Organometallics **2001,** *20,* 2759−2766 2759

Formation of Phenylene Oligomers Using Platinum−Phosphine Complexes

Nira Simhai, Carl N. Iverson, Brian L. Edelbach, and William D. Jones*

Department of Chemistry, University of Rochester, Rochester, New York 14627

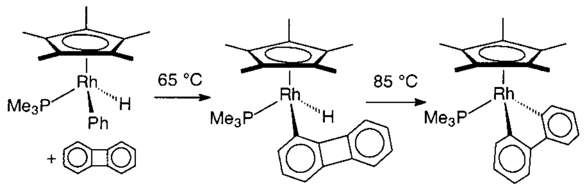
Received February 12, 2001

The reaction of biphenylene with a series of platinum bis-phosphine precursors [PtL_2] leads to a variety of C−H and C−C bond activation reactions. With L = triethylphosphine, cleavage of the carbon−carbon bond of biphenylene has been shown to catalytically form tetraphenylene. With $L_2 = Bu^t{}_2PCH_2PBu^t{}_2$, the simple C−C cleavage of biphenylene is observed. With $L = PPh_2Bu^t$, ortho metalation of the phosphine occurs to give a C−H activation product. Mechanistic details of these reactions are discussed. With L = triphenylphosphine, however, biphenylene is not cleaved by the [L_2Pt] fragment, but the independently prepared C−C insertion adduct does react with biphenylene to give five different products, including triphenylene, tetraphenylene, phenyltriphenylene, and hexaphenylene isomers.

Introduction

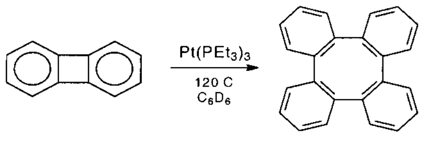
The activation of carbon−carbon bonds by homogeneous metal catalysts is an area of active research in organometallic chemistry.[1] Much of this interest is sparked by the fact that the ability to break C−C bonds is of vital importance to the petroleum industry. Selective activation of C−C bonds is crucial for petroleum refining and transformation. Unfortunately, C−C bonds are among the least reactive of all bonds, which is why this area continues to present a fundamental challenge to organometallic chemists.

Many known examples of C−C bond activation have relied on the attainment of aromaticity or relief of ring strain in order to promote C−C bond breakage.[2] Examples have also been found where an alkyl group forced into proximity with the metal leads to oxidative addition of the C−C bond.[3] One substrate that is particularly reactive is biphenylene, a molecule that contains a strained four-membered ring which can be cleaved by a variety of metal complexes.[4] In addition, such a reaction is thermodynamically favored due to the formation of two strong metal−aryl bonds. This is demonstrated by the reaction of biphenylene with $(C_5Me_5)Rh(PMe_3)(Ph)H$. The kinetic product of this reaction is $(C_5Me_5)Rh(PMe_3)$(biphenylenyl)(H), representing C−H activation at the α-carbon, but the thermodynamic product is $(C_5Me_5)Rh(PMe_3)$(2,2′-biphenyl), which results from C−C activation of one aryl−aryl bond (eq 1).[5] These types of C−C insertion products are also produced in reactions that model the hydrodesulfurization of dibenzothiophene.[6]



(1)

Rhodium and cobalt complexes of the form (C_5Me_5)-$M(C_2H_4)_2$ have also been shown to react with biphenylene to form the bimetallic species $(C_5Me_5)_2M_2$(2,2′-biphenyl).[7] A number of studies of reactions with Ni, Pd, and Pt complexes have also been conducted. Compounds containing these metals react catalytically with biphenylene in a variety of ways. One such interesting reaction involves the catalytic transformation of biphenylene to tetraphenylene using a platinum phosphine catalyst (eq 2),[8] and $Ni(COD)(PMe_3)_2$ has also



(2)

---

[1] *Topics in Organometallic Chemistry: Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer-Verlag: Berlin, 1999.

[2] (a) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222. (b) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346. Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515. Ros, R.; Lenarda, M.; Pahor, N. B.; Calligaris, M.; Delisa, P.; Randaccio, L.; Graziani, M. *J. Chem. Soc., Dalton* **1976**, 1937.

[3] Suggs, J. W.; Jun, C.-H. *J. Chem. Soc., Chem. Commun.* **1985**, 92−93. van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 13415.

[4] (a) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Kruger, C.; Tsay, Y. H. *Organometallics* **1985**, *4*, 224. (b) Lu, Z.; Jun, C.; De Gala, S. R.; Sigalas, M.; Eisenstein, O.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1877. (c) Atkinson, E. R.; Levins, P. L.; Dickelman, T. E. *Chem. Ind. (London)* **1964**, 934.

[5] Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 3647.

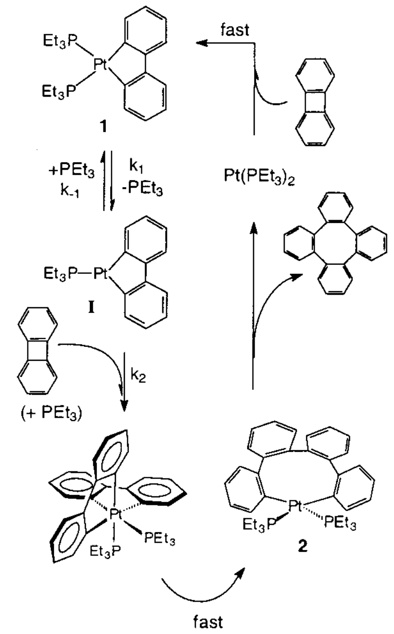
[6] Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 10855. Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 7606.

[7] Perthuisot, C.; Edelbach, B. L.; Zubris, D. E.; Jones, W. D. *Organometallics* **1997**, *16*, 2016.

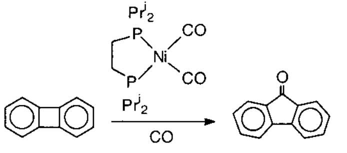
[8] (a) Edelbach, B. L.; Vicic, D. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4784. (b) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 4040.

10.1021/om010111m CCC: \$20.00

Scheme 1



been used to catalyze this reaction.[9] Another reaction uses nickel to catalytically produce fluorenone (eq 3).[8]



(3)

The catalytic mechanism of the tetraphenylene forming reaction is outlined in Scheme 1. The first step involves the dissociation of a phosphine ligand and insertion of biphenylene to give the intermediate **1**. Reversible loss of phosphine from **1** followed by C−C bond activation of another biphenylene and rapid recoordination of phosphine gives the Pt(IV) intermediate. This step is inhibited by excess phosphine, as recoordination of phosphine to species **I** occurs at a much faster rate than C−C bond cleavage. Reductive C−C coupling of adjacent aryl groups in the Pt(IV) species gives complex **2**. Tetraphenylene is then reductively eliminated, and rapid insertion of another biphenylene continues the cycle.[10] This mechanism was proposed on the basis of kinetic analysis and the identification of complexes **1**, **I**, and **2** as intermediates in the cycle. **1** was independently synthesized from $(PEt_3)_3PtCl_2$ and 2,2′-dilithiobiphenyl. Heating this complex at 120 °C in the presence of excess biphenylene resulted in a more rapid formation of tetraphenylene than when $Pt(PEt_3)_3$ was used as the catalyst.

Altering the substituents of the phosphine ligands of **1** has a pronounced effect on its reactivity and is the subject of the present study. Four different bis-phosphine platinum complexes have been investigated: [Pt(dtbpm)], [Pt(dippm)], $[Pt(PPh_2Bu^t)_2]$, and $[Pt(PPh_3)_2]$ (dtbpm = $Bu^t_2PCH_2PBu^t_2$, dippm = $Pr^i_2PCH_2PPr^i_2$). In each case, a different reactivity was observed, as presented below.

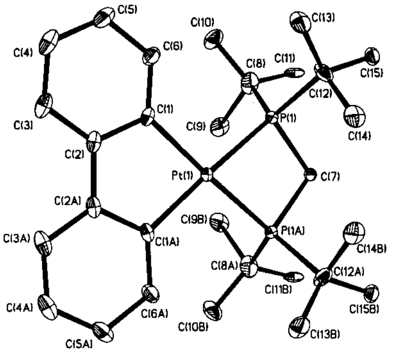
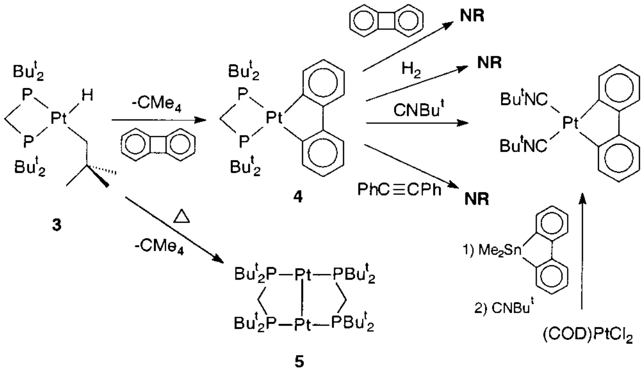


Figure 1. Thermal ellipsoid plot of (dtbpm)Pt(2,2′-biphenyl) (**4**). Ellipsoids are shown at the 30% level. There is a rotational disorder in the *tert*-butyl groups (not shown).

Scheme 2



Results and Discussion

Reactivity of [Pt(dtbpm)]. The reactive intermediate [Pt(dtbpm)] has been described by Hofmann and can be generated readily from the thermal elimination of neopentane from (dtbpm)Pt(neopentyl)H (**3**).[11] The reaction of **3** with biphenylene in THF-d_8 solution can be monitored easily by ^{31}P NMR spectroscopy. The two resonances for **3** each appear as doublets with ^{195}Pt satellites (δ 7.3, $J_{P-P} = 14$ Hz, $J_{Pt-P} = 1361$ Hz; δ −8.0, d, $J_{P-P} = 14$ Hz, $J_{Pt-P} = 1345$ Hz) and are seen to diminish as a single new singlet resonance for a product is observed at δ 4.7 ($J_{Pt-P} = 1453$ Hz). The ^1H NMR spectrum shows resonances in the aromatic region (two triplets plus two doublets), consistent with the formation of the simple C−C insertion product (dtbpm)Pt(2,2′-biphenyl) (**4**; Scheme 2). The structure of **4** was confirmed by X-ray diffraction (Figure 1) and is typical of other square-planar 2,2′-biphenyl complexes, although the P−Pt−P bond angle is fairly acute (74°). **4** can also be independently synthesized by the reaction of (dtbpm)-$PtCl_2$ with 2,2′-dilithiobiphenyl.

Unlike the PEt_3 analogue **1**, **4** does not react further with biphenylene to give a species similar to **2** or tetraphenylene. **4** does not react with CO to generate fluorenone, even at elevated temperatures (125 °C). The lack of reactivity with CO is somewhat surprising, but

---

[9] Schwager, H.; Spyroudis, S.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1990**, *382*, 191−200.

[10] Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843.

[11] (a) Hofmann, P.; Heiss, H.; Müller, G. *Z. Naturforsch.* **1987**, *42b*, 395. (b) Hofmann, P.; Heiss, H.; Neiteler, P.; Müller, G.; Lachmann, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 880. (c) Hofmann, P.; Unfried, G. *Chem. Ber.* **1992**, *125*, 659.

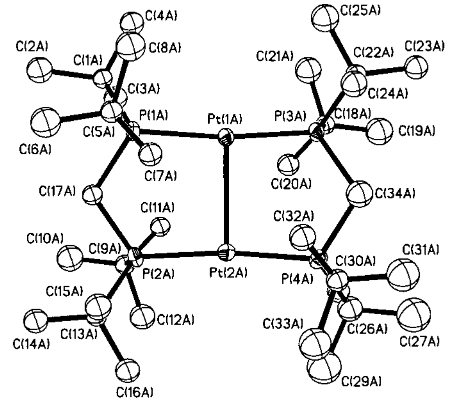


Figure 2. Thermal ellipsoid plot of $Pt_2(\mu\text{-dtbpm})_2$, (**5**). Only one of two disorder components is shown. Ellipsoids are shown at the 30% level.

Table 1. Selected Distances (Å) and Angles (deg) for $Pt_2(\mu\text{-dtbpm})_2$ (5)

	molecule			
	A	B	C	D
Bond Distances				
Pt(1)−Pt(2)	2.7948(11)	2.8078(12)	2.802(7)	2.798(5)
Pt(1)−P(1)	2.245(5)	2.250(5)	2.244(16)	2.228(15)
Pt(1)−P(3)	2.237(5)	2.249(5)	2.248(16)	2.229(15)
Pt(2)−P(2)	2.246(5)	2.232(6)	2.230(16)	2.250(15)
Pt(2)−P(4)	2.238(6)	2.242(6)	2.245(16)	2.238(16)
Bond Angles				
P(3)−Pt(1)−P(1)	172.9(2)	173.7(2)	175.0(9)	172.5(8)
P(3)−Pt(1)−Pt(2)	93.16(15)	92.53(16)	92.6(7)	93.1(6)
P(1)−Pt(1)−Pt(2)	93.97(14)	93.49(15)	92.4(6)	94.4(6)
P(4)−Pt(2)−P(2)	172.5(2)	171.9(2)	170.9(10)	173.1(8)
P(4)−Pt(2)−Pt(1)	93.78(15)	94.06(16)	93.3(7)	94.1(6)
P(2)−Pt(2)−Pt(1)	93.21(15)	93.43(17)	94.6(7)	92.7(5)
P(1)−C(17)−P(2)	114.9(9)	113.2(11)	112.9(18)	115.3(16)
P(3)−C(34)−P(4)	115.3(16)	118.7(11)	118.9(18)	115.3(17)

earlier studies showed that **1** was also unreactive toward CO. **4** also does not react with diphenylacetylene or dihydrogen, unlike **1**. It is possible that the chelating nature of the phosphine in **4** prevents the dissociation of one phosphorus, as was shown to be required in the mechanism for tetraphenylene formation (Scheme 1). However, reaction with *tert*-butyl isocyanide at 55 °C leads to phosphine displacement to give $Pt(CN\text{-}t\text{-}Bu)_2$-(2,2′-biphenyl) and free dtbpm. This product can be synthesized independently from (COD)Pt(2,2′-biphenyl) and $CNBu^t$. Also, in the absence of substrate thermolysis of **3** gives the unreactive dimer $[Pt(\mu\text{-dtbpm})]_2$ (**5**), in which the phosphine *bridges* the two metal centers.[12] The ^1H NMR spectrum for **5** shows a single *tert*-butyl environment (δ 1.47, m) and a triplet for the methylene group ($J_{P-H} = 3.7$ Hz), indicating a highly symmetric structure. The ^{31}P NMR spectrum displays a singlet with Pt satellites ($J_{Pt-P} = 4479$ Hz) at δ 84.3.

Single crystals of **5** were grown from THF solution at −20 °C, and a small crystal was used to determine the structure. The molecule crystallizes in triclinic space group $P\bar{1}$, with 2 molecules per asymmetric unit. The initial solution showed the basic skeletal framework for the two independent molecules (A and B), but a second orientation of the compound could be seen overlapping the primary orientation at a 90° angle (C and D). A successful refinement of this disorder was carried out by including the secondary orientation (molecules C and D) with a geometry constrained to be the same as that of the primary orientation (molecules A and B). The populations of the disorder partners were allowed to vary independently (15.5(2)% C, 19.7(2)% D), with each site containing one molecule total. Only the platinum and phosphorus atoms were refined anisotropically, with the carbon atoms restrained to similar ($U \pm 0.04$) isotropic values. The resulting structure is shown in Figure 2. Table 1 gives selected distances and angles.

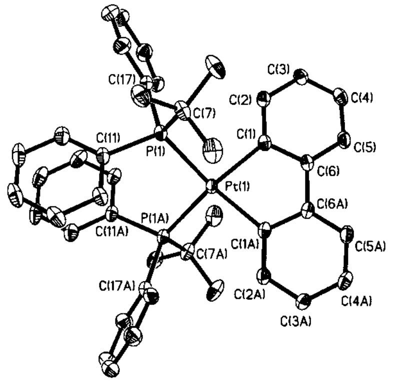


Figure 3. Thermal ellipsoid plot of $Pt(PPh_2Bu^t)_2$(2,2′-biphenyl) (**6**). Ellipsoids are shown at the 30% level.

Several features of the structure are worth noting. First, the platinum−platinum distance is 2.80 Å and is slightly longer than the Pt−Pt single bond in molecules containing Pt(I)−Pt(I) centers such as $[Pt_2(dppm)_2(CO)_2]^{+2}$ (2.642 Å)[13] or $Pt_2(dppm)_2Cl_2$ (2.651 Å).[14] The presence of a metal−metal bond, despite the presence of two formally d^{10} metal centers, has been described previously in other $d^{10}-d^{10}$ dimers and involves mixing of the empty p orbitals with the filled d orbitals to give bonding character between the metals.[12,15,16] Hofmann has reported the structure of the related compound $[Cu_2(\mu\text{-dtbpm})_2]^{2+}$, which shows similar features,[17] and the palladium dimer $[Pd(dcpe)]_2$ has also been found to have a significant Pd^0-Pd^0 interaction.[18] Second, the Pt_2P_4 unit is not planar but is twisted about the Pt−Pt bond by 20°, giving the molecule a D2 or "propeller" symmetry. The P−Pt−P bond angles are nearly linear (173°). In the overlapping of the disordered molecules (A/C or B/D), the right-handed propeller A overlaps with the left-handed propeller C, and vice versa for B and D. The *tert*-butyl groups of each molecule occupy roughly the same region of space, which accounts for the remarkable crystallization disorder that is observed.

Reactivity of (dippm)Pt(2,2′-biphenyl). The complex related to **3** but with isopropyl groups in place of *tert*-butyl groups has also been synthesized by reaction of (COD)Pt(neopentyl)Cl with dippm and $NaHB(OMe)_3$.

---

(12) This dimer was observed by Hofmann and proposed to have the structure shown in Scheme 2, but without a Pt−Pt bond.[9b] Recent results with the cyclohexylphosphine derivative give X-ray-quality crystals (Hofmann, P. Private communication).

(13) Fisher, J. R.; Mills, A. J.; Sumner, S.; Brown, M. P.; Thomson, M. A.; Puddephatt, R. J.; Frew, A. A.; Manojlovic-Muir, L.; Muir, K. W. *Organometallics* **1982**, *1*, 1421.

(14) Manojlovic- Muir, L.; Muir, K. W.; Solomun, T. *Acta Crystallogr.* **1979**, *B35*, 1237.

(15) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

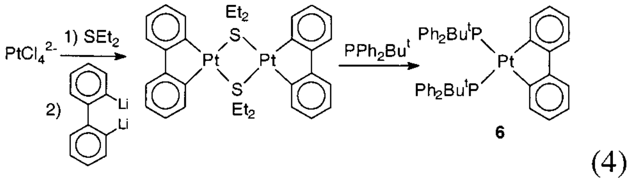
(16) Dedieu, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2074.

(17) Straub, B. F.; Rominger, F.; Hofmann, P. *Inorg. Chem.* **2000**, *39*, 2113.

(18) Pan, Y.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 3842.

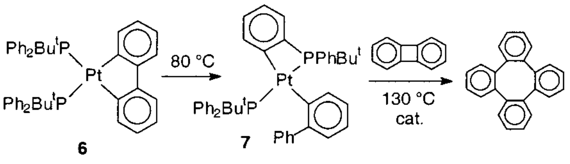
This compound loses neopentane more slowly than **3** (85 °C, 13 h) but does not give the C−C insertion product analogous to **4**. Rather, a dimer is formed exclusively, analogous to **5**. The ^{31}P NMR spectrum of the dimer appears as a singlet at δ 62.3 (with platinum satellites). No reaction of **3** with biphenylene occurs at 22 °C.

Reactivity of [Pt(PPh$_2$Bu^t)$_2$]. The synthesis of the PPh$_2$Bu^t analogue of **1** proved not to be straightforward. Reaction of (COD)Pt(2,2′-biphenyl) with PPh$_2$Bu^t failed to give the substitution product. Rather, the complex was formed by way of the diethyl sulfide complex as shown in eq 4. A single-crystal X-ray structure of **6** (Figure 3) shows square-planar coordination just as in **1** and **4**. The ^{31}P NMR spectrum of **6** shows the expected singlet (with ^{195}Pt satellites, $J_{\text{Pt-P}} = 2000$ Hz) at δ 43.64.



(4)

When a C$_6$D$_6$ solution of **6** is heated to 80 °C for 1 h, two new products are observed, each with two distinct types of phosphorus atoms, in the ^{31}P NMR spectrum (isomer A δ 32.34, d, $J_{\text{P-P}} = 14$ Hz, $J_{\text{Pt-P}} = 2054$ Hz, δ −4.10, d, $J_{\text{P-P}} = 14$ Hz, $J_{\text{Pt-P}} = 1028$ Hz; isomer B, δ 31.19, d, $J_{\text{P-P}} = 14$ Hz, $J_{\text{Pt-P}} = 2050$ Hz, δ −3.87, d, $J_{\text{P-P}} = 14$ Hz, $J_{\text{Pt-P}} = 986$ Hz). The ^{31}P−^{195}Pt coupling constants for all resonances are in the range commonly observed for phosphorus trans to an aryl ring. The products are assigned as rotamers of the ortho-metalation derivative **7** as shown in eq 5. Formation of **7** most likely occurs by way of oxidative addition of a C−H bond in **6** to give a Pt(IV) intermediate followed by reductive elimination of a 2,2′-biphenyl C−H bond. This reaction is apparently reversible, as heating **7** to 130 °C in the presence of biphenylene leads to the slow catalytic formation of tetraphenylene (~1 turnover/week).



(5)

Reactivity of [Pt(PPh$_3$)$_2$]. The reaction of Pt(PPh$_3$)$_3$ with biphenylene does not lead to the formation of a C−C insertion product. Either the fragment [Pt(PPh$_3$)$_2$] is kinetically unable to insert into the bond or the insertion product is thermodynamically unstable. The latter possibility can be disregarded, however, as the complex Pt(PPh$_3$)$_2$(2,2′-biphenyl) (**8**) can be prepared independently by reaction of Pt(PPh$_3$)$_2$Cl$_2$ with 2,2′-dilithiobiphenyl. The adduct shows a singlet in the ^{31}P NMR spectrum at δ 30.75 ($J_{\text{Pt-P}} = 2009$ Hz). A single-crystal X-ray structure of **8** is shown in Figure 4 and shows a square-planar structure similar to that of **4** and **6**.

Curiously, while the 14-electron L$_2$Pt^0 fragment does not insert into C−C bonds of biphenylene, the Pt$^{\text{II}}$ metal center in **8** appears to insert. Reaction of **8** with biphenylene at 100 °C leads to the stoichiometric formation of three major and two minor organic products (Scheme 3).

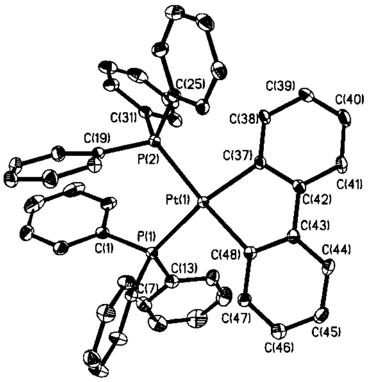


Figure 4. Thermal ellipsoid plot of Pt(PPh$_3$)$_2$(2,2′-biphenyl) (**8**). Ellipsoids are shown at the 30% level.

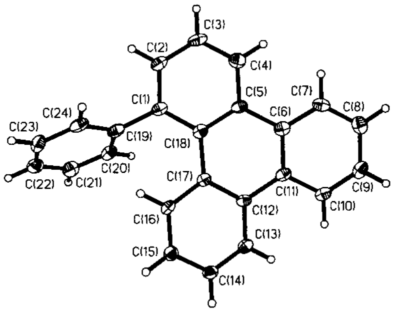
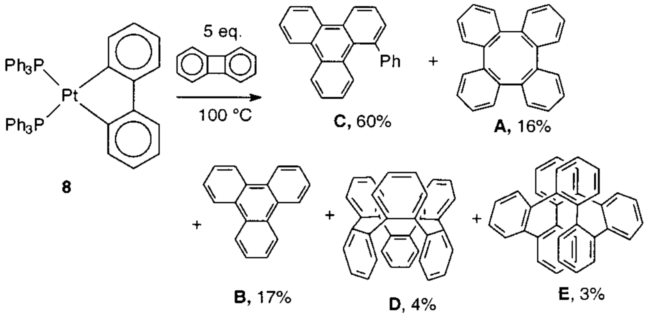


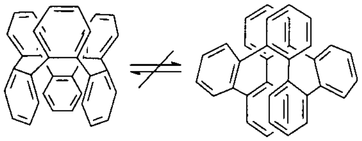
Figure 5. Thermal ellipsoid plot of phenylterphenylene (**C**). Ellipsoids are shown at the 30% level.

Scheme 3



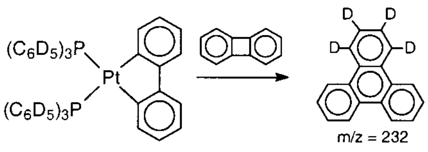
Analysis by GCMS showed the five products **A**−**E** in a 16:17:60:4:3 ratio, in order of retention time. The first product to elute (**A**; 16%) was identified as tetraphenylene, with mass 304, by comparison with an authentic sample. The next product had a mass of 228, corresponding to *triphenylene* (**B**; 17%), also by comparison with an authentic sample. The similar retention times of **A** and **B** (see the Supporting Information) appears to be attributable to the nonplanar and highly symmetrical (D_{2d}) structure of tetraphenylene. The third compound **C** was the most abundant (60%) and was identified as phenylterphenylene by comparison with an authentic sample. **C** was also identified by single-crystal X-ray diffraction (Figure 5). The two minor products **D** (4%) and **E** (3%) had long retention times and each displayed m/z 456. None of the five compounds showed significant fragmentation at 70 eV ionization energy, consistent with their formation as fused ring systems of the type (C$_6$H$_4$)$_n$, where $n = 3$, 4, or 6.

The three major products (**A**−**C**) were isolated by preparative TLC, but insufficient quantities of the long-retention-time products (**D**, **E**) were isolated to permit complete characterization. ^{1}H NMR spectra of **A**−**C** were consistent with their identification as triphenylene, tetraphenylene, and phenylterphenylene. Products **D** and **E** can be tentatively identified by their masses and by making a basic assumption. In the catalytic transformation of biphenylene to tetraphenylene, aryl−aryl C−C single bonds were made and broken. Consequently, one might expect products of the type $(C_{12}H_8)_n$ by a series of ring-opening/ring-forming metatheses. The masses of the unknown products are consistent with even-numbered combinations of phenylene rings, $(C_6H_4)_6$. Compounds **D** and **E** with m/z 456 can therefore be assigned as two isomers of hexaphenylene, which are known compounds produced in the decomposition of M(2,2′-biphenyl)$_3$ compounds in the literature.[19] They do not interconvert even at elevated temperatures (eq 6). No independent samples of hexaphenylene were available to confirm this assignment.


(6)

Determination of the Origin of Triphenylene. Triphenylene presents an anomaly because it has an odd number of phenylene rings, unlike the other products. Since the biphenylene substrate consisted of an even number of rings, the presence of triphenylene may have indicated more complex C−C bond cleavage. That is, this product may have resulted from breaking both aryl−aryl bonds in biphenylene. Alternatively, triphenylene may have come from activation of one of the triphenylphosphine ligands on the catalyst, which underwent P−C bond cleavage[20] over the reaction.

To probe these two possibilities, the reaction was repeated with a modified catalyst. The *perdeutero* derivative $[P(C_6D_5)_3]_2$Pt(2,2′-biphenyl) was synthesized, and the reaction with biphenylene was performed as before. Examination of the product by GCMS showed a peak for triphenylene with a mass of 232 was observed, indicating that one of the phenylene rings has arisen from the phosphine ligand (eq 7). It was therefore determined that the third phenylene ring in triphenylene does indeed come from the metal ligands and not from biphenylene cleavage.



(7)

Conclusions

Reaction of biphenylene with Pt(dtbpm)(neopentyl)H gives the expected C−C insertion adduct, but no further reaction chemistry. Reaction of Pt(PPh$_2$Bu^t)$_2$(2,2′-biphenyl) with biphenylene leads to the formation of a phosphine ortho-metalated product, which can also participate in the catalytic dimerization of biphenylene to give tetraphenylene. Reaction of biphenylene with $(PPh_3)_2$Pt(2,2′-biphenyl) leads to the major product phenyltriphenylene, followed by tetraphenylene and then triphenylene. The presence of triphenylene is shown to occur via P−C activation of the phosphine ligand phenyl groups. Two unique isomers of hexaphenylene were also observed in the product mixture.

Experimental Section

General Considerations. All manipulations were performed under an N_2 atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. glovebox. Tetrahydrofuran, toluene, and diethyl ether were distilled from dark purple solutions of benzophenone ketyl. Alkane solvents were made olefin-free by stirring over H_2SO_4, washing with aqueous $KMnO_4$ and water, and distilling from dark purple solutions of tetraglyme/benzophenone ketyl. Tetrahydrofuran-d_8, benzene-d_6, and CD_2Cl_2 were purchased from Cambridge Isotope Lab. The liquids were distilled under vacuum from dark purple solutions of benzophenone ketyl or dried over 4 Å molecular sieves and stored in ampules with Teflon-sealed vacuum-line adaptors. PPh_2Cl was purchased from Strem Chemical Co. The preparations of $Pt(PPh_3)_2Cl_2$,[21] [(2,2′-biphenyl)Pt(μ-SEt$_2$)]$_2$,[22] (dtbpm)PtCl$_2$,[23] (dtbpm)Pt(neopentyl)H,[11] (COD)Pt(neopentyl)Cl,[24] (COD)Pt(2,2′-biphenyl),[25] (^{t}BuNC)$_2$Pt(2,2′-biphenyl),[25] (LiTMEDA)$_2$(2,2′-biphenyl),[26] Me$_2$Sn(2,2′-biphenyl),[26] bis(diisopropylphosphino)methane,[27] and biphenylene[28] were all prepared according to literature procedures.

All NMR spectra were recorded on a Bruker AMX400 (^{1}H, ^{31}P) spectrometer. All ^{1}H and ^{31}P chemical shifts are reported in ppm (δ) relative to residual solvent resonances or 85% phosphoric acid. Analyses were obtained from Desert Analytics. A Siemens SMART system with a CCD area detector was used for X-ray structure determination. Gas chromatography−mass spectrometry was performed on a 5890 Series II gas chromatograph fitted with an HP 5970 Series mass selective detector.

Reaction of (dtbpm)Pt(neopentyl)H (3) with Biphenylene. **3** (10 mg, 0.017 mmol) and biphenylene (13.3 mg, 0.087 mmol) were placed in a resealable NMR tube and dissolved in 0.6 mL of THF. The reaction mixture was heated to 55 °C and was judged complete after 1.5 h, on the basis of changes in the ^{31}P NMR spectrum (see text). The major product (>90%) was **4**, although a small amount of the dimer Pt$_2$(μ-dtbpm)$_2$ (**5**, ~5%) and other uncharacterized products (~5%) were observed. The volatile materials were removed under vacuum, the excess biphenylene was removed by sublimation, and the residue was redissolved in $CDCl_3$. ^{1}H and ^{31}P NMR spectra of the major product were consistent with the C−C-activated Pt(II) complex **4**.

---

(19) Wittig, G.; Rümpler, K.-D. *Liebigs Ann. Chem.* **1971**, 1. Irngartinger, H. *Isr. J. Chem.* **1972**, *10*, 635. Ernst, L.; Mannschreck, A.; Rümpler, K.-D. *Org. Magn. Reson.* **1973**, *5*, 125. Irngartinger, H. *Acta Crystallogr.* **1973**, *B29*, 894. Hirschler, M. M.; Taylor, R. *J. Chem. Soc., Chem. Commun.* **1980**, 967.

(20) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171.

(21) Bailar, J. C.; Itatani, H. *Inorg. Chem.* **1965**, *4*, 1618.

(22) Zelewsky, A.; Cornioley-Bevschel, C. *Inorg. Chem.* **1987**, *26*, 3334.

(23) Hofmann, P.; Heiss, H.; Muller, G. *Z. Naturforsch.* **1987**, *42B*, 395.

(24) Brainard, R. L.; Miller, T. M.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1481.

(25) Uson, R.; Vicente, J.; Cirac, J. A.; Chicote, M. T. *J. Organomet. Chem.* **1980**, *198*, 105.

(26) Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. *J. Organomet. Chem.* **1982**, *228*, 107.

(27) Novikova, Z. S.; Prischenko, A. A.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1977**, *47*, 775.

(28) Logullo, F. M.; Seitz, A. H.; Friedman, L. In *Organic Syntheses*; Yates, P., Ed.; Wiley: New York, 1968; Vol. 48, pp 54−59.

Preparation of (dtbpm)Pt(2,2′-biphenyl) (4). 2,2′-Dilithiobiphenyl, used in situ from Bu^{n}Li (0.81 mmol, 0.3 mL of 2.6 M hexanes solution) and 2,2′-dibromobiphenyl (120 mg, 0.39 mmol) in 6 mL of Et_2O at 0 °C, was added dropwise to a solution of (dtbpm)$PtCl_2$ (200 mg, 0.35 mmol) in 10 mL of toluene. The yellow reaction mixture was quenched with 10 mL of H_2O after stirring at room temperature for 42 h. The mixture was extracted with 50 mL each of toluene and THF. The organic portion was dried with $MgSO_4$, and the solvents were removed in vacuo. Recrystallization from CH_2Cl_2 and Et_2O at −15 °C yielded yellow crystals (103 mg, 45%). ^{1}H NMR ($CDCl_3$): δ 7.67 (br t, J_{Pt-H} = 62 Hz, 2 H, $H_{ortho-Pt}$), 7.31 (d, J = 8.8 Hz, 2 H), 6.92 (t, J = 7.0 Hz, 2 H), 6.76 (t, J = 7.2 Hz, 2 H), 3.52 (t, J_{P-H} = 7.6 Hz, 2 H, PCH_2P), 1.49 (d, J_{P-H} = 12.8 Hz, 36 H, $(CH_3)_3CP$). ^{31}P NMR ($CDCl_3$); δ 4.7 (t, J_{Pt-P} = 1445 Hz). Mp: did not melt or decompose under 255 °C. Anal. Calcd (found): C, 53.44 (53.38); H, 7.12 (7.16).

Reaction of (dtbpm)Pt(2,2′-biphenyl) with H_2. **4** (8 mg, 0.012 mmol) was placed in a resealable NMR tube with a gas bulb attached and placed under vacuum. A 0.60 mL portion of THF-d_8 was added to the tube by vacuum transfer, and the headspace (approximately 5 mL) was filled with 1 atm of H_2. No change was observed in the reaction mixture following 4.5 days of thermolysis at 120 °C. Extended heating at 150 °C resulted in no change in the NMR spectrum.

Reaction of (dtbpm)Pt(2,2′-biphenyl) with PhC≡CPh. **4** (8.1 mg, 0.012 mmol) and diphenylacetylene (10.9 mg, 0.61 mmol) were placed in a NMR tube and dissolved in 0.60 mL of THF-d_8. The mixture was frozen in liquid N_2 and quickly flame-sealed. No change was observed in the reaction mixture following 4.5 days of thermolysis at 120 °C. Extended heating at 150 °C resulted in no change in the NMR spectrum.

Reaction of (dtbpm)Pt(2,2′-biphenyl) with CO. **4** (8 mg, 0.012 mmol) was placed in a resealable NMR tube and placed under vacuum. A 0.60 mL portion of THF-d_8 was added to the tube by vacuum transfer, and the headspace was filled with 1 atm of CO. No change was observed in the reaction mixture following 4 days of thermolysis at 85 °C. Extended heating at 150 °C resulted in no change in the NMR spectrum.

Reaction of (dtbpm)Pt(2,2′-biphenyl) with Bu^{t}NC. **4** (8.1 mg, 0.012 mmol) was placed in a resealable NMR tube and dissolved in 0.60 mL of C_6D_6. Bu^{t}NC (14 μL, 0.12 mmol) was added to the solution via syringe. The mixture was allowed to react overnight at room temperature. ^{1}H and ^{31}P NMR indicated complete conversion to (^{t}BuNC)$_2$Pt(2,2′-biphenyl) and free dtbpm.

Thermolysis of (dtbpm)Pt(neopentyl)H (3). **3** (8.0 mg, 0.014 mmol) was placed in a resealable NMR tube and dissolved in 0.6 mL of THF-d_8. The tube was frozen in liquid N_2 and flame-sealed. Formation of the dimer $Pt_2(\mu\text{-dtbpm})_2$ (**5**) was complete after heating for 1.5 h at 55 °C. ^{1}H NMR (THF-d_8): δ 1.94 (t, J_{P-H} = 3.7 Hz, J_{Pt-H} = 34 Hz, 4 H, PCH_2P), 1.47 (m, 72 H, ^{t}Bu methyls). ^{31}P NMR (THF-d_8): δ 84.3 (m, J_{Pt-P} = 4479 Hz, J_{Pt-P} = 41 Hz).

Preparation of (dippm)Pt(neopentyl)Cl. Bis(diisopropylphosphino)methane (87 mg, 0.35 mmol) in 1.5 mL of CH_2Cl_2 was added dropwise to (COD)Pt(neopentyl)Cl (120 mg, 0.29 mmol) in 2 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 1 h, and then the volatile materials were removed by vacuum. A total of 103 mg (63%) of white (dippm)Pt(neopentyl)Cl was isolated by column chromatography (CH_2Cl_2, SiO_2, 14 × 2.5 cm). ^{1}H NMR ($CDCl_3$): δ 2.70 (dd, J_{P-H} = 9.6 Hz, J_{P-H} = 7.6 Hz, J_{Pt-H} = 39 Hz, 2 H, PCH_2P), 2.41 (m, 2 H, ^{i}Pr H), 2.29 (m, 2 H, ^{i}Pr H), 1.62 (dd, J_{P-H} = 7.6 Hz, J_{P-H} = 3.6 Hz, J_{Pt-H} = 63 Hz, 2 H, $CH_2C(CH_3)_3$), 1.4−1.2 (m, 24 H, ^{i}Pr methyls), 1.04 (s, 9 H, $CH_2C(CH_3)_3$). ^{31}P NMR ($CDCl_3$); δ −12.4 (d, J_{Pt-P} = 1152 Hz, J_{P-P} = 42 Hz, trans neopentyl), −15.4 (d, J_{Pt-P} = 4019 Hz, J_{P-P} = 42 Hz, trans Cl).

Preparation of (dippm)Pt(neopentyl)H. $NaHB(OMe)_3$ (59 mg, 0.46 mmol) in 1.5 mL of THF was added dropwise to a solution of (dippm)Pt(neopentyl)Cl (101 mg, 0.18 mmol) in 1 mL of THF. The reaction was stirred at room temperature for 2 h and then quenched with 8 mL of cold H_2O at 0 °C. The mixture was extracted with 4 × 10 mL of Et_2O. The organic portion was then washed with 3 × 10 mL of H_2O, dried with $MgSO_4$, and evaporated under vacuum to yield a waxy solid. Recrystallization from toluene and hexanes at −15 °C yielded tan crystals (27 mg, 28%). ^{1}H NMR (THF-d_8): δ 3.11 (t, J_{P-H} = 8.4 Hz, 2 H, PCH_2P), 2.27 (m, 2 H, ^{i}Pr H), 2.03 (m, 2 H, ^{i}Pr H), 2.00 (dd, J_{P-H} = 9.2 Hz, J_{P-H} = 6.8 Hz, J_{Pt-H} = 85 Hz, 2 H, $CH_2C(CH_3)_3$), 1.3−1.1 (m, 24 H, ^{i}Pr methyls), 0.97 (s, 9 H, $CH_2C(CH_3)_3$), −3.68 (dd, $J_{P(trans)-H}$ = 212 Hz, $J_{P(cis)-H}$ = 12 Hz, J_{Pt-H} = 1304 Hz, 1 H, Pt−H). ^{31}P NMR (THF-d_8): δ −1.8 (d, J_{Pt-P} = 1369 Hz, J_{P-P} = 22 Hz), −12.4 (d, J_{Pt-P} = 1377 Hz, J_{P-P} = 22 Hz).

Thermolysis of (dippm)Pt(neopentyl)H. (dippm)Pt(neopentyl)H (7.8 mg, 0.015 mmol) was placed in a resealable NMR tube and dissolved in 0.6 mL of THF-d_8. Formation of the dimer, $Pt_2(\mu\text{-dippm})_2$, was complete after heating for 13 h at 85 °C. ^{1}H NMR (THF-d_8): δ 2.08 (broad septet, 8 H, J_{H-H} = 6.8 Hz, ^{i}Pr H), 1.79 (t, 4 H, J_{P-H} = 3.6 Hz, J_{Pt-H} = 42 Hz, PCH_2P), 1.29 (m, 24 H, ^{i}Pr methyls), 1.22 (m, 24 H, ^{i}Pr methyls). ^{31}P NMR (THF-d_8): δ 62.3 (m, J_{Pt-P} = 4312 Hz, J_{Pt-P} = 89 Hz).

Preparation of PPh$_2$Bu^t. A 6.145 g (0.0278 mmol) portion of PPh_2Cl was dissolved in 45 mL of Et_2O, and 18.2 mL of Bu^{t}Li (1.7 M in pentane, 0.031 mmol) was added slowly with cooling in an ice bath. The solution was warmed to room temperature and then refluxed overnight. The dark brown solution was separated from the LiCl precipitate and the solvent removed under vacuum (0.1 Torr). The product was isolated by vacuum distillation (∼55 °C). ^{1}H NMR (THF-d_8): δ 1.47 (d, J_{P-H} = 12.2 Hz, 9 H), 7.3 (m, 6 H), 7.55 (m, 4 H). ^{31}P NMR (THF-d_8): δ 20.24 (s).

Preparation of (PPh$_2$Bu^t)$_2$Pt(2,2′-biphenyl) (6). A slurry of 89.6 mg (0.102 mmol) of [(2,2′-biphenyl)Pt(μ-SEt$_2$)]$_2$ in 15 mL of THF was treated with 0.6 mmol of PPh$_2$Bu^t (0.37 mL of 1.63 M solution). After 75 min, all of the solid had dissolved to give a clear yellow solution. The THF was removed under vacuum and the residue washed with benzene to remove excess phosphine. The product remained as pale yellow air-stable crystals and was recrystallized from CH_2Cl_2. Data for **6** are as follows. ^{1}H NMR (THF-d_8): δ 8.151 (br s, 4 H), 7.600 (br s, 8 H), 7.426 (t, J = 7.3 Hz (Pt satellites), 2 H), 7.288 (d, J, 7.3 Hz, 2 H), 6.876 (br s, 2 H), 6.789 (t, J = 7.3 Hz, 2 H), 6.609 (br s, 6 H), 6.377 (t, J = 7.3 Hz, 2 H), 1.197 (d, J = 13.3 Hz, 18 H). ^{31}P NMR (THF-d_8): δ 43.64 (s, J_{Pt-P} = 2000 Hz). Anal. Calcd (found) for **6**·2CH_2Cl_2: C, 55.15 (54.59); H, 5.03 (5.16).

Thermolysis of (PPh$_2$Bu^t)$_2$Pt(2,2′-biphenyl) (6). A 10 mg portion of **6** was dissolved in 0.6 mL of THF-d_8 and placed in a resealable NMR tube. The sample was heated to 80 °C, and after 1 h the starting material had been replaced by a new product, identified spectroscopically as rotamers of the ortho-metalation product **7**. Data for **7** are as follows. ^{1}H NMR (THF-d_8): isomer A, δ 7.86 (t, J = 8 Hz, 2 H), 7.63 (d, J = 8 Hz, 2 H), 7.33 (m, 2 H), 7.20−7.00 (m, 20 H), 6.93 (m, 2 H), 0.770, 1.146 (d, J = 10.2 Hz, 9 H), 0.735 (d, J = 9.8 Hz, 9 H); isomer B, δ 0.818 (d, J = 14.0 Hz, 9 H), 0.696, d, J = 13.8 Hz, 9 H), other resonances obscured. ^{31}P NMR (THF-d_8): isomer A, δ 32.34 (d, J_{P-P} = 14 Hz, J_{Pt-P} = 2054 Hz), −4.10 (d, J_{P-P} = 14 Hz, J_{Pt-P} = 1028 Hz); isomer B, δ 31.19 (d, J_{P-P} = 14 Hz, J_{Pt-P} = 2050 Hz), −3.87 (d, J_{P-P} = 14 Hz, J_{Pt-P} = 986 Hz).

Reaction of (PPh$_2$Bu^t)$_2$Pt(2,2′-biphenyl) with Biphenylene. A sample of 9 mg of **6** (0.0108 mmol) and 8.2 mg (0.054 mmol) of biphenylene was dissolved in 0.6 mL of THF-d_8 and placed in a resealable NMR tube. The sample was heated to 130 °C and the reaction monitored by periodic recording of ^{1}H NMR spectra. Over a period of 40 days, the biphenylene was seen to be converted catalytically into tetraphenylene (∼1 turnover/week).

Table 2. Summary of Crystallographic Data for 4, 5, 6, 8, and C

	4	5	6	8	C
Crystal Parameters					
chem formula	$PtP_2C_{29}H_{46}$	$Pt_2P_4C_{34}H_{76}$	$PtP_2C_{44}H_{46}$	$PtP_2C_{48}H_{38}\cdot CH_2Cl_2\cdot 2H_2O$	$C_{24}H_{32}$
fw	651.69	999.01	831.84	992.77	320.50
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
space group (No.)	*Pnma*	$P\bar{1}$	*C*2/*c*	$P2_1/n$	$P2_1/c$
Z	4	4	4	4	8
a, Å	16.28370(10)	11.9290(12)	15.3446(4)	16.7917(2)	19.1209(11)
b, Å	19.9282(2)	17.0879(17)	12.6371(3)	13.4726(2)	5.7541(3)
c, Å	8.47700(10)	22.465(2)	18.6507(5)	20.30490(10)	29.742(2)
α, deg	90	72.623(2)	90	90	90
β, deg	90	83.087(2)	92.6390(10)	107.6270(10)	108.057(2)
γ, deg	90	71.827(2)	90	90	90
V, Å^3	2750.83(5)	4150.4(7)	3612.7(2)	4377.86(9)	3111.2(3)
ρ_{calcd}, g cm^{-3}	1.574	1.599	1.529	1.506	1.368
cryst dimens, mm^3	0.22 × 0.22 × 0.36	0.04 × 0.10 × 0.24	0.16 × 0.18 × 0.24	0.24 × 0.26 × 0.38	0.12 × 0.16 × 0.24
temp, °C	−80	−80	−80	−80	−80
Measurement of Intensity Data					
radiation (*λ*, Å)	Mo (0.710 73)	Mo (0.710 73)	Mo (0.710 73 Å	Mo (0.710 73)	Mo (0.710 73)
frame range, deg/time, s	0.3/30	0.3/30	0.3/5	0.3/5	0.3/30
2*θ* range, deg	4.1−56.8	2.6−45.0	4.1−56.6	3.6−56.6	2.9−46.5
no. of data collected	16 337	17 867	10 764	26 434	10 983
no. of unique data	3430	10 842	4201	10 185	4260
no. of obsd data ($I > 2\sigma(I)$)	3083		3779		2717
agreement between equiv data (R_{int})	0.0264	0.0712	0.0295	0.0211	0.0601
no. of params varied	196	763	213	488	433
μ, mm^{-1}	5.232	6.908	4.003	3.438	0.076
abs cor	SADABS	SADABS	SADABS	SADABS	SADABS
range of transmissn factors	0.616−0.928	0.593−0.928	0.678−0.928	0.927−0.733	0.566−0.862
$R1(F_o)$, $wR2(F_o^2)$ ($I > 2\sigma$)	0.0196, 0.0452	0.0753, 0.1665	0.0282, 0.0509	0.0410, 0.1441	0.0839, 0.1467
$R1(F_o)$, $wR2(F_o^2)$ (all data)	0.0244, 0.0467	0.1395, 0.1977	0.0361, 0.0531	0.0488, 0.1493	0.1413, 0.1682
goodness of fit	1.079	0.934	1.073	1.209	1.118

Preparation of $(PPh_3)_2Pt$(2,2′-biphenyl) (8). A 1.185 g (1.50 mmol) portion of $Pt(PPh_3)_2Cl_2$ was dissolved in 50 mL of Et_2O and a solution of 2,2′-dilithiobiphenyl (1.32 mL, 2.4 M in hexanes, 3.18 mmol) added dropwise via syringe. The solution turned yellow-green over a few hours, after which 10 mL of water was added. The organic layer was separated, dried with $MgSO_4$, and evaporated to give yellow crystals of the product (0.75 g, 73%). Data for **8** are as follows. ^1H NMR (THF-d_8): *δ* 7.491 (t, *J* = 8.4 Hz, 12 H); 7.252 (dm, *J* = 7.4 Hz, 2 H); 7.206 (td, *J* = 7.5, 1.3 Hz, 6 H); 7.081 (td, *J* = 6.9, 1.3 Hz, 12 H); 6.837 (td, *J* = 6.7, 2.7 Hz, 2 H); 6.660 (t, *J* = 7.5 Hz, 2 H); 6.093 (tm, *J* = 7.4 Hz, 2 H). ^{31}P NMR (THF-d_8): *δ* 30.75 (s, J_{Pt-P} = 2009 Hz). Anal. Calcd (found) for **8**: C, 66.13 (66.08); H, 4.39 (4.68).

Reaction $(PPh_3)_2Pt$(2,2′-biphenyl) of with Biphenylene. A 144.5 mg (0.85 mmol) portion of biphenylene was dissolved in ∼1.3 mL of THF, and 871 mg (0.188 mmol) of $(PPh_3)_2Pt$(2,2′-biphenyl) was added. The mixture was heated to 100 °C and refluxed for 2 h. The solvent and excess biphenylene were removed by sublimation (60 °C, 0.04 Torr). The products were isolated by preparative TLC, using hexane as the eluent, on SiO_2. Characterization was accomplished by GC/MS and ^1H NMR spectroscopy and comparison with authentic samples. Yields of each product were determined from the areas of the GC trace and are as follows: phenyltriphenylene, 60%; tetraphenylene, 16%; triphenylene, 17%; centrosymmetrical hexaphenylene, 4%; helical hexaphenylene, 3%.

Synthesis of $(PPh_3\text{-}d_{15})_2PtCl_2$. An 81 mg (0.168 mmol) portion of $(COD)PtCl_2$ was dissolved in ∼3 mL of CH_2Cl_2. A 103 mg (0.37 mmol) amount of PPh_3-d_{15} was added, and the solution turned yellow. The reaction mixture was stirred at room temperature for 20 min, after which it was layered with ether and cooled to −20 °C. A total of 82.9 mg (0.101 mmol) of white crystals was recovered by filtration, a 74% yield.

Synthesis of $(LiTMEDA)_2$(2,2′-biphenyl). A 1.57 g (5.0 mmol) portion of 2,2′-dibromobiphenyl was dissolved in 50 mL of diethyl ether. The solution was cooled to 0 °C, after which 1.46 g (12.5 mmol) of tetramethylethylenediamine and 6.6 mL of a 1.6 M solution (10.5 mmol) of *n*-BuLi were added. The bright yellow mixture was stirred at 0 °C for 30 min and then warmed to room temperature and stirred for 1 h. The flask was cooled in a −20 °C freezer overnight, and 0.82 g of yellow crystals was isolated (41% yield).

Synthesis of $(PPh_3\text{-}d_{15})_2Pt$(2,2′-biphenyl). A 124 mg (0.151 mmol) portion of $(PPh_3\text{-}d_{15})_2PtCl_2$ was combined with 95 mg of the dilithio−biphenyl−TMEDA complex and dissolved in 15 mL of THF. This mixture was stirred for approximately 20 min, during which time the solution became clear. The solvent was removed in vacuo, and ∼20 mL of toluene was added. The white precipitate (LiCl) was removed by filtration and the solvent removed by vacuum. A total of 79 mg (0.087 mmol) of the yellow product was isolated (58% yield).

X-ray Structure Determinations of 4, 5, 6, 8, and C. Single crystals of **4**, **5**, **6**, **8**, and **C** were mounted under Paratone-8277 on glass fibers and immediately placed under 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 2*θ* angle of 56.54°) for all of the crystals. The total data collection time was 4−12 h. Frames were integrated with the Siemens SAINT program 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.[29] Data were corrected for absorption using the program SADABS.[30] Space group assignments were made on the basis of systematic absences and intensity statistics by using the

---

(29) 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.

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

XPREP program (Siemens, SHELXTL 5.04). The structures were solved by using direct methods and refined by full-matrix least-squares on F^2.[31] For all of the structures, the non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogens were included in idealized positions. **4** was found to have a rotational disorder in the *tert*-butyl groups. It was modeled by including two *tert*-butyl groups at 50% occupancy, with the *tert*-butyl groups restrained to have similar geometries by keeping C−C nearest-neighbor distances, C−C next-nearest-neighbor distances, and P−C distances similar. **6** lies on a 2-fold axis. **8** also contained one CH_2Cl_2 and two water molecules in the asymmetric unit. **5** and **C** have two independent molecules within the asymmetric unit. In addition, **5** showed a disorder in which a fraction of the molecules of **5** were rotated by 90°. The disorder model described in the text was employed with molecule C being constrained to the same geometry as molecule B and molecule D constrained to the same geometry as molecule A. The populations of A and B were allowed to vary independently. The phosphorus and platinum atoms were refined with anisotropic thermal parameters, carbon atoms were refined isotropically, and hydrogens were included in idealized positions. Table 2 gives a summary of relevant crystallographic data. 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 structures.

Acknowledgment is made to the U.S. Department of Energy (Grant No. FG02-86ER113596) for their support of this work. We also thank Prof. Peter Hofmann for valuable discussions concerning his studies of the dimer **5** and related species.

Supporting Information Available: Figures giving GCMS traces for the reaction of **8** with biphenylene and tables of crystallographic data for **4**, **5**, **6**, **8**, and **C**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010111M

---

[31] Using the SHELX95 package, $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $wR2 = \{[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [f^0(\text{Max } 0, F_o^2) + (1 - f)F_c^2]$.