] that have been observed in organic cyclization reactions with *gem*-

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[†] Contribution #8606.

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[1] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Organometallic Chemistry of Transition Metals: Principles and Use*; University Science Books: Mill Valley, CA, 1987. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; John Wiley & Sons: New York, 2001.

[2] For some leading references, see: (a) Freixa, Z.; Van Leeuwen, P. W. N. M. *Dalton Trans.* **2003**, 1890. (b) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741. (c) Casey, C. P.; Whiteker, G. T.; Melville, M. G.; Petrovich, L. M.; Gavney, J. A.; Powell, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 5535. (d) Casey, C. P.; Whiteker, G. T. *Isr. J. Chem.* **1990**, *30*, 299. (e) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (f) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Wemkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946.

[3] Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442, and references therein.

[4] For explanations and discussion of the *gem*-dialkyl effect, see: (a) Parrill, A. L.; Dolata, D. P. *J. Mol. Struct. (THEOCHEM)* **1996**, *370*, 187. (b) Jung, M.; Gervay, J. *J. Am. Chem. Soc.* **1991**, *113*, 224. (c) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735.

[5] Marcone, J. E.; Moloy, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 8527.

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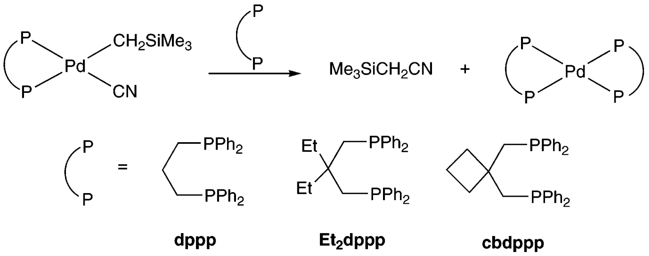
Scheme 1

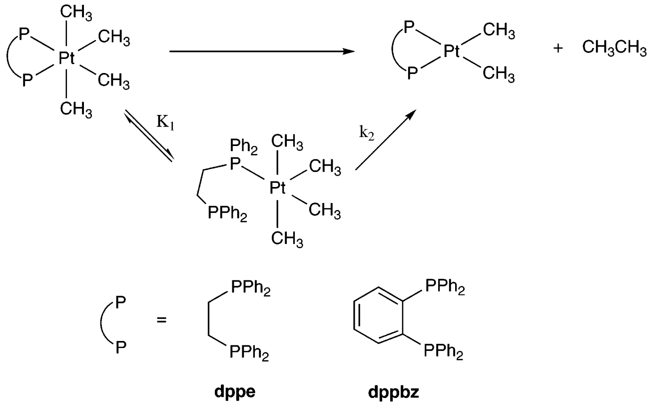


dialkyl substitutions.[4] However, instead of the rate variation expected if the reaction proceeded via phosphine dissociation (Et_2dppp, cbdppp < dppp), the authors found that the rates varied only slightly (less than 4×) following the order Et_2dppp < dppp < cbdppp.[5] Thus, the reaction was proposed to proceed *without* chelate opening. When a larger group of bidentate ligands were compared in this reductive elimination reaction, an overall rate variation of 10^4 was observed with dppe (1,2-bis(diphenylphosphino)ethane) < cbdppp < dppp < Et_2dppp < DIOP (2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis((diphenylphosphino)butane). This trend was attributed to the effect of increasing the bite angle of the bisphosphine ligands on direct C−C coupling from the four-coordinate Pd(II) center.[2a,5,7] What remained unclear from the study, however, is whether *gem*-dialkyl substitution at a carbon within a chelating ligand would indeed register a significant effect on the rate of a reaction involving chelate opening as a preliminary reaction step. That is, can *gem*-dialkyl substitution in the backbone of a phosphine chelate be used as a test for chelate opening during a reaction?

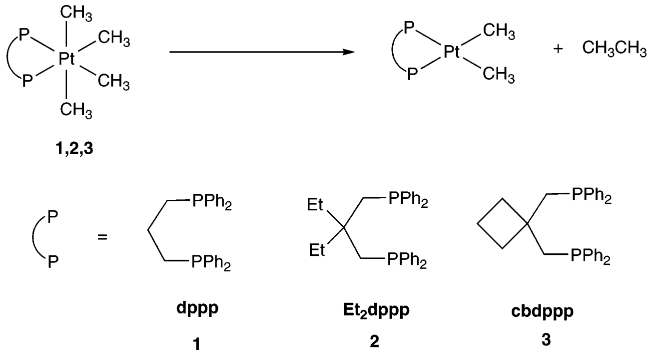
While the *gem*-dialkyl effect has been frequently employed in organic chemistry, there are considerably fewer examples of its application in inorganic and organometallic systems. Shaw has argued that to effectively employ the *gem*-dialkyl effect in systems having tetrahedral atoms that are larger than carbon, e.g., phosphorus or metals, larger groups such as *tert*-butyl, rather than methyl or ethyl, would be required.[8] Indeed, Shaw made excellent use of bulky organic substituents on phosphorus to promote cyclometalation reactions and to favor the formation of large chelate rings.[8] Another illustration of the effective use of the *gem*-dialkyl effect on the thermodynamics of inorganic systems dates back almost fifty years. Through the measurement of formation constants, it was shown that Cu and Ni complexes of 2,2-dimethyl-1,3-propanediamine were more stable than those of 1,3-propanediamine.[9] However, the kinetic effects of *gem*-dialkyl substitution on inorganic and organometallic reactions have not been adequately explored.

Recently, strong evidence was presented that carbon−carbon reductive elimination from a Pt(IV) tetramethyl complex with a chelating bidentate ligand proceeds via preequilibrium opening of the phosphine chelate.[3] In this study, the rates of reductive elimination of ethane from L_2PtMe_4 (L_2 = dppe and dppbz (1,2-bis(diphenylphosphino)benzene)) were measured and compared (Scheme 2). Combined with the results of a variety of other mechanistic experiments, the observation of a difference of 2 orders of magnitude in reactions rates between the complex containing dppe and that containing the more rigid dppbz ligand provided strong support that for reductive elimination of ethane from dppePtMe$_4$ one end of the phosphine dissociates to form a five-coordinate intermediate prior to carbon−carbon coupling. Evidence was also presented that phosphine chelate opening in this system was kinetically viable as a preliminary step, or in other words, the rate of phosphine dissociation exceeds that of C−C reductive elimination.[3] Thus, this L_2PtMe_4 system is ideally suited for analyzing whether the *gem*-dialkyl effect is useful as a means to detect such chelate opening. In addition, studies of this system should provide the first estimate of the magnitude of rate inhibition to be expected upon such *gem*-dialkyl substitution in a reaction involving preequilibrium chelate opening. Herein, we report the results of such a study in which the six-coordinate d^6 Pt(IV) complexes, L_2PtMe_4, where L_2 = dppp (**1**), Et_2dppp (**2**), and cbdppp (**3**), have been synthesized and characterized, and the kinetics of their thermolysis reactions to produce ethane and L_2PtMe_2 measured and compared.

Scheme 2



Scheme 3



Results and Discussion

Synthesis and Characterization of L_2PtMe_4. The complexes L_2PtMe_4 (L_2 = dppp (**1**), Et_2dppp (**2**), cbdppp (**3**), Scheme 3) were prepared either by the reaction of bisphosphine ligand L_2 with $Pt_2Me_8(\mu\text{-}SMe_2)_2$ or by the reaction of L_2PtMe_3I, generated in situ from L_2 and $[PtMe_3I]_4$, with MeMgCl. Complexes **1**−**3** were recrystallized from methylene chloride/pentane solutions and characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis.

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[7] Brown, J. M.; Guiry, P. J. *Inorg. Chim. Acta* **1994**, *220*, 249.
[8] Shaw, B. L. *Adv. Chem. Ser.* **1982**, *196*, 101.
[9] Hares, G. B.; Fernelius, C.; Douglas, B. D. *J. Am. Chem. Soc.* **1956**, *78*, 1816.

The NMR data for complexes **1**, **2**, and **3** are very similar. In the ^{1}H NMR spectra, values of Pt−H coupling constants for Pt−CH_3 groups are nearly identical. For Pt−CH_3 *trans* to methyl, $^2J_{Pt-H}$ is 43 Hz for **1** and 44 Hz for both **2** and **3**. For Pt−CH_3 *trans* to phosphorus, $^2J_{Pt-H}$ is 59 Hz for **1** and **2** and 60 Hz for **3**. In addition, the value of the P−H coupling constant for the Pt-bound methyl groups varies only slightly with the phosphine ligand. For Pt−CH_3 *trans* to methyl, $^3J_{P-H}$ is 5.7 Hz for **1** and **2** and 6.0 Hz for **3**. For Pt−CH_3 *trans* to phosphorus, $^3J_{P-H}$ is 6.0 for **1**, 6.7 for **2**, and 6.8 for **3**. In the ^{31}P{^{1}H} NMR spectra, it is seen that the Pt−P coupling constants are also similar: 1084 Hz for **1**, 1082 Hz for **2**, and 1068 Hz for **3**.

The similarity in the spectroscopic data of complexes **1**, **2**, and **3** indicates that the three complexes have very similar structures. This is analogous to the virtually identical ν_{CN} stretches found for the Pd complexes, $L_2Pd(CN)CH_2SiMe_3$ (L_2 = dppp, Et$_2$dppp, cbdppp),[5] further suggesting that there are negligible electronic differences between the members of this ligand set. Additional evidence that the three ligands, dppp, Et$_2$dppp, and cbdppp, coordinate to the metal to form similar six-membered rings is that only minimal differences in P−M−P angles are observed. The P−Pt−P angles of the Pt(II) complexes L_2PtMe_2 (L_2 = Et$_2$dppp and cbdppp) have been reported as 95.82(4)° and 95.39(5)°, respectively.[10] For direct comparison to these complexes, crystals of dpppPtMe$_2$ were grown and analyzed by X-ray diffraction; a P−Pt−P of 93.56(4)° was found.[11] Thus, despite predictions on the basis of the Thorpe−Ingold hypothesis (P−Pt−P angle predicted to vary as L_2 = cbdppp > dppp > Et$_2$dppp),[5] the six-membered chelate ring containing the large metal and two phosphorus atoms is apparently able to effectively minimize the strain caused by changes in the C−C−C angle resulting from the *gem*-dialkyl substitutions. Although there is a variation of almost 5° in the C−C−C internal chelate angles of the L_2PtMe_2 complexes (dppp (114.22°), cbdppp (111.3°), Et$_2$dppp (109.3°)), the P−Pt−P angles for the three Pt(II) complexes are within 2° of one another. As implied by the virtually identical NMR coupling constants (J_{Pt-H}, J_{P-H}, and J_{Pt-P}) for the methyl and phosphine ligands attached to Pt in complexes **1**−**3**, comparable minimal differences in the P−Pt−P bond angles are expected for the analogous Pt(IV) complexes, **1**−**3**.

In summary, relevant spectroscopic and crystallographic data support that the structures of complexes **1**, **2**, and **3** are similar. Thus, any differences in observed reaction rates for reductive elimination from these complexes cannot be readily attributed to ground state structural or electronic differences between them.

Thermolysis of Complexes 1−3. When the Pt(IV) complexes (dppp)PtMe$_4$ (**1**), (Et$_2$dppp)PtMe$_4$ (**2**), and (cbdppp)PtMe$_4$ (**3**) were heated in C_6D_6 at 165 °C, ethane and the corresponding Pt(II) product, L_2PtMe_2, formed as the exclusive products (Scheme 3). The reactions exhibited clean and reproducible first-order kinetic behavior, and representative kinetic data are shown in Figure 1. The rate constants for the reductive elimination reactions of **1**−**3** are presented in Table 1.

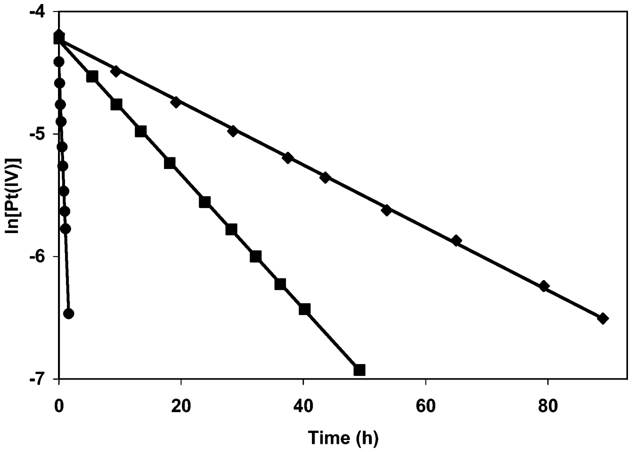

Figure 1. First-order kinetic plots of the disappearance of L_2PtMe_4 (● = **1**, ♦ = **2**, ■ = **3**) in C_6D_6 at 165 °C.

Table 1. First-Order Rate Constants for the Reductive Elimination of Ethane from 1−3 in C_6D_6 at 165 °C

complex	k_{obs} (s^{-1})
(dppp)PtMe$_4$ (**1**)	$(3.3 \pm 0.2) \times 10^{-4}$
(Et$_2$dppp)PtMe$_4$ (**2**)	$(7.3 \pm 0.2) \times 10^{-6}$
(cbdppp)PtMe$_4$ (**3**)	$(1.6 \pm 0.1) \times 10^{-5}$
(dppe)PtMe$_4$[3]	$(4.2 \pm 0.1) \times 10^{-6}$

It is of interest to first compare the rate constant for reductive elimination from **1** ($k_{obs} = (3.3 \pm 0.2) \times 10^{-4}$ s^{-1}) to that measured for reductive elimination from dppePtMe$_4$ ($k_{obs} = (4.2 \pm 0.1) \times 10^{-6}$ s^{-1})[3] under the same conditions; an increase of almost 80 times is observed upon substituting dppp for dppe. Since a detailed mechanistic study of carbon−carbon reductive elimination from dppePtMe$_4$ provided strong evidence that the reaction proceeds via preliminary chelate opening,[3] it is reasonable to attribute the faster reaction of dpppPtMe$_4$ to the increased flexibility provided by the three-carbon chain of dppp versus the two-carbon chain of dppe. However, it has been reported that the same replacement in $L_2Pd(CN)(CH_2SiMe_3)$ led to an increase of 24 times in the rate of C−CN reductive elimination, and acceleration in this system was attributed to the increase in bite angle on going from dppe (natural bite angle of 85°) to dppp (natural bite angle of 91°), with the reaction proposed to proceed via a direct pathway not involving ligand chelate opening.[5] Similarly, an increase of 46 times was observed for the same dppe to dppp substitution in the rates of ethane elimination from $L_2Ni(CH_3)_2$.[12] In this Ni system, the authors left open the question of whether the rate difference was due to a distortion of the starting complex structure (ligand bite angle) or a result of chelate opening on the reaction path. Note that in the Pd and Ni systems, the P−M−P angle of the tetrahedral M(0) product will be significantly greater than in the starting square planar M(II) complex. In contrast, for the Pt example, the octahedral Pt(IV) starting complex and the square

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(10) Smith, D. C., Jr.; Haar, C. M.; Stevens, E. D.; Nolan, S. P.; Marshall, W. J.; Moloy, K. G. *Organometallics* **2000**, *19*, 1427.

(11) Complete crystallographic data for dpppPtMe$_2$·1/2($C_6H_5CH_3$) supplied as CIF in the Supporting Information ($C_{65}H_{27}P_4Pt_2$, MW = 1367.27, colorless prism, monoclinic, space group = $P2_1/c$, T = 130(2) K, a = 12.1540(2) Å, b = 14.9520(3) Å, c = 18.4300(3) Å, α = 90°, β = 120.5791(10)°, γ = 90°, Z = 2, R_1 ($I > 2\sigma(I)$) = 0.0354, wR_2 (all data) = 0.0928, GOF (F^2) = 1.044).

(12) Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1980**, *192*, 265.

planar Pt(II) product have similar P−Pt−P angles.[13] Overall, it then appears difficult to distinguish the effects of increased bite angle and increased flexibility on substitution of dppp for dppe, compromising this substitution as an unambiguous test for chelate opening.

In contrast, spectral and crystallographic data imply that the P−M−P angles for coordinated dppp, Et_2dppp, and cbdppp are similar and the ground state structures of **1**, **2**, and **3** highly comparable. Thus, rate differences in reductive elimination from **1**, **2**, and **3** should be directly attributable to differences in the flexibility of the chelate caused by the *gem*-dialkyl substitution. These differences in the rates of reductive elimination reactions to form ethane and L_2PtMe_2 from **1**, **2**, and **3** are significant (Table 1). The *gem*-dialkyl-substituted dppp complexes, $Et_2dpppPtMe_4$ (**2**) and $cbdpppPtMe_4$ (**3**), eliminate ethane 45 times and 21 times slower, respectively, than the unsubstituted dppp complex **1**. This substantial difference in the rates of elimination from **2** and **3** compared to that of **1** is consistent with the proposal that these reductive eliminations follow the mechanism previously supported for ethane elimination from the analogous bisphosphine Pt(IV) tetramethyl complex (dppe)$PtMe_4$.[3] In this case, chelate opening occurs as a preequilibrium step and is followed by rate-determining carbon−carbon coupling from the resultant five-coordinate intermediate.[14] The results reported here demonstrate that *gem*-dialkyl substituents can significantly affect the rates of reactions wherein partial chelate dissociation is involved as an initial step. Thus, the *gem*-dialkyl effect shows considerable potential as a viable method for detection of chelate opening on the reaction pathway.

As noted earlier, *gem*-dialkyl substitution has been widely used in organic chemistry to accelerate cyclization reactions, to stabilize cyclic structures, and as a mechanistic tool.[4] Its application in inorganic and organometallic chemistry, however, has been primarily limited to thermodynamic observations, i.e., favoring ring-closed structures with *gem*-dialkyl substitution.[8,9] As such, its potential as a diagnostic tool in kinetic/mechanistic analyses of metal-based systems has not yet been recognized. However, it is interesting that the kinetic results for the organometallic system reported here can in fact be explained on the basis of thermodynamics. The reductive elimination of ethane consists of an equilibrium step of chelate opening (K_1) followed by rate-determining carbon−carbon bond formation (k_2) ($k_{obs} = K_1k_2$; see Scheme 2).[14] Assuming that the *gem*-dialkyl substitution destabilizes the chelate-opened form, the overall rate constant is decreased by diminishing the equilibrium constant (K_1) for the preliminary ligand dissociation step. Thus, the reductive eliminations from *gem*-dialkyl-substituted **2** and **3** are much slower than from unsubstituted **1**. Note that changing the identity of the *gem*-alkyl substituents does not appear to have a significant effect, as there is only a small difference (ca. 2×) in the rates of the reductive elimination from **2** (Et_2dppp) and **3** (cbdppp). This is similar to thermodynamic observations by Busch in which although the formation constants for Ni(II) and Cu(II) complexes of *gem*-substituted 1,1-R_2-1,3-propanediamine were in general greater than that of 1,3-propanediamine, there was little variation found in Ni(II) formation constants with the size of R for 1,1-R_2-1,3-propanediamine (R = Me, Et) or with ring size for 1,1-di(aminomethyl)cycloR′ (R′ = propane, butane, pentane, hexane).[15]

In summary, *gem*-dialkyl substitution on the dppp backbone led to a significant decrease in the rate of reductive elimination from **2** and **3** as compared to **1**. This rate inhibition illustrates that the *gem*-dialkyl effect has potential as a mechanistic probe for preliminary chelate opening on a reaction pathway. The results reported here also offer the first insight into the magnitude of a kinetic effect that might be expected by such substitution. Our kinetic results parallel earlier observations of the *gem*-dialkyl effect on the thermodynamics of chelation in inorganic and organometallic systems.

Experimental Section

General Considerations. Unless otherwise noted, all reactions were carried out under a N_2 atmosphere in a Vacuum Atmospheres VAC-MO-40-M drybox. Pentane and CH_2Cl_2 were dried over CaH_2. Benzene, THF, diethyl ether, and toluene were dried over sodium and benzophenone. All solvents were distilled before use. Benzene-d_6 and dioxane were dried over sodium benzophenone and vacuum transferred prior to use. ^1H NMR, ^{31}P NMR, ^{13}C NMR, DEPT-135, HMQC, and HMBC spectra were collected on Bruker DPX, DRX, and AVANCE spectrometers. The ^1H NMR spectra were referenced to residual protiated solvent, and chemical shifts are reported in parts per million downfield of tetramethylsilane. The ^{13}C NMR, DEPT-135, HMQC, and HMBC spectra were referenced to residual solvent peaks or a known chemical shift standard. ^{31}P NMR spectra were referenced to an external standard of 85% phosphoric acid, and all chemical shifts are reported in parts per million (ppm) downfield of this reference. Coupling constants are reported in hertz (Hz). Elemental analyses were performed by Atlantic Microlab, Inc.

$Pt_2Me_8(\mu\text{-}SMe_2)_2$,[16] $[PtMe_3I]_4$,[17] Et_2dppp,[18] and cbdppp[19] were prepared according to literature procedures. Unless otherwise noted, all other reagents were used as supplied from commercial sources.

Synthesis and Characterization of (dppp)$PtMe_4$ (1). Under nitrogen, dppp (169 mg, 0.409 mmol) and $[PtMe_3I]_4$ (146 mg, 0.0994 mmol) in THF (10 mL) were allowed to stir overnight. The solvent was removed under vacuum and toluene (10 mL) was added to the residue. MeMgCl (2.8 M in THF, 0.8 mmol) was added, and the reaction was allowed to stir overnight. The reaction was exposed to air, and water (0.5 mL) was slowly added to the reaction mixture (0 °C) to quench the excess MeMgCl. The volatiles were removed under vacuum. CH_2Cl_2 (10 mL) was added to dissolve the Pt compounds. The suspension was filtered through tightly packed glass wool, and the volatiles were removed from the filtrate under vacuum.

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[13] The PPtP angle is 86.04(3)° in (dppe)$PtMe_4$ (ref 3) and 84.73(5)° in dppe$PtMe_2$ (ref 10).

[14] The precedent of the dppe$PtMe_4$ reaction wherein rate-determining C−C coupling occurs after preequilibrium phosphine chelate opening[3] strongly argues against the possibility of rate-determining phosphine dissociation in the analogous dppp system. The rate of phosphine dissociation from Pt(IV) for the more flexible dppp should be even greater than that of the dppe ligand.

[15] Newman, M. S.; Busch, D. H.; Cheney, G. E.; Gustafson, C. R. *Inorg. Chem.* **1972**, *11*, 2890.

[16] Lashanizadehgan, M.; Rashidi, M.; Huz, J. E.; Puddephatt, R. J.; Ling, S. S. M. *J. Organomet. Chem.* **1984**, *269*, 317.

[17] Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

[18] Bianchini, C.; Lee, H. M.; Meli, A.; Moneti, S.; Vizza, F.; Fontani, M.; Zanello, P. *Macromolecules* **1999**, *32*, 4183.

[19] Prepared analogously to Et_2dppp (ref 18) via the reaction of $(CH_2)_3C(CH_2OTs)_2$ (Houk, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1987**, *109*, 6825) with $LiPPh_2$.

This material contained 84% (**1**) and 16% (dppp)PtMe$_2$ (determined by ^{31}P{^{1}H} NMR). Recrystallization from THF/pentane afforded white crystals of **1** in 15% yield (37.3 mg). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 0.62 (t, w/Pt satellites, 6H, $^2J_{\mathrm{Pt-H}} = 43$, $^3J_{\mathrm{P-H}} = 5.7$, Pt−CH_3 *trans* to methyl), 1.08 (t, w/Pt satellites, 6H, $^2J_{\mathrm{Pt-H}} = 59$, $^3J_{\mathrm{P-H}} = 6.0$, Pt−CH_3 *trans* to phosphorus), 1.55 (br m, 2H, P−CH$_2$−CH_2−CH$_2$−P), 2.16 (br m, 4H, P−CH_2−CH$_2$−CH_2−P), 7.04 and 7.33 (br m, 12H, 8H, phenyl protons). ^{13}C{^{1}H} NMR (50 MHz, CD$_2$Cl$_2$): δ −5.52 (t, w/Pt satellites, $^1J_{\mathrm{Pt-C}} = 408$, $^2J_{\mathrm{P-C}} = 4.7$, Pt−CH$_3$ *trans* to methyl), 8.65 (dd, w/Pt satellites, $^1J_{\mathrm{Pt-C}} = 546$, *cis* $^2J_{\mathrm{P-C}} = 7.7$, *trans* $^2J_{\mathrm{P-C}} = 124$, Pt−CH$_3$ *trans* to phosphorus), 20.19 (s, P−CH$_2$−CH$_2$−CH$_2$−P), 24.36 (virtual coupling pattern,[20] P−CH$_2$−CH$_2$−CH$_2$−P), 128.3, 130.2, and 133.9 (phenyl carbons). ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$): δ −32.9 (s, w/Pt satellites, $^1J_{\mathrm{Pt-P}} = 1084$). Anal. Calcd for C$_{31}H_{38}P_2$Pt: C, 55.77; H, 5.74. Found: C, 56.06; H, 5.85.

Synthesis and Characterization of (Et$_2$dppp)PtMe$_4$ (2) and (cbdppp)PtMe$_4$ (3). Et$_2$dpppPtMe$_4$ (**2**) and cbdpppPtMe$_4$ (**3**) were prepared by a method adapted from a procedure reported for a similar compound.[16] Pt$_2$Me$_8$(μ-SMe$_2$)$_2$ (21.8 mg, 0.0343 mmol) and diphosphine ligand (0.0700 mmol) were dissolved in toluene (2 mL), and the solution was allowed to stir for 3 h in a sealed reaction vessel. The solvent was removed under vacuum, and the product was recrystallized from methylene chloride layered with pentane at −35 °C. **Et$_2$dpppPtMe$_4$ (2):** Colorless blocks were produced (34.0 mg, 76% yield). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 0.35 (t, $^3J_{\mathrm{H-H}} = 7.2$, 6H, CH$_2$−CH_3), 0.66 (t, w/Pt satellites, 6H, $^2J_{\mathrm{Pt-H}} = 44$, $^3J_{\mathrm{P-H}} = 5.7$, Pt−CH_3 *trans* to methyl), 0.92 (q, 4H, $^3J_{\mathrm{H-H}} = 7.3$, CH_2−CH$_3$), 1.19 (t, w/Pt satellites, 6H, $^2J_{\mathrm{Pt-H}} = 59$, $^3J_{\mathrm{P-H}} = 6.7$, Pt−CH_3 *trans* to phosphorus), 2.62 (m, 4H, P−CH_2), 7.04 and 7.57 (br m, 12H, 8H, phenyl protons). ^{13}C{^{1}H} NMR (50 MHz, C$_6$D$_6$): δ −4.33 (t, w/Pt satellites, $^1J_{\mathrm{Pt-C}} = 411$, $^2J_{\mathrm{P-C}} = 4.3$, Pt−CH$_3$ *trans* to methyl), 7.51 (s, CH$_2$−CH$_3$), 9.42 (dd, w/Pt satellites, $^1J_{\mathrm{Pt-C}} = 548$, *cis* $^2J_{\mathrm{P-C}} = 6.5$, *trans* $^2J_{\mathrm{P-C}} = 124$, Pt−CH$_3$ *trans* to phosphorus), 32.8 (vt[20] with apparent $J = 15.5$, P−CH$_2$), 34.0 (vt[20] with apparent $J = 5.7$, CH$_2$−CH$_3$), 39.9 (s, quaternary carbon), 130.1, 134.5, and 135.2 (phenyl carbons). ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$): δ −35.0 (s, w/Pt satellites $^1J_{\mathrm{Pt-P}} = 1082$). Anal. Calcd for C$_{35}H_{46}P_2$Pt: C, 58.08; H, 6.41. Found: C, 58.14; H, 6.40. **For cbdpppPtMe$_4$ (3):** A white powder was produced (36.0 mg, 68% yield). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 0.64 (t, w/Pt satellites, 6H, $^2J_{\mathrm{Pt-H}} = 44$, $^3J_{\mathrm{P-H}} = 6.0$, Pt−CH_3 *trans* to methyl), 1.15 (t, w/Pt satellites, 6H, $^2J_{\mathrm{Pt-H}} = 60$, $^3J_{\mathrm{P-H}} = 6.8$, Pt−CH_3 *tran*s to phosphorus), 1.27 (t, 4H, $^3J_{\mathrm{H-H}} = 7.2$, CH_2−CH$_2$−CH_2), 1.47 (p, 2H, $^3J_{\mathrm{H-H}} = 7.7$, CH$_2$−CH_2−CH$_2$), 2.79 (q, 4H, $^3J_{\mathrm{H-H}} = 8.0$, $^2J_{\mathrm{P-H}} = 5.7$, P−CH_2), 7.04 and 7.49 (br m, 12H, 8H, phenyl signals). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ −5.02 (t, w/Pt satellites, $^1J_{\mathrm{Pt-C}} = 411$, $^2J_{\mathrm{P-C}} = 4.3$, Pt−CH$_3$ *trans* to methyl), 7.96 (dd, w/Pt satellites, $^1J_{\mathrm{Pt-C}} = 543$, *cis* $^2J_{\mathrm{P-C}} = 6.6$, *trans* $^2J_{\mathrm{P-C}} = 124$, Pt−CH$_3$ *trans* to phosphorus), 16.4 (s, CH$_2$−CH$_2$−CH$_2$), 35.6 (vt[20] with apparent $J = 15.4$, P−CH$_2$), 38.6 (vt[20] with apparent $J = 6.7$, CH$_2$−CH$_2$−CH$_2$), 40.5 (s, quaternary carbon), 127.8, 129.8, and 133.8 (phenyl carbons). ^{31}P{^{1}H} (202 MHz, C$_6$D$_6$): δ −35.2 (s, w/Pt satellites $^1J_{\mathrm{Pt-P}} = 1068$ Hz). Anal. Calcd for C$_{34}$H$_{42}$P$_2$Pt: C, 57.70; H, 5.98. Found: C, 56.95; H, 5.93.

Kinetics Experiments. In a typical kinetics experiment, the platinum compound (**1**, **2**, or **3**, 3−6 mg) was loaded into a Wilmad 504-PP medium-walled NMR tube that was sealed onto a 14/20 joint. A stopcock adapter was attached to the tube, then the tube was evacuated and deuterated solvent was added via vacuum transfer. Dioxane, the internal standard, was added via a known volume bulb, and the tube was flame-sealed under vacuum. An initial ^{1}H NMR spectrum was collected. The tube was immersed in a Neslab Excal EX-250 HT elevated temperature oil bath at 165 °C for a specified amount of time and then quickly cooled in an ice bath. As a safety precaution, the tubes were surrounded by stainless steel jackets during heating and rapid cooling. Three ^{1}H NMR spectra were acquired after each heating period, and the integration values were averaged. The reaction progress was quantified by integration of the ligand backbone methylene signal relative to the dioxane. The tube was frozen at −20 °C when not in the oil bath or spectrometer. Reactions were monitored for a minimum of three half-lives, and the rate constant was calculated by a least squares linear regression method. Samples were then heated to completion, and mass balance was confirmed by the integration of products against the internal standard.

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Supporting Information Available: X-ray crystallographic data for (dppp)PtMe$_2$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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