

Catalytic Hydrogenolysis of Biphenylene with Platinum, Palladium, and Nickel Phosphine Complexes

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The catalytic hydrogenolysis of biphenylene was carried out using Pt, Pd, and Ni phosphine complexes under an atmosphere of H₂ between 56 and 120 °C. The Pt species Pt(PET₃)₃, (PET₃)₂Pt(2,2'-biphenyl), **1**, *trans*-(PET₃)₂PtH₂, and *trans*-(PET₃)₂Pt(α -biphenyl)H, **4**, were all viable catalysts. The resting state species in each case was complex **4**. At 80 °C under an atmosphere of H₂, **4** reductively eliminates biphenyl and forms *trans*-(PET₃)₂PtH₂. Free PET₃ inhibits the rate of reductive elimination from **4** and the overall rate of hydrogenolysis. The novel Pt(IV) dihydride *trans,cis*-(PET₃)₂Pt(2,2'-biphenyl)H₂ was synthesized and characterized by X-ray analysis. *trans,cis*-(PET₃)₂Pt(2,2'-biphenyl)H₂ undergoes unimolecular reductive elimination to give **2**. On the basis of these results a catalytic cycle is proposed. A mixture of [(dippe)PtH]₂ and (dippe)PtH₂ (dippe = bis(diisopropylphosphino)ethane) was also capable of catalyzing the hydrogenolysis of biphenylene under an atmosphere of H₂ at 120 °C. The rate of hydrogenolysis increases as the concentration of biphenylene, H₂, and (dippe)PtH₂ increases. These observations are consistent with the C–C bond activation of biphenylene occurring via (dippe)PtH₂, not [(dippe)Pt⁰]. The rate of catalytic hydrogenolysis was not affected by the length of the chelating phosphine bridge. The Ni complex [(dippe)NiH]₂ was the most efficient catalyst for the hydrogenolysis of biphenylene (16 turnovers/day at 56 °C). The resting state species was (dippe)Ni(2,2'-biphenyl).

Introduction

Homogeneous C–C bond cleavage and functionalization by transition metal complexes is currently an active area of research in organometallic chemistry. Stoichiometric C–C bond activation by several metal complexes has been reported.^{1–4} Most of these examples rely on relief of ring strain,¹ attainment of aromaticity,² or intramolecular addition in which the C–C bond is forced into close proximity to the metal.³ Catalytic C–C bond activation is less common.^{1k,3a,4} To our knowledge, catalytic hydrogenolysis of C–C bonds in homogeneous

solution has been achieved on two separate occasions. First, the hydrogenolysis of biphenylene to biphenyl was reported with (C₅Me₅)Rh(PMe₃)H₂.^{4e} Second, Milstein and co-workers recently reported the catalytic hydrogenolysis and hydrosilation of a strong C–C bond using a rhodium complex.^{4h}

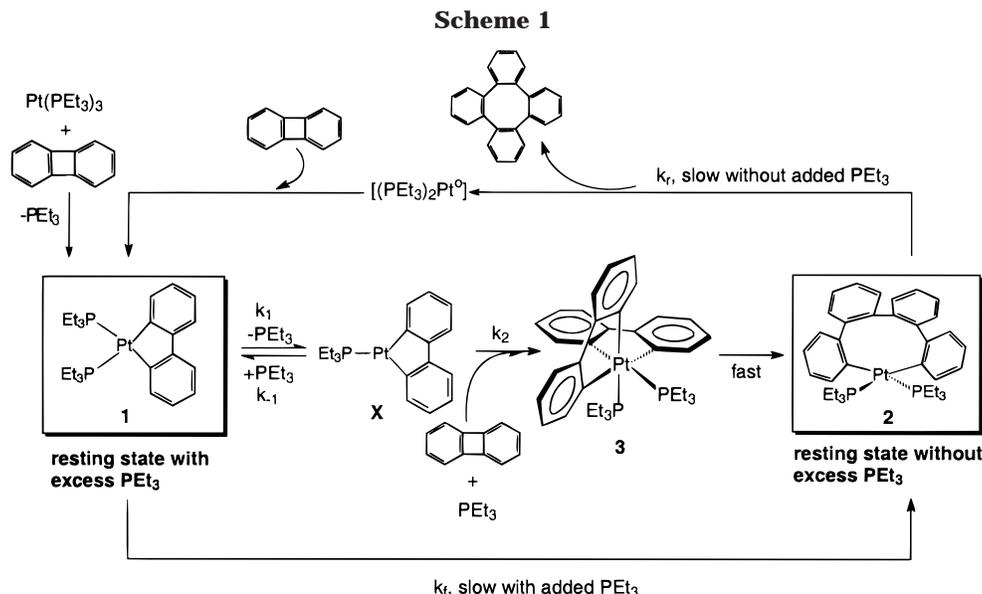
Recently, we reported that tetraphenylene can be formed catalytically from biphenylene via catalytic carbon–carbon bond activation and formation by platinum and palladium phosphine complexes.^{4g} The operating catalytic cycle was determined and is shown in Scheme 1. One important discovery made concerning this catalytic cycle was that as the ratio of free phosphine to biphenylene increases, the rate of catalysis decreases. This observation is consistent with the formation of intermediate **X** via phosphine loss from **1**. Intermediate **X** can either re-coordinate phosphine or

(1) (a) Adams, D. M.; Chatt, J.; Guy, R. G.; Sheppard, N. *J. Chem. Soc.* **1961**, 738–742. (b) Bailey, N. A.; Gillard, R. D.; Keeton, M.; Mason, R.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1966**, 396–398. (c) McQuillin, F. J.; Powell, K. C. *J. Chem. Soc., Dalton Trans.* **1972**, 2123–2129. (d) Barretta, A.; Cloke, F. G. N.; Feigenbaum, A.; Green, M. L. H.; Gourdon, A.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1981**, 156–158. (e) Barretta, A.; Chong, K. S.; Cloke, F. G. N.; Feigenbaum, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1983**, 861–864. (f) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, 3, 1795–1803. (g) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Krüger, C.; Tsay, Y. H. *Organometallics* **1985**, 4, 4–231. (h) Schwager, H.; Spyroudis, S.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1990**, 382, 191–200. (i) Lu, Z.; Jun, C.-H.; de Gala, S. R.; Sigalas, M.; Eisenstein, O.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1877–1880. (j) Lu, Z.; Jun, C.-H.; de Gala, S. R.; Eisenstein, O.; Crabtree, R. H. *Organometallics* **1995**, 14, 1168–1175. (k) Perthuisot, C.; Edelbach, B. E.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, 16, 2016–2023. (l) Shaltout, R. M.; Sygula, R.; Sygula, A.; Fronczek, F. R.; Stanley, G. G.; Rabideau, P. W. *J. Am. Chem. Soc.* **1997**, 120, 8835–8836.

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(3) (a) Suggs, J. W.; Jun, C.-H. *J. Chem. Soc., Chem. Commun.* **1985**, 92–93. (b) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, 364, 699–701. (c) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, 370, 42–44. (d) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1165–1166. (e) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, 117, 9774–9775. (f) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, 118, 12406–12415. (g) Gandelman, M.; Vigalok, A.; Shimon, L. J. W.; Milstein, D. *Organometallics* **1997**, 16, 3981–3986.

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cleave the C–C bond of biphenylene. We demonstrated that recoordination of phosphine is several orders of magnitude more rapid than C–C bond cleavage of a second biphenylene molecule. When (depe)Pt(2,2'-biphenyl) (depe = bis(diethylphosphino)ethane) was used, the catalytic formation of tetraphenylene was completely inhibited.

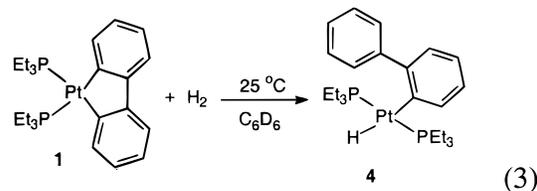
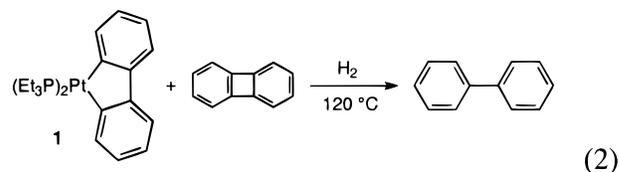
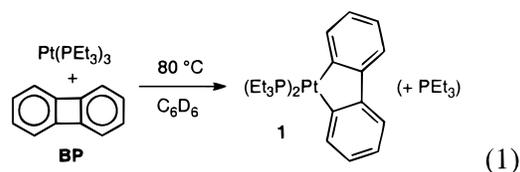
In this paper we demonstrate that addition of H₂ to a mixture containing complex **1** and biphenylene inhibits the formation of tetraphenylene and leads to the catalytic hydrogenolysis of biphenylene instead. Furthermore, the rate of hydrogenolysis is shown to vary depending on the concentration of H₂ and the metal employed. The rate of hydrogenolysis of biphenylene was also monitored with various chelating phosphines on Pt, Pd, and Ni. Finally, catalytic cycles are proposed for the various systems that were evaluated.

Results and Discussion

1. Catalytic Hydrogenation of Biphenylene with Nonchelating Pt Phosphines. The thermolysis of Pt(PEt₃)₃ in toluene-*d*₈ with 5 equiv of biphenylene (BP) at 120 °C under 0.92 atm of H₂ resulted in the catalytic formation of biphenyl (1 turnover/12 days). Initially, the only Pt species observed was (PEt₃)₃PtH₂.⁵ However, as the catalysis progressed, the ³¹P{¹H} NMR spectrum revealed the presence of one dominant Pt-bound phosphine species at δ 16.05 (s, *J*_{Pt–P} = 2862 Hz), as well as free PEt₃.

a. Identification of Intermediates in the Catalytic Reaction. It has been demonstrated that in the absence of H₂, Pt(PEt₃)₃ inserts into the C–C bond of biphenylene at 80 °C to give (PEt₃)₂Pt(2,2'-biphenyl), **1**, and free PEt₃ (eq 1).^{4g} Therefore, **1** was heated at 120 °C with 5 equiv of biphenylene under 0.92 atm of H₂. Biphenyl was formed catalytically with a more rapid turnover rate (1 turnover/4.5 days, eq 2) than with Pt(PEt₃)₃ as the catalyst precursor, suggesting that free PEt₃ inhibits the catalytic reaction. The resting state species was the same as with Pt(PEt₃)₃ as the starting

material. With **1** as the catalyst precursor, a small amount of (PEt₃)₂Pt(2,2'''-terphenyl), **2**, was seen early on in the catalysis, and this complex disappeared as a small amount of tetraphenylene was produced. Complex **2** is an intermediate in the catalytic formation of tetraphenylene from biphenylene when (PEt₃)₂Pt(2,2'-biphenyl) is heated in the presence of biphenylene with no H₂ present (Scheme 1).^{4g}



The resting state species described in the two catalytic reactions above was produced independently by stirring **1** under an atmosphere of H₂ at room temperature (*t*_{1/2} ~ 12 h). On the basis of ¹H NMR and ³¹P NMR spectroscopy the resting state species was assigned as *trans*-(PEt₃)₂Pt(α-biphenyl)H, **4** (eq 3). No other intermediates were observed when monitoring the reaction by ¹H NMR and ³¹P NMR spectroscopy. Added PEt₃ (0.2 M) had no effect on the rate of formation of **4**. The aromatic region of the ¹H NMR spectrum of **4** integrated to nine protons and the hydride region displayed a 1:2:1 triplet at δ –7.450 (C₆D₆, *J*_{Pt–P} = 639.9, *J*_{H–P} = 20.0

(5) Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muettterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543–3544.

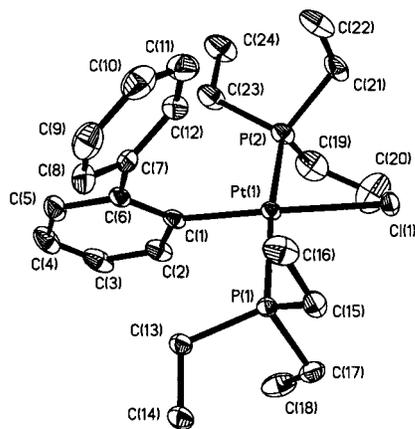
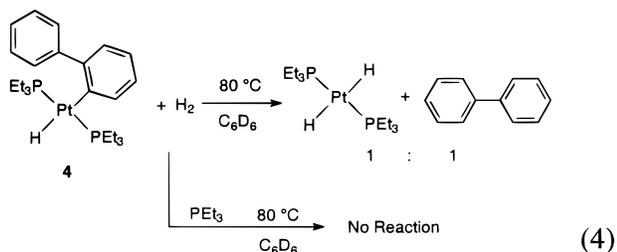


Figure 1. ORTEP drawing of $(\text{PEt}_3)_2\text{Pt}(o\text{-C}_6\text{H}_4\text{Ph})\text{Cl}$, **5**. Ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

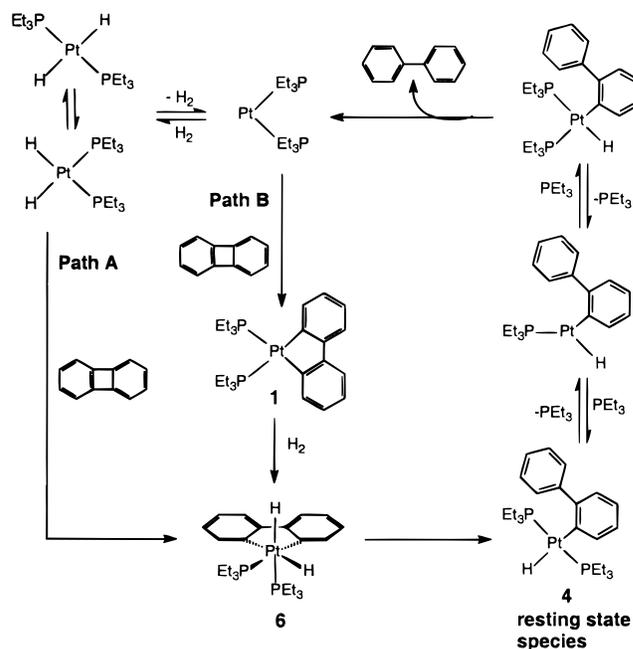
Hz), which integrated to one proton. This pattern is consistent with the hydride coupling to two equivalent cis phosphines. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consisted of a singlet at δ 16.25 (THF- d_6 , $J_{\text{Pt-P}} = 2854$ Hz). The magnitude of this $^{31}\text{P}\{^1\text{H}\}$ coupling constant is similar to that observed in other Pt(II) complexes with trans phosphines in C_6D_6 (cf. *trans*- $(\text{PEt}_3)_2\text{Pt}(\alpha\text{-biphenyl})\text{-phenyl}$) (δ 4.40, $J_{\text{Pt-P}} = 2871$ Hz) and *trans*- $(\text{PEt}_3)_2\text{Pt}(\alpha\text{-biphenyl})(\alpha\text{-biphenylenyl})$ (δ 5.02, $J_{\text{Pt-P}} = 2805$ Hz).^{4g} Chlorination of **4** with CCl_4 results in the formation of *trans*- $(\text{PEt}_3)_2\text{Pt}(\alpha\text{-biphenyl})\text{Cl}$, **5**. With the exception of a lack of a hydride resonance, the ^1H NMR spectrum and the platinum phosphorus coupling constant of **5** (THF- d_6 , $J_{\text{Pt-P}} = 2825$ Hz) are very similar to those of complex **4**. The solid-state structure of the chloro derivative was determined by X-ray crystallography (Figure 1). Compound **5** is a square planar platinum(II) species with trans phosphines and trans biphenyl and chloro groups. When **4** was heated at 120°C with excess biphenylene under H_2 , biphenyl was formed catalytically with the same turnover rate reported for complex **1**. The resting state species was complex **4**. In this case there was no evidence for the formation of $(\text{PEt}_3)_2\text{Pt}(2,2''\text{-terphenyl})$ or tetraphenylene.

Before complex **4** can reductively eliminate biphenyl it must first undergo a trans to cis isomerization. Stang et al. demonstrated that reductive elimination of unsaturated trans organic groups from Pt(II) bisphosphine complexes occurs via reversible dissociation of phosphine to give a 14-electron complex from which isomerization to the cis isomer can occur.⁶ In the present study, complex **4** was heated to 80°C under an atmosphere of H_2 . The products of the reaction were *trans*- $(\text{PEt}_3)_2\text{PtH}_2$ and biphenyl in a one-to-one ratio (eq 4).



However, when the same reaction was run in the presence of excess PEt_3 (0.044 M), no reaction occurred.

Scheme 2



This is consistent with reversible phosphine loss to give a three-coordinate complex from which trans to cis isomerization can occur prior to reductive elimination. It was not possible to determine whether phosphine recoordinates to the metal center prior to or after reductive elimination.^{6,7}

trans- $(\text{PEt}_3)_2\text{PtH}_2$ is also a viable intermediate in the catalytic formation of biphenyl. When *trans*- $(\text{PEt}_3)_2\text{PtH}_2$ was heated at 120°C under 0.92 atm of H_2 in the presence of excess biphenylene, biphenyl was formed catalytically with the same turnover rate as with complexes **1** or **4**. *trans*- $(\text{PEt}_3)_2\text{PtH}_2$ slowly disappears and complex **4** again becomes the resting state species. There was no $(\text{PEt}_3)_2\text{Pt}(2,2''\text{-terphenyl})$ or tetraphenylene formed.

On the basis of the above results the catalytic cycle shown in Scheme 2 is proposed. Complexes $\text{Pt}(\text{PEt}_3)_3$, **1**, **4**, and *trans*- $(\text{PEt}_3)_2\text{PtH}_2$ are all viable catalyst precursors in the formation of biphenyl. In all cases, the resting state species is complex **4**. If *trans*- $(\text{PEt}_3)_2\text{PtH}_2$ is the initial starting material, isomerization to

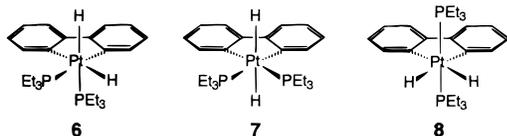
(6) Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 3356–3362. He did not rule out rapid phosphine coordination prior to reductive elimination from the cis complex.

(7) Experimental and theoretical evidence suggests the phosphine loss occurs prior to reductive elimination in *cis*-bis(phosphine) $\text{M}^{\text{II}}\text{R}_2$ systems ($\text{M} = \text{Pd}, \text{Pt}$), where R is an alkyl group: (a) DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601–3607. (b) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868–1880. (c) Gille, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933–4941. (d) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182–4186. (e) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725. (f) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396–3403. (g) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857–1867. However, when at least one organic group is unsaturated, reductive elimination often occurs directly from the four-coordinate species: (h) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174–4181. (i) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1031–1046, and references therein. (j) Ozawa, F.; Kurihara, K.; Fujimori, M.; Hidaka, T.; Toyoshima, T.; Yamamoto, A. *Organometallics* **1989**, *8*, 180–188. (k) Calhorda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*, 1431–1438. (l) Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1980**, *192*, 265–274. (m) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916.

cis-(PEt_3)₂PtH₂ can occur. Trogler et al. have established that a toluene-*d*₈ solution of *trans*-(PEt_3)₂PtH₂ contains 3% of the *cis* isomer.⁸ At this point there are two possible pathways available (Scheme 2). Path A involves C–C bond cleavage of biphenylene by *cis*-(PEt_3)₂PtH₂ to give the Pt(IV) dihydride (**6**). Complex **6** then undergoes rapid intramolecular reductive elimination to give complex **4**. Complex **4** is the resting state species as a result of requisite phosphine loss prior to the reductive elimination of biphenyl. The required loss of phosphine prior to reductive elimination is also the source of phosphine inhibition on the overall catalytic turnover rate. Reductive elimination of biphenyl from **4** leads to [(PEt_3)₂Pt⁰], which can either add H₂ to give *cis*-(PEt_3)₂PtH₂ (path A) or insert into the C–C bond of biphenylene to give **1** (path B). Complex **1** may oxidatively add H₂ to give complex **6** and the cycle continues. *cis*-(PEt_3)₂PtH₂ may also be a source of [(PEt_3)₂Pt⁰] via reductive elimination of H₂. Theoretical calculations have shown that reductive elimination of H₂ from *cis*-L₂PtH₂ (L = PH₃ or PMe₃) has a barrier between 18 and 42 kcal/mol.⁹ The enthalpy of activation for reductive elimination of H₂ from (PMe₃)₂PtH₂ has been calculated to be 20.8 kcal/mol in a noncoordinating solvent.¹⁰

Under the present conditions it is not possible to discriminate between paths A and B. Path B is viable since it is known that [(PEt_3)₂Pt⁰] is capable of cleaving the C–C bond of biphenylene to give **1**.^{4g} Furthermore, it has been demonstrated that complex **1** goes on to give **4** under H₂. However, direct C–C bond cleavage of biphenylene by (PMe₃)₂PtH₂ (path A) cannot be ruled out. Previously we have demonstrated that the C–C bond of biphenylene can be cleaved by another Pt(II) species, (PEt_3)Pt(2,2'-biphenyl), **X** (Scheme 1).^{4g}

b. Identification of a Pt(IV) Intermediate. Complex **6** was not observed during the course of catalysis, nor was it observed when complex **1** was stirred under H₂ at room temperature to give **4**. However, H₂ oxidative addition to **1** or C–C bond cleavage of biphenylene by *cis*-(PEt_3)₂PtH₂ would generate a Pt(IV) dihydride, but is **6** the correct formulation? Three possible Pt(IV) stereoisomers may arise from the reaction of **1** with H₂, as shown below. Structure **7** can be discounted based on the *trans* orientation of the hydrides. Concerted oxidative addition of H₂ to **1** would generate a Pt(IV) center with *cis* hydrides.



Structure **8** was formed independently by addition of NaB(OMe)₃H to *trans,cis*-(PEt_3)₂Pt(2,2'-biphenyl)(OTf)₂.

(8) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 1138–1140.

(9) (a) Noell, J. O.; Hay, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4578–4584. (b) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 6928–6937. (c) Low, J. J.; Goddard, W. A., III. *Organometallics* **1986**, *5*, 609–622. (d) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115–6128. (e) Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7482–7492. (f) Balazs, A. C.; Johnson, K. H.; Whitesides, G. M. *Inorg. Chem.* **1982**, *21*, 2162–2174.

(10) Packett, D. L.; Trogler, W. C. *Inorg. Chem.* **1988**, *27*, 1768–1775.

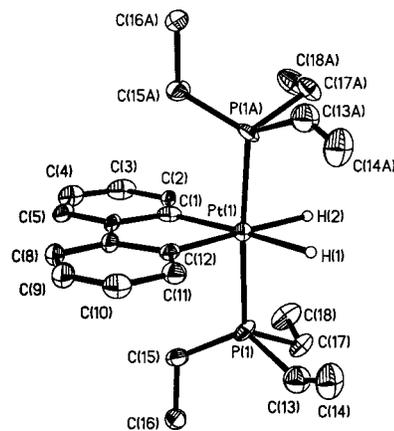
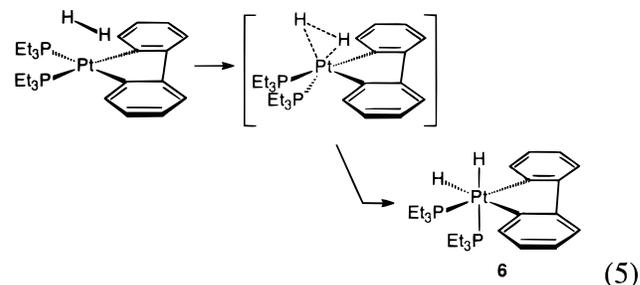


Figure 2. ORTEP drawing of (PEt_3)₂Pt(2,2'-biphenyl)H₂, **8**. Ellipsoids are shown at the 30% level. Hydrogen atoms other than on Pt have been omitted for clarity.

The aromatic region of the ¹H NMR spectrum integrated to eight protons with a splitting pattern very similar to the known Pt(IV) species *trans,cis*-(PEt_3)₂Pt(2,2'-biphenyl)Br₂ and *trans,cis*-(PEt_3)₂Pt(2,2'-biphenyl)HBr.^{4g} The hydride resonance was a triplet at δ –10.619 with corresponding platinum satellites ($J_{\text{Pt-H}} = 637.4$, $J_{\text{P-H}} = 15.8$ Hz) and integrated to two protons. The ³¹P{¹H} NMR spectrum consisted of a singlet at δ –0.978 ($J_{\text{Pt-P}} = 1897$ Hz). The platinum–phosphorus coupling constant is very similar to that observed in the two Pt(IV) species reported above. Based on these data, compound **8** was assigned as *trans,cis*-(PEt_3)₂Pt(2,2'-biphenyl)H₂. Single-crystal X-ray crystallography confirmed the structure of compound **8** (Figure 2). To our knowledge this is the first X-ray crystal structure of a neutral monomeric Pt(IV) dihydride. The solid-state structure shows an octahedral complex with *trans* phosphines and *cis* hydrides (located and included, but not refined).

Heating complex **8** at 65 °C in C₆D₆ led to the formation of complex **4** ($t_{1/2} \sim 300$ h). This observation rules out **8** as an intermediate in the catalytic cycle since complex **1** goes on to form **4** at room temperature ($t_{1/2} \sim 12$ h). Therefore, complex **6** is the most probable Pt(IV) dihydride intermediate in the catalytic cycle. Furthermore, H₂ approach parallel to the plane of complex **1** would be expected to cause a folding down of one of the phosphine groups, resulting in the all-*cis* ligand orientation shown in complex **6** (eq 5). The

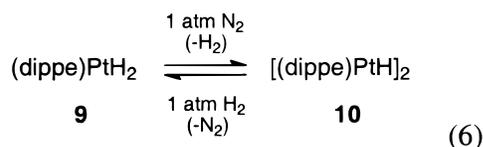


stability of complex **8** relative to **6** may be explained by a simple steric argument. In complex **8** the phosphines are orientated *trans* to one another, thereby providing maximum steric relief.

As stated earlier, the formation of **4** from **1** was not inhibited by added phosphine. This suggests that phosphine dissociation from **1** does not occur prior to the rate-determining step when H₂ adds to complex **1** to give **4**. An earlier study^{4g} demonstrated that excess phosphine severely inhibits the C–C activation of biphenylene by complex **1**, and detailed kinetic studies revealed that phosphine dissociation from **1** is required before insertion into the C–C bond of biphenylene. The fact that H₂ addition does not require phosphine dissociation may simply be a result of the increased ability of the smaller H₂ molecule (vs biphenylene) to approach the square planar complex of **1**. However, a difference in mechanism based upon electronic differences cannot be ruled out.

2. Catalytic Hydrogenation of Biphenylene with Chelating Pt Phosphines. In the system discussed above, phosphine loss from complex **4** is necessary for trans to cis isomerization to occur prior to the reductive elimination of biphenyl. Consequently, reductive elimination of biphenyl (or possibly trans to cis isomerization in the three-coordinate intermediate) is the rate-limiting step in the catalytic cycle. We reasoned that the rate of catalysis might increase if a chelating phosphine was used. A chelating phosphine might eliminate the need for phosphine dissociation since the ligands would already be in a cis orientation. Therefore, (dippe)PtH₂, **9**, was synthesized¹¹ for this purpose. Complex **9** might be a source of [(dippe)Pt⁰] via reductive elimination of H₂, or **9** might be capable of cleaving the C–C bond of biphenylene directly via oxidative addition.

Schwartz and Anderson have established that a reversible chemical equilibrium exists between the monomer **9** and the dimer [(dippe)PtH]₂, **10** (eq 6).¹¹



When a mixture of **9** and **10** (3.2:1 based on ¹H NMR spectroscopy at room temperature) was heated at 120 °C in a sealed NMR tube with excess biphenylene under 702 mm H₂, biphenyl was formed catalytically. Although no sign of *cis*-(dippe)Pt(biphenyl)H could be detected, the turnover *rate* did not increase as anticipated. The concentration and ratio of **9**:**10** remained essentially constant throughout the reaction (based on ¹H NMR spectroscopy at room temperature). Initially, these were the only two metal species observed; however, as the catalysis progressed, a small amount of (dippe)Pt(2,2'-biphenyl), **11**, was detected. Complex **11** was independently synthesized and a solid-state structure was obtained. Complex **11** shows the expected square planar geometry with only a slight deviation from planarity (±0.12 Å, Figure 3).

The effect of H₂ pressure on the rate of hydrogenolysis of biphenylene was tested by performing the same reaction under 130 mm H₂. In this case the ratio of **9**:**10** remained at approximately 0.85:1 during the course of

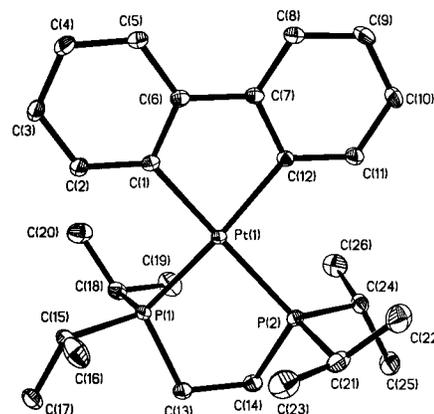
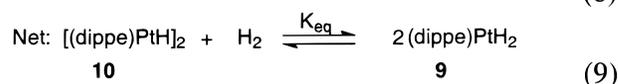
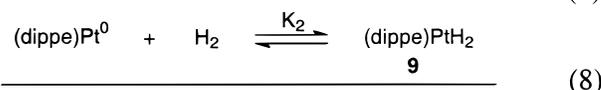
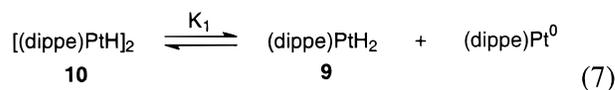


Figure 3. ORTEP drawing of (dippe)Pd(2,2'-biphenyl), **11**. Ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

the reaction. The rate of biphenyl production for the reaction with 702 mm H₂ was 3.8 times more rapid than the reaction with 130 mm H₂. The increase in rate is consistent with the increased concentration of monomer **9**.

The increase in the monomer-to-dimer ratio (**9**:**10**) observed with an increase in H₂ pressure can be explained by the following two independent equilibria (eqs 7 and 8). Equation 9 is the net equilibrium reaction, and eq 10 shows that an increase in H₂ pressure leads to a larger increase in the monomer concentration relative to the dimer concentration, as seen in our experiments. At 23 °C, $K_{\text{eq}} = 0.30 \text{ M atm}^{-1}$ (see Supporting Information).

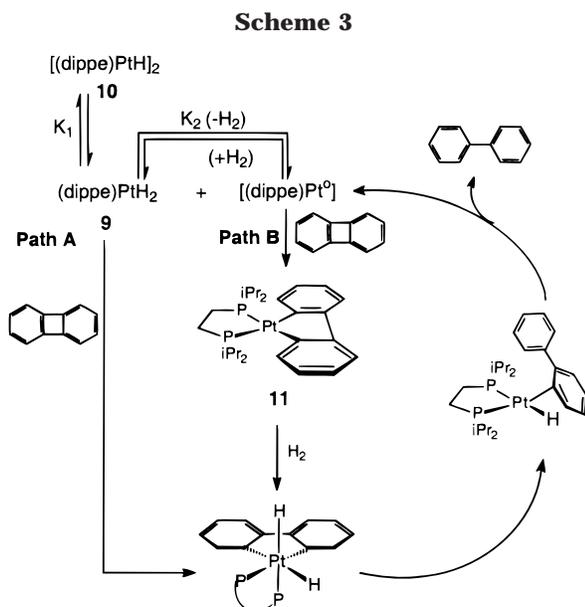


$$K_{\text{eq}} = K_1 K_2 = \frac{[\text{(dippe)PtH}_2]^2}{[\text{[(dippe)PtH]}_2] \cdot P_{\text{H}_2}} \quad (10)$$

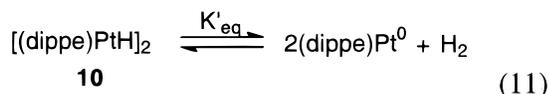
The effect of biphenylene concentration on the rate of hydrogenolysis of biphenylene was also tested at 702 mm H₂, where the concentration of monomer was held constant. The concentration of biphenylene was increased by a factor of 3.5 (0.14 M vs 0.56 M). The rate of biphenyl production was 2.3 times faster with the higher biphenylene concentration. The rate of formation of complex **11** was also 3.5 times faster in the case of higher biphenylene concentration.

A quantitative interpretation of the above results is not readily attainable for several reasons. The solubility of H₂ at 120 °C in a sealed NMR tube is not easily measured. Furthermore, the monomer:dimer ratio is not known under the reaction conditions (120 °C vs room temperature). *Qualitatively*, however, these results suggest that the majority of C–C bond cleavage is occurring by way of the Pt(II) species **9** rather than

(11) Schwartz, D. J.; Anderson, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 4014–4025.



$[(dippe)Pt^0]$. Combining eq 7 with the reverse of eq 8 gives eq 11, with equilibrium constant K'_{eq} (eq 12).



$$K'_{eq} = \frac{K_1}{K_2} = \frac{[(dippe)Pt^0]^2 \cdot P_{H_2}}{[(dippe)PtH]_2} \quad (12)$$

$$[(dippe)Pt^0] = \sqrt{\frac{K'_{eq} \cdot [(dippe)PtH]_2}{P_{H_2}}} \quad (13)$$

Rearrangement of eq 12 for $[(dippe)Pt^0]$ gives eq 13, which shows that increasing the H_2 concentration results in a decrease in $[(dippe)Pt^0]$ concentration; therefore, if C–C bond cleavage of biphenylene was occurring via $[(dippe)Pt^0]$, the rate of biphenyl production should slow with an increase in H_2 concentration. The opposite was observed; an increase in H_2 concentration resulted in an increase in biphenyl production. Furthermore, the fact that the rate of increase in biphenyl production matched the increase in the ratio of **9**:**10** with increasing H_2 concentration is strong evidence that the C–C bond of biphenylene is being cleaved by complex **9** more rapidly than by $[(dippe)Pt^0]$. Increasing the biphenylene concentration at constant H_2 pressure (702 mm Hg) also resulted in an increased rate of biphenyl production. This observation is also consistent with rate-determining C–C cleavage of biphenylene via **9**.

Scheme 3 lays out the proposed catalytic cycle using $(dippe)PtH_2$. In path A, C–C activation of biphenylene occurs via complex **9** to give a Pt(IV) dihydride from which rapid intramolecular reductive elimination occurs to give *cis*-(*dippe*)Pt(biphenyl)H. Neither of these species were observed. Reductive elimination of biphenyl from *cis*-(*dippe*)Pt(biphenyl)H generates $[(dippe)Pt^0]$, which can rapidly add H_2 to give **9** or cleave the C–C bond of biphenylene to give **11**. As mentioned earlier, complex **11** is slowly produced as the catalysis

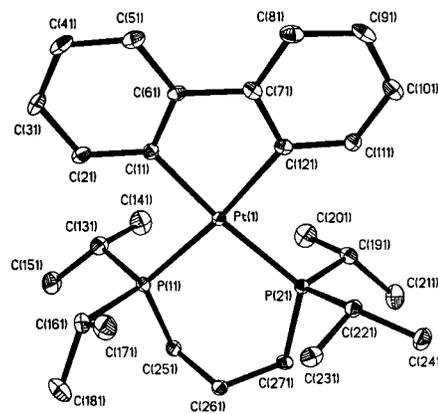


Figure 4. ORTEP drawing of $(dippp)Pt(2,2'$ -biphenyl). Ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

progresses. Complex **11** then oxidatively adds H_2 to give *cis*-(*dippe*)Pt(biphenyl)H, and the cycle continues. The slow growth of complex **11** throughout the catalysis suggests that some C–C cleavage is occurring via $[(dippe)Pt^0]$. However, this pathway can be eliminated if an NMR tube containing a large reservoir of H_2 is used, ensuring that the solution always contains its equilibrium quantity of H_2 to trap $[(dippe)Pt^0]$.

The 3 carbon bridged phosphine analogue of **9** was also examined for hydrogenolysis. The synthesis of $(dippp)PtH_2$ proceeds as for **9**, but the complex was found to exist only as the monomeric species in solution. An X-ray structure of the putative C–C insertion complex, prepared by independent synthesis, is shown in Figure 4. Despite the fact that $(dippp)PtH_2$ exists solely as the monomer, the rate of biphenylene hydrogenolysis was found to be the same as for the mixture of **9** and **10**.

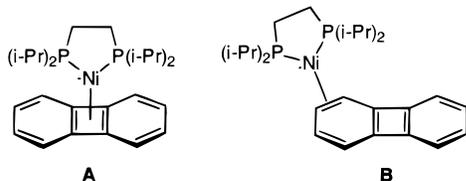
The chelating phosphine Pt complexes did not enhance the rate of biphenyl production as anticipated. Most likely this resulted from the fact that two new stable resting state species were formed in the case of the chelating phosphine complexes: **9** and **10**. In the nonchelating system, *cis*-(PEt_3)₂PtH₂ was not observed during the course of catalysis, and the resting state species was complex **4**.

3. Effect of Metal on the Rate of Catalysis. It is well established that reductive elimination occurs faster from Pd complexes than their Pt analogues. Therefore, $(PEt_3)_2Pd(2,2'$ -biphenyl) was heated with excess biphenylene at 50 °C under 0.92 atm of H_2 . Biphenyl was produced catalytically (initial turnover rate = 3.3 turnovers/day). Initially the resting state species was $(PEt_3)_2Pd(2,2'$ -biphenyl). However as the catalysis progressed, $Pd(PEt_3)_3$ also formed as a result of decomposition of the starting material (free Pd was also observed) and the rate of biphenyl production decreased. When $Pd(PEt_3)_3$ was used as the catalyst precursor, the hydrogenolysis of biphenylene proceeded at a rate of 2.2 turnovers/day at 70 °C, with the resting state being $(PEt_3)_2Pd(2,2'$ -biphenyl). This observation is consistent with H_2 addition to $(PEt_3)_2Pd(2,2'$ -biphenyl) being the rate-limiting step in the overall catalytic cycle, not reductive elimination from *trans*-(PEt_3)₂Pd(α -biphenyl)H, if a cycle similar to that in Scheme 2 is correct. *trans*-(PEt_3)₂Pd(α -biphenyl)H was formed independently by reacting $(PEt_3)_2Pd(2,2'$ -biphenyl) with 1 atm H_2 in

the presence of excess PEt_3 . This species could not be isolated since reductive elimination of biphenyl occurs immediately upon removal of PEt_3 . However, the complex was characterized by ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ spectroscopies. The ^1H NMR spectrum is very similar to that of the Pt analogue. The hydride resonance is observed at -7.761 (t, $J_{\text{P-H}} = 14.3$ Hz, 1 H), and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consisted of a singlet at δ 20.90.

Finally, the reactivity of $[(\text{dippe})\text{NiH}]_2$ ¹² was explored since reductive elimination from Ni is more rapid than either Pd or Pt complexes. A chelating ligand was employed to minimize the amount of decomposition that might occur during the hydrogenolysis. Compared to the Pt and Pd systems employed, $[(\text{dippe})\text{NiH}]_2$ proved to be the most efficient catalyst precursor for the hydrogenolysis of biphenylene, with a turnover rate of 16/day at 50°C under 0.92 atm of H_2 . The resting state species throughout the course of catalysis was $(\text{dippe})\text{Ni}(2,2'\text{-biphenyl})$, again indicating that the rate-limiting step in the cycle is H_2 addition to $(\text{dippe})\text{Ni}(2,2'\text{-biphenyl})$ not reductive elimination from a presumed $(\text{dippe})\text{Ni}(\alpha\text{-biphenyl})\text{H}$ species.

Within minutes of biphenylene addition to $[(\text{dippe})\text{NiH}]_2$ at room temperature, ^1H NMR spectroscopy (C_6D_6) revealed the presence of a new nickel complex as well as $[(\text{dippe})\text{NiH}]_2$. The aromatic region of the spectrum exhibited an AA'BB' multiplet similar to free biphenylene with broad signals at δ 6.71 and 6.64. The low-temperature (278 K) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (THF-d_8) of this intermediate revealed a new singlet at δ 75.31. Two possible structures that are consistent with the data are shown as **A** and **B**. Structure **A** displays



the nickel atom coordinated in an η^4 fashion to the four-membered ring of biphenylene. In this structure, there are only two types of aromatic protons which would give rise to the observed AA'BB' pattern in the ^1H NMR spectrum. In structure **B**, the nickel atom is coordinated in an η^2 fashion to biphenylene. Rapid migration about the biphenylene molecule would render all ortho protons equivalent and all meta protons equivalent, again leading to the observed AA'BB' pattern. A $^{13}\text{C}\{^1\text{H}\}$ -JMOD experiment in THF-d_8 solvent helps to distinguish between these two structures. The presence of a quaternary carbon at δ 157.07 (similar to free biphenylene) and two CH carbons at δ 123.45 and δ 121.37 (upfield relative to free biphenylene) is most consistent with an η^2 complex as in structure **B**. Migration of the nickel around the biphenylene perimeter would equilibrate all the α , β , and quaternary carbons and also effectively eliminate any C-P coupling.

A detailed dynamic study of $(\text{dippe})\text{Ni}(\text{C}_{10}\text{H}_8)$ (C_{10}H_8 = naphthalene) indicated that naphthalene is η^2 -coordinated in solution and that η^2 migration of $(\text{dippe})\text{Ni}$ around the naphthalene ring occurs.¹³ A solid-state

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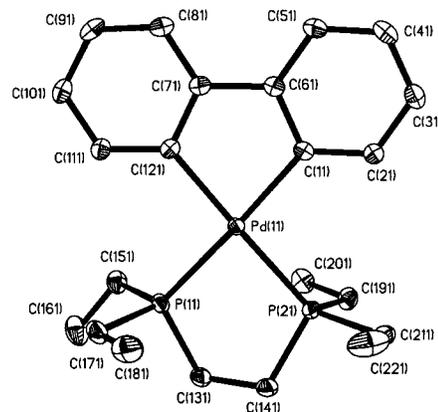


Figure 5. ORTEP drawing of $(\text{depe})\text{Pd}(2,2'\text{-biphenyl})$. Ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

crystal structure of $(\text{dippe})\text{Ni}(\text{C}_{10}\text{H}_8)$ showed that the naphthalene molecule is η^2 -bonded to the P_2Ni unit.¹⁴ Stanger and Vollhardt have evidence that above -30°C the P_2Ni moiety of $[\text{bis}(\text{trialkylphosphine})\text{nickel}](\eta^2\text{-anthracene})$ (alkyl = Et, Bu) migrates around the anthracene ring via a series of η^2 - η^3 coordination modes.¹⁵

4. Effect of the Chelate on the Rate of Catalysis.

In the case of the Pd and Ni systems described above, the resting state species were $(\text{PEt}_3)_2\text{Pd}(2,2'\text{-biphenyl})$ and $(\text{dippe})\text{Ni}(2,2'\text{-biphenyl})$, respectively. If the catalytic cycle shown in Schemes 2 and 3 are correct, this suggests that H_2 addition to give the corresponding species $(\text{PEt}_3)_2\text{Pd}(2,2'\text{-biphenyl})\text{H}_2$ and $(\text{dippe})\text{Ni}(2,2'\text{-biphenyl})\text{H}_2$ is the rate-limiting step in the overall catalysis. Harrod has proposed that the major enthalpic barrier for oxidative addition to square planar complexes arises as a result of the requisite deformation of the ligands in the plane around the metal in order to accommodate the incoming molecule.¹⁶ Consequently, we reasoned that a chelating bisphosphine ligand with a longer backbone might be more readily distorted on approach of the incoming ligand than a chelating bisphosphine with a shorter backbone, yet could still help maintain the overall thermal stability of the complex. The result would be a lower enthalpic barrier to oxidative addition of H_2 and a more efficient catalyst for the hydrogenolysis of biphenyl. To test this idea, the following complexes were prepared: $(\text{depe})\text{Pd}(2,2'\text{-biphenyl})$, $(\text{depp})\text{Pd}(2,2'\text{-biphenyl})$ (depp = bis(diethylphosphino)propane), and $(\text{depb})\text{Pd}(2,2'\text{-biphenyl})$ (depb = bis(diethylphosphino)butane). The solid-state structure of each compound was determined by X-ray crystallography (Figures 5–7). It is readily apparent that the chelating backbone becomes more distorted as the number of carbons in the backbone increases in order to accommodate a square planar geometry around the Pd atom. The average distortion of the phosphorus atoms from a square plane were 0.009, 0.054, and 0.105 Å, respectively.

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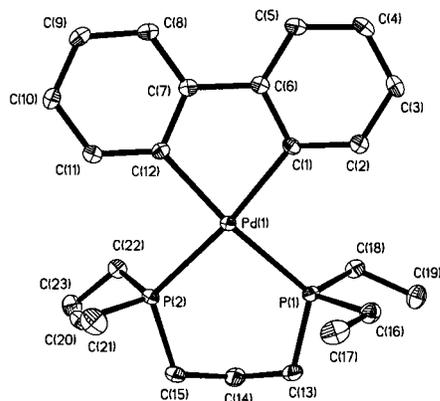


Figure 6. ORTEP drawing of (depp)Pd(2,2'-biphenyl). Ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

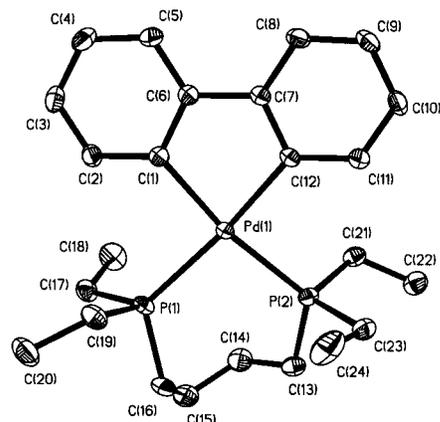


Figure 7. ORTEP drawing of (depb)Pd(2,2'-biphenyl). Ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

Table 1. Catalytic Turnover Rate for the Hydrogenolysis of Biphenylene to Biphenyl with Various Pd Species^a

metal complex	turnover rate/24 h
(depe)Pd(2,2'-biphenyl)	0.70
(depp)Pd(2,2'-biphenyl)	0.52
(depb)Pd(2,2'-biphenyl)	0.94

^a Condition for catalysis: [Pd complexes] = 0.033 M; [biphenylene] = 0.166 M. All reactions were run at 95 °C in a sealed NMR tube in pyridine-*d*₅.

These complexes were heated at 95 °C in the presence of excess biphenylene under 0.92 atm of H₂. The resting state species in each case was the starting metal complex. While there was no discernible trend in the rate of hydrogenolysis of biphenylene between the three complexes (Table 1), these experiments do not rule out the distortion hypothesis since the catalytic rate of these three species was slower than that of the nonchelating case (PEt₃)₃Pd(2,2'-biphenyl) (vide supra). An alternative explanation for the lack of increase in the turnover rate is that there is no correlation between the ease of distortion of the square planar complex and the length of the backbone of the chelating ligand.

Conclusions

The catalytic formation of tetraphenylene from biphenylene by Pt(PEt₃)₃ or (PEt₃)₂Pt(2,2'-biphenyl) can

be eliminated by the addition of H₂ to the reaction mixture, resulting in the catalytic formation of biphenyl instead. The formation of tetraphenylene required prior phosphine dissociation from (PEt₃)₂Pt(2,2'-biphenyl) to give the 14-electron species (PEt₃)Pt(2,2'-biphenyl), which then inserted into a second molecule of biphenylene, ultimately leading to the formation of tetraphenylene. However, the room-temperature addition of H₂ to (PEt₃)₂Pt(2,2'-biphenyl) to give complex **4** was not inhibited by added phosphine, implying that prior phosphine dissociation from (PEt₃)₃Pt(2,2'-biphenyl) is not a prerequisite for H₂ addition. The reductive elimination of biphenyl from **4** was inhibited by added phosphine since phosphine loss is required to achieve a cis geometry, from which reductive elimination can occur.

Addition of a chelating phosphine to eliminate the need for the required cis to trans isomerization *did not* result in an increased turnover rate. Rather, two new resting states appeared: [(dippe)PtH]₂ and (dippe)PtH₂. Experimental evidence suggests that the C–C bond cleavage of biphenylene is occurring via the Pt(II) species (dippe)PtH₂ more rapidly than the Pt(0) species [(dippe)Pt⁰]. Changing the metal to Pd eliminated the formation of the hydride species and resulted in a more rapid hydrogenolysis rate. In this case the resting state was (depe)Pd(2,2'-biphenyl), implying that addition of H₂ is the rate-limiting step in the catalytic cycle. Increasing the length of the phosphine backbone had no effect on the turnover rate.

The metal used had the greatest overall effect on the rate of hydrogenolysis. [(dippe)NiH]₂ catalyzed the hydrogenolysis of biphenylene at a rate of 16 turnovers/day at 50 °C. The resting state species was (dippe)Ni(2,2'-biphenyl), which is consistent with the rate-determining step being the oxidative addition of H₂.

Experimental Section

General Considerations. All manipulations were performed under an N₂ atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. glovebox. Tetrahydrofuran, benzene, and toluene were distilled under nitrogen from dark purple solutions of benzophenone ketyl. Alkane solvents were made olefin-free by stirring over H₂SO₄, washing with aqueous KMnO₄ and water, and distilling from dark purple solutions of tetraglyme/benzophenone ketyl. Benzene-*d*₆, tetrahydrofuran-*d*₈, and toluene-*d*₈ were purchased from Cambridge Isotope Lab, distilled under vacuum from dark purple solutions of benzophenone ketyl, and stored in ampules with Teflon-sealed vacuum line adapters. The preparations of Pt(PEt₃)₃,¹⁷ Pd(PEt₃)₃,¹⁸ *trans*-(SEt₂)₂PdCl₂,¹⁹ 2,2'-dilithiobiphenyl,²⁰ *cis*-PtCl₂(PEt₃)₂,²¹ [Pt(2,2'-biphenyl)(SEt₂)₂]₂,²² (PEt₃)₂Pt(2,2'-biphenyl),^{4g} (PEt₃)₂Pd(2,2'-biphenyl),^{4g} *trans*,*cis*-(PEt₃)₂Pt(2,2'-biphenyl)Br₂,^{4g} [(dippe)NiH]₂, and (dippe)Ni(2,2'-biphenyl)¹² have been previously reported. The (P–P)PtCl₂ complexes were made from (cod)PtCl₂ and the corresponding phosphines. The (P–P)PdCl₂ complexes were made from (tmeda)PdCl₂ and

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the corresponding phosphines. The dippe²³ and dippp²⁴ ligands were prepared by published procedures. The depp and depb ligands were prepared in a manner similar to the dippp ligand. *trans*-Pt(PET₃)₂H₂,²⁵ Pt(PET₃)₂(C₂H₄),²⁶ [(dippe)PtH]₂,¹¹ and Pt-(dippe)H₂²⁷ were prepared as previously described. Alternatively, [(dippe)PtH]₂ and Pt(dippp)H₂ can be prepared as described below. Biphenylene and NaB(OCH₃)₃H were purchased from Aldrich Chemical Co., 2,2'-dibromobiphenyl was purchased from Alfa Aesar (Avocado), and the depe ligand and triethylphosphine were purchased from Strem Chemical Co. The liquids were stirred over sieves, freeze-pump-thaw degassed three times, and vacuum-distilled prior to use.

All ¹H NMR and ³¹P NMR spectra were recorded on a Bruker AMX400 spectrometer. All ¹H chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced using chemical shifts of residual solvent resonances (THF-*d*₆, δ 1.73, toluene-*d*₆, δ 2.09, C₆D₆, δ 7.15, CDCl₃, δ 7.24, CD₂Cl₂, δ 5.32). ³¹P NMR spectra were referenced to external 30% H₃PO₄ (δ 0.0). GC-MS was conducted on a 5890 Series II gas chromatograph fitted with an HP 5970 series mass selective detector. Analyses were obtained from Desert Analytics. A Siemens SMART system with a CCD area detector was used for X-ray structure determination.

Preparation of *trans*-(PET₃)₂Pt(α-biphenyl)H, 4. A Teflon-sealed ampule was charged with 2 mL of C₆D₆, (PET₃)₂-Pt(2,2'-biphenyl) (60 mg, 0.103 mmol), PET₃ (18 μL, 0.103 mmol), and 1 atm of H₂. The solution was heated to 80 °C and stirred for 12 h. ¹H NMR spectroscopy indicated the quantitative formation of **1**. The solvent, PET₃, and H₂ were removed under vacuum to give a clear slightly yellow air-sensitive oil. Compound **1** can also be formed by stirring (PET₃)₂Pt(2,2'-biphenyl) under 1 atm of H₂ at room temperature. NMR data for **1**: ¹H NMR (THF-*d*₆): δ 7.984 (d, *J*_{H-H} = 7.4 Hz, 2 H), δ 7.643 (d, *J*_{Pt-H} = 45.5, *J*_{H-H} = 7.4, 1 H), δ 7.255 (d, *J*_{H-H} = 7.4 Hz, 1 H), δ 7.207 (t, *J*_{H-H} = 7.4 Hz, 2 H), δ 7.112 (d, *J*_{H-H} = 7.4 Hz, 1 H), δ 6.909–6.813 (m, 2 H), 1.622–1.384 (overlapping multiplets, 12 H), 0.912 (1:4:6:4:1 quintet, *J*_{H-H} = 8.4, *J*_{P-H} = 8.4 Hz, 18 H), -7.770 (t, *J*_{Pt-H} = 640, *J*_{P-H} = 20.3 Hz, 1 H). ³¹P{¹H} NMR (C₆D₆): δ 16.25 (s, *J*_{Pt-P} = 2854 Hz).

Preparation of *trans*-(PET₃)₂Pt(α-biphenyl)Cl, 5. CCl₄ (0.1 mL) was added to a THF solution of *trans*-(PET₃)₂Pt(α-biphenyl)H (62 mg, 0.10 mmol). The mixture was stirred for 2 h. The solvent was removed, and the off-white air-stable solid was purified on a thick-layer silica chromatography plate with 1:1 hexanes–benzene (*R*_f = 0.2) to give white crystals. Yield: 80%. X-ray quality crystals were grown by dissolving **5** in a minimum of hexanes at room temperature and cooling to -25 °C. NMR data for **5**: ¹H NMR (THF-*d*₆): δ 8.119 (d, *J*_{H-H} = 7.9 Hz, 2 H), δ 7.681 (d, *J*_{Pt-H} = 66.9, *J*_{H-H} = 7.9, 1 H), δ 7.302 (t, *J*_{H-H} = 7.9 Hz, 1 H), δ 7.240–7.154 (m, 2 H), δ 7.112 (d, *J*_{H-H} = 7.4 Hz, 1 H), δ 6.909 (t, *J*_{H-H} = 7.9 Hz, 1 H), δ 6.874–6.814 (m, 1 H), 1.683–1.494 (overlapping multiplets, 12 H), 0.926 (1:4:6:4:1 quintet, *J*_{H-H} = 8.2, *J*_{P-H} = 8.2 Hz, 18 H). ³¹P{¹H} NMR (THF-*d*₆): δ 12.95 (s, *J*_{Pt-P} = 2825 Hz). Anal. Calcd for C₂₄H₃₉P₂PtCl: C, 46.49; H, 6.34. Found: C, 46.39; H, 6.40.

Preparation of *trans,cis*-(PET₃)₂Pt(2,2'-biphenyl)(OTf)₂. *trans,cis*-(PET₃)₂Pt(2,2'-biphenyl)Br₂ (400 mg, 0.55 mmol) was suspended in 10 mL of THF. A solution of silver triflate (1.0 mmol, 257 mg) was added dropwise at room temperature to the stirred suspension. The mixture was stirred at room temperature for 36 h. Most of the AgBr was removed by filtering through a Celite plug. The solvent was removed under vacuum, the resulting white solid was dissolved in benzene, and the residual AgBr was removed by again filtering through a Celite plug. *trans,cis*-(PET₃)₂Pt(2,2'-biphenyl)(OTf)₂ was used without isolation in the formation of **8**. ¹H NMR (THF-*d*₆): δ 7.939 (d, *J*_{Pt-H} = 41.3, *J*_{H-H} = 7.8, Hz, 2 H), 7.559 (d, *J*_{H-H} = 7.0 Hz, 2 H), 7.281 (t, *J*_{H-H} = 7.8 Hz, 2 H), 7.069 (t, *J*_{H-H} = 7.8 Hz, 2 H), 1.975–1.800 (m, 12 H), 0.763 (1:4:6:4:1

quintet, *J*_{P-H} = 7.5, *J*_{H-H} = 7.5 Hz, 18 H). ³¹P{¹H} NMR (THF-*d*₆): δ 18.30 (s, *J*_{Pt-P} = 1747 Hz).

Preparation of *trans,cis*-(PET₃)₂Pt(2,2'-biphenyl)H₂, 8. *trans,cis*-(PET₃)₂Pt(2,2'-biphenyl)(OTf)₂ (~0.55 mmol) was dissolved in 50 mL of THF and cooled to -50 °C. NaB(OCH₃)₃H (1.1 mmol, 141 mg) was dissolved in 10 mL of THF and added dropwise to the cooled solution. The solution turned light brown upon addition of NaB(OCH₃)₃H. The mixture was allowed to warm to room temperature and stirred an additional 15 min. The solvent was removed under vacuum, and a yellow solution was extracted by washing the resulting brown sludge with hexanes (3 × 10 mL). The hexane solution was concentrated to 2 mL and cooled to -25 °C. White crystals precipitated. The mother liquor was separated, concentrated to 1 mL, and cooled to -25 °C. White air-sensitive crystals of *trans,cis*-(PET₃)₂Pt(2,2'-biphenyl)H₂ formed (total yield: 50 mg, 28% yield), which were suitable for X-ray diffraction. ¹H NMR (C₆D₆): δ 8.146 (d, *J*_{Pt-H} = 26.9, *J*_{H-H} = 6.7, Hz, 2 H), 7.884 (d, *J*_{H-H} = 7.6 Hz, 2 H), 7.309 (t, *J*_{H-H} = 8.4 Hz, 2 H), 7.143 (t, *J*_{H-H} = 7.5 Hz, 2 H), 1.380–1.243 (m, 12 H), 0.680 (1:4:6:4:1 quintet, *J*_{P-H} = 7.5, *J*_{H-H} = 7.5 Hz, 18 H), -10.619 (t, *J*_{Pt-H} = 637.4, *J*_{P-H} = 15.8, Hz, 2 H). ³¹P{¹H} NMR (C₆D₆): δ -0.978 (s, *J*_{Pt-P} = 1897 Hz). Anal. Calcd for C₂₄H₄₀P₂Pt: C, 49.22; H, 6.88. Found: C, 49.27; H, 6.88.

Preparation of *trans*-(PET₃)₂Pd(α-biphenyl)H. (PET₃)₂-Pd(2,2'-biphenyl) (11.4 mg, 0.023 mmol) and PET₃ (3.4 μL, 0.023 mmol) were combined in a resealable NMR tube containing 0.5 mL of THF-*d*₆. One atmosphere of H₂ was added. After 38 days at room temperature, the ¹H NMR spectrum shows no more (PET₃)₂Pd(2,2'-biphenyl), but a new compound designated as *trans*-(PET₃)₂Pd(α-biphenyl)H was observed. NMR data for *trans*-(PET₃)₂Pd(α-biphenyl)H: ¹H NMR (THF-*d*₆): δ 7.907 (d, *J*_{H-H} = 8.1 Hz, 2 H), δ 7.609–7.552 (m, 1 H), δ 7.169–7.101 (m, 2 H), δ 6.889–6.809 (m, 2 H), δ 6.889–6.802 (m, 2 H), 1.525–1.285 (overlapping multiplets, partially obscured by PET₃, 12 H), 0.921 (1:4:6:4:1 quintet, *J*_{H-H} = 8.2, *J*_{P-H} = 8.2 Hz, 18 H), -7.761 (t, *J*_{P-H} = 14.3 Hz, 1 H). ³¹P{¹H} NMR (C₆D₆): δ 20.90 (s).

Preparation of (dippe)Pt(2,2'-biphenyl), 11. This compound was prepared by two different methods. The first method involved dissolving [Pt(2,2'-biphenyl)(SET₂)₂] (100 mg, 0.114 mmol) in 10 mL of CH₂Cl₂. The dippe ligand (60 mg, 0.229 mmol) was added dropwise at room temperature, and the solution was observed to lighten slightly as the addition proceeded. The resulting mixture was stirred for 1 h at room temperature. The solvent was removed under vacuum, and the yellow solid was washed with hexanes and cold acetone to give air-stable yellow crystals (50 mg, 36% yield). X-ray quality crystals were grown by dissolving in methylene chloride and layering with hexanes. In the second method, a solution of 2,2'-dilithiobiphenyl (from 380 mg (1.20 mmol) of 2,2'-dibromobiphenyl) in THF (7 mL) was added dropwise to a stirred suspension of (dippe)PtCl₂ (500 mg, 0.947 mmol) in 30 mL of THF at room temperature. The reaction mixture was stirred for 3 h, during which time the solution became clear orange. The reaction was quenched with 10 mL of H₂O. The organic layer was separated and dried with MgSO₄, and the solvent removed under vacuum. Rinsing the resulting yellow solid with cold acetone resulted in air-stable yellow crystals (404 mg, 70% yield). NMR data for **11**: ¹H NMR (CD₂Cl₂): δ 7.708 (dd, *J*_{Pt-H} = 51.2, *J*_{H-H} = 7.6, *J*_{P-H} = 7.6 Hz, 2 H), 7.379 (d, *J*_{H-H} = 7.7 Hz, 2 H), 6.981 (t, *J*_{H-H} = 7.6 Hz, 2 H), 6.850 (t, *J*_{H-H} = 7.6 Hz, 2 H), 2.558 (sept, CHMe₂, *J*_{H-H} = 7.6 Hz, 4 H), 1.784 (m, PCH₂CH₂P, 4 H), 1.263 and 1.228 (dd, CHMeMe', *J*_{P-H} = 15.2, *J*_{H-H} = 7.6 Hz, 24 H). ³¹P{¹H} NMR (CD₂Cl₂): δ 66.74 (s, *J*_{Pt-P} = 1854 Hz). Anal. Calcd for C₂₆H₄₀P₂Pt: C, 51.22 H, 6.61. Found: C, 51.07; H, 6.70.

Alternative Preparation of [(dippe)PtH]₂. Super-Hydride (1.53 mmol from 1.53 mL of a 1 M solution in THF) was added dropwise at room temperature to a stirred suspension

of (dippe)PtCl₂ in hexanes (405 mg, 0.77 mmol). Over 6 h the (dippe)PtCl₂ slowly dissolved and a yellow solution formed. A gummy white precipitate of LiCl was also observed. The solution was filtered, the residue washed with hexanes, and the solvent removed from the combined extracts under vacuum to give a yellow solid in 81% yield. The ³¹P{¹H} NMR spectrum showed a 95:5% ratio of [(dippe)PtH]₂ to (dippe)PtH₂.

Preparation of (dipp)Pt(2,2'-biphenyl). A solution of 2,2'-dilithiobiphenyl (from 336 mg (1.08 mmol) of 2,2'-dibromobiphenyl) in ether (7 mL) was added dropwise to a stirred suspension of (dipp)PtCl₂ (530 mg, 0.980 mmol) in 30 mL of THF at room temperature. The reaction mixture was stirred for 3 h, during which time the solution became clear orange. The reaction was quenched with 10 mL of H₂O. The organic layer was separated and dried with MgSO₄, and the solvent removed under vacuum. Rinsing the resulting yellow solid with cold acetone resulted in air-stable yellow/green crystals (425 mg, 70% yield). NMR data: ¹H NMR (CD₂Cl₂): δ 7.599 (dd, *J*_{Pt-H} = 47.4, *J*_{H-H} = 7.6, *J*_{P-H} = 7.6 Hz, 2 H), 7.397 (d, *J*_{H-H} = 7.5 Hz, 2 H), 6.996 (t, *J*_{H-H} = 7.6 Hz, 2 H), 6.879 (t, *J*_{H-H} = 7.6 Hz, 2 H), 2.741 (sept, *CHMe*₂, *J*_{H-H} = *J*_{P-H} = 7.6 Hz, 4 H), 2.086 (m, PCH₂CH₂CH₂P, 2 H), 1.902 (m, PCH₂CH₂CH₂P, 4 H), 1.298 and 1.263 (dd, *CHMeMe'*, *J*_{P-H} = 17.6, *J*_{H-H} = 7.4 Hz, 24 H). ³¹P{¹H} NMR (CD₂Cl₂): δ 15.32 (s, *J*_{Pt-P} = 1878 Hz). Anal. Calcd for C₂₇H₄₂P₂Pt: C, 51.99; H, 6.79. Found: C, 51.93; H, 6.73.

Preparation of (depe)Pd(2,2'-biphenyl). A solution 2,2'-dilithiobiphenyl (from 686 mg (2.2 mmol) of 2,2'-dibromobiphenyl) in ether (15 mL) was added dropwise to a stirred suspension of *trans*-(SEt₂)₂PdCl₂ (400 mg, 1.12 mmol) in 20 mL of diethyl ether at -78 °C. The temperature was then brought to -15 °C with a NaCl/H₂O bath, and the reaction mixture was stirred for 5 min, during which time the solution darkened to a dark orange. The mixture was recooled to -78 °C, and depe (454 mg, 2.2 mmol) was added dropwise. A tan precipitate formed immediately upon addition of the phosphine ligand. The solution was slowly warmed to room temperature and stirred an additional 1 h. The reaction was quenched with 10 mL of H₂O. The organic layer was extracted with CH₂Cl₂, separated, and dried with MgSO₄, and the solvent removed under vacuum. The resulting yellow solid was washed with several portions of diethyl ether to remove any remaining phosphine. Rinsing the resulting yellow solid with cold acetone gave air-stable yellow crystals (260 mg, 50% yield). X-ray quality crystals were obtained by dissolving the solid in CH₂Cl₂ and layering with hexanes. NMR data for (depe)Pd(2,2'-biphenyl): ¹H NMR (CD₂Cl₂): δ 7.377 (dd, *J*_{H-H} = 7.6, *J*_{P-H} = 7.6 Hz, 2 H), 7.355 (d, *J*_{H-H} = 8.0 Hz, 2 H), 6.962 (t, *J*_{H-H} = 7.8 Hz, 2 H), 6.833 (t, *J*_{H-H} = 7.5 Hz, 2 H), 2.051–1.757 (m, 12 H, PCH₂CH₂P and CH₃CH₂P), 1.161 (1:2:1:2:1 quintet, *J*_{P-H} = 16.5, *J*_{H-H} = 7.9 Hz, 12 H). ³¹P{¹H} NMR (CD₂Cl₂): δ 45.49 (s). Anal. Calcd for C₂₂H₃₂P₂Pd: C, 56.84; H, 6.94. Found: C, 56.47; H, 6.93.

Preparation of (depp)Pd(2,2'-biphenyl). A similar preparation as that described for (depe)Pd(2,2'-biphenyl) can be used; however, the yield is low (24%). A higher yield preparation is given. A solution of 2,2'-dilithiobiphenyl (from 728 mg (2.33 mmol) of 2,2'-dibromobiphenyl) in ether (12 mL) was added dropwise to a stirred suspension of (depp)PdCl₂ (843 mg, 2.12 mmol) in 30 mL of THF at room temperature. The resulting mixture turned yellow and then formed an orange solution. Within 1 h a precipitate began to form. The reaction mixture was stirred for a total of 4 h and then quenched with 10 mL of H₂O. The organic layer was separated, washed five times with H₂O, and dried with MgSO₄. The solvent was removed under vacuum. Rinsing the resulting yellow solid with cold acetone gave air-stable yellow crystals (547 mg, 54% yield). X-ray quality crystals were grown by dissolving the solid in CH₂Cl₂ and layering with hexanes. NMR data for (depp)Pd(2,2'-biphenyl): ¹H NMR (CD₂Cl₂): δ 7.392 (t, *J*_{H-H} = 6.4, 2 H), 7.365 (d, *J*_{H-H} = 8.2 Hz, 2 H), 6.967 (t, *J*_{H-H} = 7.6

Hz, 2 H), 6.837 (t, *J*_{H-H} = 7.6 Hz, 2 H), 2.165–1.935 (m, 6 H), 1.891–1.713 (m, 8 H), 1.169 (quintet, *J*_{P-H} = 16.4, *J*_{H-H} = 8.2 Hz, 12 H). ³¹P{¹H} NMR (CD₂Cl₂): δ 2.46 (s). Anal. Calcd for C₂₃H₃₄P₂Pd: C, 57.69; H, 7.16. Found: C, 57.45; H, 7.32.

Preparation of (depb)Pd(2,2'-biphenyl). A solution 2,2'-dilithiobiphenyl (from 604 mg (1.94 mmol) of 2,2'-dibromobiphenyl) in ether (10 mL) was added dropwise to a stirred suspension of (depb)PdCl₂ (725 mg, 1.76 mmol) in 25 mL of THF at room temperature. The resulting mixture turned yellow, and then orange as (depb)PdCl₂ dissolved. The reaction mixture was stirred for a total of 4 h and then quenched with 10 mL of deoxygenated H₂O. The organic layer was separated, washed five times with deoxygenated H₂O, and dried with MgSO₄ (under N₂). The solvent was removed under vacuum. Rinsing the resulting yellow solid with cold acetone gave yellow crystals (205 mg, 24% yield). X-ray quality crystals were grown by dissolving the solid in CH₂Cl₂ and layering with hexanes. The product is air stable as a solid but slowly decomposes in solution if exposed to air. NMR data for (depb)Pd(2,2'-biphenyl): ¹H NMR (CD₂Cl₂): δ 7.390 (q, *J*_{H-H} = 7.0 Hz, 2 H), 7.353 (d, *J*_{H-H} = 8.0 Hz, 2 H), 6.969 (t, *J*_{H-H} = 7.5 Hz, 2 H), 6.836 (t, *J*_{H-H} = 7.5 Hz, 2 H), 2.143–2.019 (m, 4 H), 1.965–1.780 (m, 12 H), 1.169 (1:4:6:4:1 quintet, *J*_{P-H} = 15.6, *J*_{H-H} = 7.6 Hz, 12 H). ³¹P{¹H} NMR (CD₂Cl₂): δ 12.18 (s). Anal. Calcd for C₂₄H₃₆P₂Pd: C, 58.45; H, 7.36. Found: C, 58.53; H, 7.24.

General Procedure for Catalysis with Nonchelating Pt Phosphines. A solution containing the metal complex (0.033 M) and biphenylene (5 equiv, 0.22 M) was prepared in toluene-*d*₈ and added to a resealable NMR tube. The NMR tube was charged with 0.92 atm of H₂ and heated at 120 °C in a constant-temperature oil bath thermostatically controlled (±0.5 °C). The NMR tube was removed at various intervals and cooled to room temperature, and a ¹H NMR spectrum was recorded. The catalytic turnover number was calculated by plotting the concentration of biphenyl vs time. At early reaction times, the rate of biphenyl formation was constant since the concentration of biphenylene and H₂ were nearly constant. These initial rates were used to calculate the turnover rate. The methyl peak of toluene-*d*₈ was used as an internal standard.

General Procedure for Catalysis with Chelating Pt Phosphines at Different Pressures of H₂. Two resealable NMR tubes were charged with [(dippe)PtH]₂ (20 mg, 0.049 M) and biphenylene (16.7 mg, 0.24 M). The first NMR tube was charged with 130 mm H₂ and stirred at room temperature for 1 h. Integration of the ¹H NMR spectrum revealed a 1:1 ratio of [(dippe)PtH]₂:(dippe)PtH₂, **9:10**. The NMR tube was heated at 120 °C in a constant-temperature oil bath thermostatically controlled (±0.5 °C). The NMR tube was removed at various intervals and cooled to room temperature, and a ¹H NMR spectrum was recorded. The catalytic turnover number was calculated as above. The ratio of **9:10** remained at approximately 0.85:1 throughout the course of the reaction. The second NMR tube was charged with 702 mm H₂ and stirred at room temperature for 1 h. Integration of the ¹H NMR spectrum revealed a 3.2:1 ratio of **9:10**. The tube was heated in the same manner as discussed above (the ratio of **9:10** stayed at approximately 3:2:1), and the catalytic turnover rate was calculated.

General Procedure for Catalysis with Chelating Pt Phosphines with Different Concentrations of Biphenylene. Two resealable NMR tubes were charged with [(dippe)PtH]₂ (10 mg, 0.017 M). The first tube was charged with 13.4 mg (0.14 M) of biphenylene. The second tube was charged with 53.6 mg (0.56 M) of biphenylene. Then 702 mm H₂ was added to each tube. Each tube was stirred for 3 h at room temperature to establish an equilibrium ratio between **9** and **10** (6:1). The NMR tubes were heated at 120 °C in a constant-temperature oil bath thermostatically controlled (±0.5 °C), removed at various intervals, and cooled to room temperature,

Table 2. Summary of Crystallographic Data for 5, 8, 11, (dipp)Pt(2,2'-biphenyl), (depe)Pd(2,2'-biphenyl), (depp)Pd(2,2'-biphenyl), and (depb)Pd(2,2'-biphenyl)

crystal parameters	5	8	11	(dipp)Pt(2,2'-biphenyl)	(depe)Pd(2,2'-biphenyl)	(depp)Pd(2,2'-biphenyl)	(depb)Pd(2,2'-biphenyl)
chemical formula	C ₂₄ H ₃₉ ClP ₂ Pt	C ₂₄ H ₄₀ P ₂ Pt	C ₂₆ H ₄₀ P ₂ Pt	C ₂₇ H ₄₂ P ₂ Pt	C ₂₂ H ₃₂ P ₂ Pd	C ₂₃ H ₃₄ P ₂ Pd	C ₂₄ H ₃₆ P ₂ Pd
fw	620.03	585.59	609.61	623.64	464.82	478.84	492.87
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group, Z	P2 ₁ /c, 4	Pmn2 ₁ , 2	P2 ₁ /n, 4	P2 ₁ /c, 8	C2/c, 24	P2 ₁ /n, 4	P2 ₁ /c, 4
a, Å	9.9326(2)	13.1226(1)	10.1697(1)	18.6934(4)	24.2761(2)	12.4108(1)	9.9794(1)
b, Å	13.6947(2)	10.1708(2)	13.4373(1)	14.0978(3)	13.4416(2)	13.5356(1)	13.5881(2)
c, Å	19.3064(3)	9.3403(2)	18.5698(2)	20.6100(5)	38.9652(7)	13.2064(1)	16.7499(2)
α, deg	90	90	90	90	90	90	90
β, deg	95.142(1)	90	105.49(1)	108.846(1)	98.47(1)	97.652(1)	94.506(1)
γ, deg	90	90	90	90	90	90	90
vol, Å ³	2615.56(8)	1246.63(3)	2445.50(4)	5140.3(2)	12575.9(3)	2198.76(3)	2264.28(5)
temp, °C	-80	-80	-80	-80	-80	-80	-80
ρ _{calc} , g cm ⁻³	1.575	1.560	1.656	1.612	1.473	1.447	1.446
no. of data collected	15694	7833	15093	29885	37373	13155	13584
no. of unique data	6100	2977	5804	11827	14623	5166	5288
no. of params varied	259	141	270	557	676	239	676
R1(F _o), wR2(F _o ²), (I > 2σ(I))	0.0208, 0.0478	0.0445, 0.1089	0.0214, 0.0481	0.0397, 0.0632	0.0522, 0.0930	0.0241, 0.0521	0.0338, 0.0655
R1(F _o), wR2(F _o ²), all data	0.0250, 0.0491	0.0544, 0.1135	0.0269, 0.0498	0.0617, 0.0689	0.0641, 0.0979	0.0314, 0.0546	0.0446, 0.0693
goodness of fit	1.051	1.010	1.072	1.013	1.144	1.063	1.083

and a ¹H NMR spectrum was recorded. The turnover rate was calculated as discussed above.

X-ray Structural Determination of 5, 8, 11, (dipp)Pt(2,2'-biphenyl), (depe)Pd(2,2'-biphenyl), (depp)Pd(2,2'-biphenyl), and (depb)Pd(2,2'-biphenyl). A single crystal of each compound was mounted under Paratone-8277 on a glass fiber and immediately placed in a cold nitrogen stream at -80 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD area detector system equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 5–30 s/frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of 56.54°). The total data collection time was approximately 4 h for 5 s/frame exposures and 13 h for 30 s/frame exposures. Frames were integrated with the Siemens SAINT program to 0.75 Å for all of the data sets. The unit cell parameters for all of the crystals were based upon the least-squares refinement of three-dimensional centroids of >5000 reflections.²⁸ Data were corrected for absorption using the program SADABS.²⁹ Space

group assignments were made on the basis of systematic absences and intensity statistics by using the XPREP program (Siemens, SHELXTL 5.04). The structures were solved by using direct methods and refined by full-matrix least-squares on F². Most structures contained one molecule within the asymmetric unit with the following exceptions: compound **8** was found to lie on a mirror plane, with Z = 2; (dippe)Pt(2,2'-biphenyl) was found to have two molecules within the asymmetric unit, as was (dipp)Pt(2,2'-biphenyl); (depe)Pd(2,2'-biphenyl) was found to have three molecules within the asymmetric unit. For all of the structures, the non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogens were included in idealized positions giving data: parameter ratios greater than 10:1. The Pt-bound hydrides in **8** were located from the difference Fourier map and were included but not refined. **8** was also refined as a racemic twin (0.20/0.80) since the Flack parameter deviated substantially from zero. Further experimental details of the X-ray diffraction studies are provided in Table 2 and in the Supporting Information. Positional parameters for all atoms, anisotropic thermal parameters, all bond lengths and angles, and fixed hydrogen positional parameters are given in the Supporting Information for all of the structures.

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Supporting Information Available: Details of the calculation of the equilibrium constant in eq 9 and tables of coordinates, thermal parameters, and bond distances and angles for **5**, **8**, **11**, (dipp)Pt(2,2'-biphenyl), (depe)Pd(2,2'-biphenyl), (depp)Pd(2,2'-biphenyl), and (depb)Pd(2,2'-biphenyl) (57 pages). Ordering information is given on any current masthead page.

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(28) It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10× the listed value.

(29) The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect A* **1995**, 51, 33–38.