Palladium Complexes Bearing Novel Strongly Bent Trans-Spanning Diphosphine Ligands: Synthesis, Characterization, and Catalytic Activity

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The new air-stable chelating diphosphine ligands 1,8-bis(diisopropylphosphino)triptycene (**2**) and 1-(diisopropylphosphino)-8-(diphenylphosphino)triptycene (**3**) were synthesized in 51−73% yield from readily available starting materials. The examination of their coordination modes in the palladium(II) complexes [$PdCl_2$(**2**)] (**4**) and [$PdCl_2$(**3**)] (**5**) by means of ^{1}H, ^{13}C, and ^{31}P NMR is consistent with the formation of trans-spanned complexes. X-ray analysis of **4** and **5** confirmed the structure but disclosed a strong distortion of the palladium centers from the expected square-planar geometry toward a butterfly-like environment. Further investigation revealed that **2** can also behave as a binucleating ligand, forming the quasi-closed halogen-bridged dipalladium complex **6**, featuring an unusual nonplanar $Pd_2(\mu\text{-}Cl)_2Cl_2$ core. The catalytic activity of the new ligands and complexes was tested in palladium-catalyzed cross-coupling reactions of aryl chlorides with phenylboronic acid.

Introduction

During the past few decades, enormous efforts have been devoted to the synthesis of transition-metal complexes as promoters for a variety of homogeneous catalytic transformations. Initially, research has been focused on the nature of transition metals as a primary factor responsible for the catalytic interconversion. Consequently, many successful processes were developed utilizing transition-metal catalysts bearing ligands as simple as triphenylphosphine. However, numerous studies describing effects of the metal environment on chemo-, regio-, and stereoselective formation of products have made the ligand design a domain of current research activity. In recent years, catalysts bearing "wide bite angle" and "trans-chelating" diphosphines have received much attention.[1] For example, heteroaromatic Xantphos-like ligands demonstrated outstanding reactivity in rhodium-[2] and platinum-catalyzed[3] oxo processes, palladium-catalyzed Tsuji reactions,[4] carbon−carbon[5] and carbon−nitrogen[6] bond-forming reactions. Steric and electronic effects of the ligand bite on the reactivity/selectivity of the catalyst were rationalized using both theoretical and experimental studies.[7]

Flexibility or, more precisely, the ability of a ligand to adapt a wide range of coordination angles is another important factor affecting the overall efficiency of a transformation by stabilizing different intermediates that form over the course of a catalytic cycle. Although the predicted flexibility range of the Xantphos-like chelates is relatively wide,[8] their ability to conform to different geometries may be limited. First, an excessive rigidity of the frame along with overly remote donor groups (e.g., DBFphos) sometimes prevents the formation of stable complexes.[9] Second, as was evidenced by X-ray analysis, the heteroatom in the vertex of the heteroarene skeleton may coordinate the metal center in a relatively strong fashion. As a result, the metal is often locked at a more or less fixed location, which is dictated by the metal−heteroatom interaction but not by the metal preferences.[10]

Of course, a more flexible trans-coordinating mode can be achieved by utilizing flexible long alkyl chain chelates;[11]

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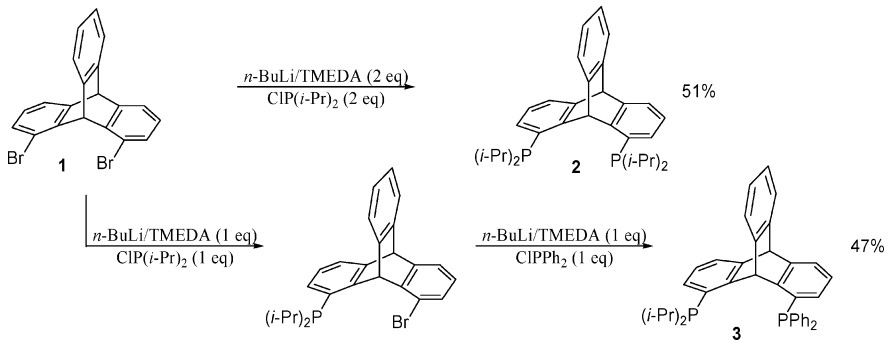
Scheme 1. Preparation of 2 and 3



however, complex mixtures of cis/trans isomers along with poorly soluble oligomeric byproducts form even under high-dilution conditions.[12] Alternatively, a substantial degree of flexibility (apparently, at the expense of conformational instability)[13−16] can be reached by employing a rigid spacer possessing pliable methylene-tethered donors. For example, phenanthrene-based (TransPhos),[13] diferrocene-based (TRAP),[14] biphenyl-based (BISBI),[15] and *m*-terphenyl-based[16] diphosphines have been synthesized, characterized, and tested in different catalytic transformations.

Recently we became interested in studying the coordination and catalytic activity of transition-metal complexes bearing as yet unexplored[17] roof-shaped diphosphine chelates based on the barrelene framework. We assumed that the strongly bent triptycene-based ligands possessing adequately large P−P distances would be able to coordinate transition metals in a trans-chelating mode. On the other hand, a rotation of the phosphine donors around the C−P bonds would allow for the flexible coordination of transition metals, independent of their size and identity, and therefore, various geometries may be adopted (Figure 1).

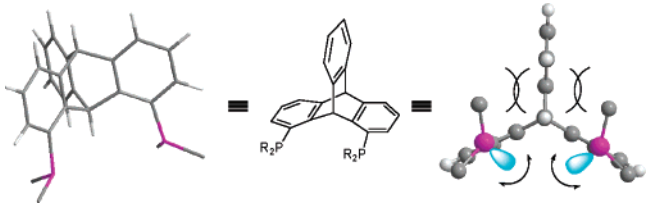


Figure 1. Triptycene-based diphosphines.

Another attractive feature of the triptycene skeleton is its modularity. Numerous efficient synthetic strategies for differently substituted barrelene-like compounds (including chiral), which allow tuning steric and electronic properties of a potential catalyst by varying such parameters as donor−donor distance, bite angle, and steric environment around the catalytic site, are available.[18]

Herein we wish to report on the synthesis and characterization of palladium complexes bearing the novel trans-spanning ligands 1,8-bis(diisopropylphosphino)triptycene (**2**) and 1-(diisopropylphosphino)-8-(diphenylphosphin)otriptycene (**3**). The interesting geometry of these complexes, as well as the unexpected ability of **2** to form uncommon bimetallic quasi-closed chloro-bridged compounds will be discussed. In addition, we will describe the use of **2** and **3** in the catalytic coupling of aryl chlorides with arylboronic acids (Suzuki reaction).

Results and Discussion

Ligand Synthesis. Scheme 1 summarizes the synthetic pathway to **2** and **3** from the readily accessible 1,8-dibromotriptycene (**1**), which can be prepared from the commercially available starting materials on a 20−40 g scale.[19] Compound **2** was obtained in 51% yield by subsequent treatment of **1** with *n*-BuLi/TMEDA and chlorodiisopropylphosphine. The synthesis of **3** was accomplished using a two-step protocol, as outlined in Scheme 1. In this case, **1** was initially converted into a monophosphine derivative via selective monolithiation with the *n*-BuLi/TMEDA complex in THF and subsequent quenching with chlorodiisopropylphosphine. It is worth noting that the monolithiation takes place smoothly and results in the formation of the ca. 95% pure intermediate. Additional *n*-BuLi/electrophile (chlorodiphenylphosphine) treatment leads to the desired dissymmetric **3** in good yield.

The $^{31}P\{^{1}H\}$ NMR spectrum of **2** in THF-d_8 displays a single resonance frequency at δ −4.75 ppm, which is ascribed to the

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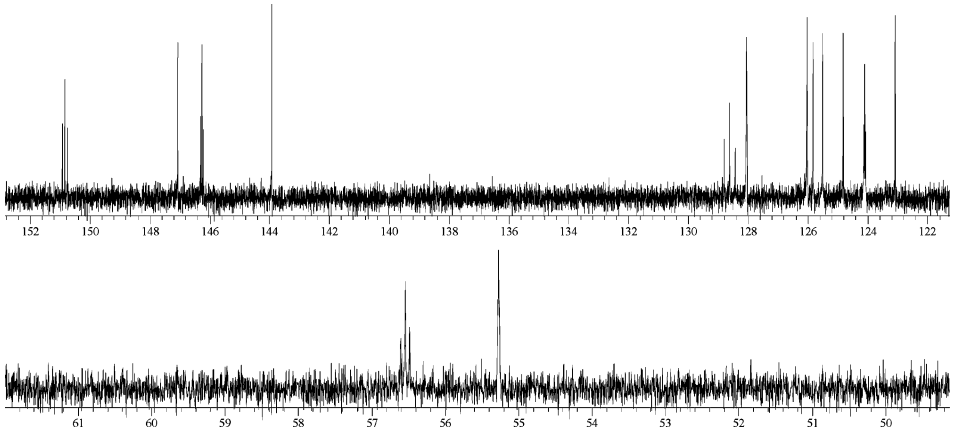
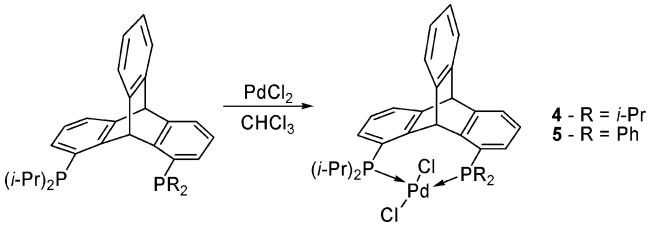


Figure 2. $^{13}C\{^1H\}$ NMR (100 Hz) spectrum of **4** in $CDCl_3$: (top) aromatic carbons; (bottom) methine carbons.

Scheme 2. Preparation of 4 and 5



identical phosphine groups. Resonances for two different phosphorus nuclei of the dissymmetric **3** appear separately as a set of doublets centered at δ −9.26 and −18.05 ppm with a $^{31}P-^{31}P$ coupling constant of 20 Hz. Since the phosphorus moieties are connected through six bonds, this splitting originates from the through-space spin coupling due to the close proximity of the two phosphorus atoms.[20] Unfortunately, our attempts to obtain single crystals of **2** and **3** suitable for X-ray analysis failed; thus, we can only hypothesize that lone pairs of the phosphine groups converge in the cavity produced by ring planes, giving rise to such a "communication" (Figure 1). We also found that the ligands are air-stable and they could be kept for months on the shelf without notable oxidation.

Transition-Metal Complexes. Ligands **2** and **3** were then reacted with stoichiometric amounts of $PdCl_2(CH_3CN)_2$ in chloroform at room temperature, resulting in the formation of complexes **4** and **5** in 94 and 88% yields, respectively (Scheme 2). $^{31}P\{^1H\}$ NMR measurements indicated that the complexation of the palladium with the ligands was complete within 20−30 min at room temperature.

The $^{31}P\{^1H\}$ NMR spectrum of complex **4** displays a sharp singlet with a resonance frequency of 33.93 ppm. The splitting of the phosphorus-coupled carbon signals into 1:2:1 triplets was observed in the ^{13}C NMR spectrum of **4** (Figure 2). Similar triplets have been observed in numerous compounds, forming AXX′ spin systems where the two phosphorus nuclei couple with a large coupling constant,[21] characteristic of the trans diphosphine complexes.[22]

Although the $^{31}P-^{31}P$ coupling constant could not be directly determined for **4**, the dissymmetric **5** exhibited, as expected, an AB pattern (δ 38.06 and 14.47 ppm) due to the coupling established by two different phosphorus nuclei coordinated to the same Pd center. The magnitude of the coupling constant measured as $^2J_{P-P} = 576$ Hz revealed a trans-chelation mode of the two phosphorus donors.

Remarkably, the signal ascribed to the central methine hydrogen atom in both the symmetrical and dissymmetrical complexes appears in the ^1H NMR spectra at a very low field (δ 9.41 ppm for **4** and 9.13 ppm for **5**), suggesting a close proximity of the hydrogen to the metal center.

Suitable single crystals of **4** and **5**, grown by the slow diffusion of pentane into their saturated solutions in chloroform at room temperature, were subjected to X-ray diffraction

Table 1. Crystal Data and Structure Refinement Details for 4−6

	5	**4**	**6**
empirical formula	$C_{32}H_{40}Cl_2P_2Pd$	$C_{39.5}H_{37.5}Cl_6P_2Pd$	$C_{35}H_{43}Cl_{13}P_2Pd_2$
fw	663.88	730.07	1199.28
temp (K)	295(1)	173(1)	173(1)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
unit cell dimens			
a (Å)	12.7444(12)	12.0089(13)	15.3648(9)
b (Å)	11.9870(11)	12.6271(14)	22.1329(12)
c (Å)	19.6856(18)	15.4198(17)	14.2719(8)
α (deg)	90	67.500(2)	90
β (deg)	95.124(2)	74.016(2)	106.9380(10)
γ (deg)	90	65.386(2)	90
V (Å^3)	2995.3(5)	1945.1(4)	4642.9(5)
Z	4	2	4
calcd density (Mg/m^3)	1.472	1.525	1.716
abs coeff (mm^{-1})	0.925	1.000	1.618
F(000)	1368	905	2384
cryst size (mm)	0.27 × 0.22 × 0.20	0.25 × 0.21 × 0.07	0.31 × 0.16 × 0.08
θ range, data collecn (deg)	1.60−27.00	1.86−27.00	1.66−27.00
	$-16 < h < 16$	$-15 < h < 15$	$-19 < h < 19$
	$-15 < k < 15$	$-16 < k < 16$	$-28 < k < 28$
	$-25 < l < 25$	$-19 < l < 19$	$-18 < l < 18$
no. of rflns collected	33 511	21 940	52 101
no. of indep rflns	6549	8406	10150
refinement method		full-matrix least squares on F^2	
no. of data/ restraints/ params	6549/0/353	8406/0/484	10 150/0/561
goodness of fit on F^2	1.061	1.064	0.966
final R indices ($I > 2\sigma(I)$)			
R1	0.0254	0.0336	0.0374
wR2	0.0717	0.0925	0.0892
R indices (all data)			
R1	0.0291	0.0376	0.0543
wR2	0.0732	0.0947	0.0937

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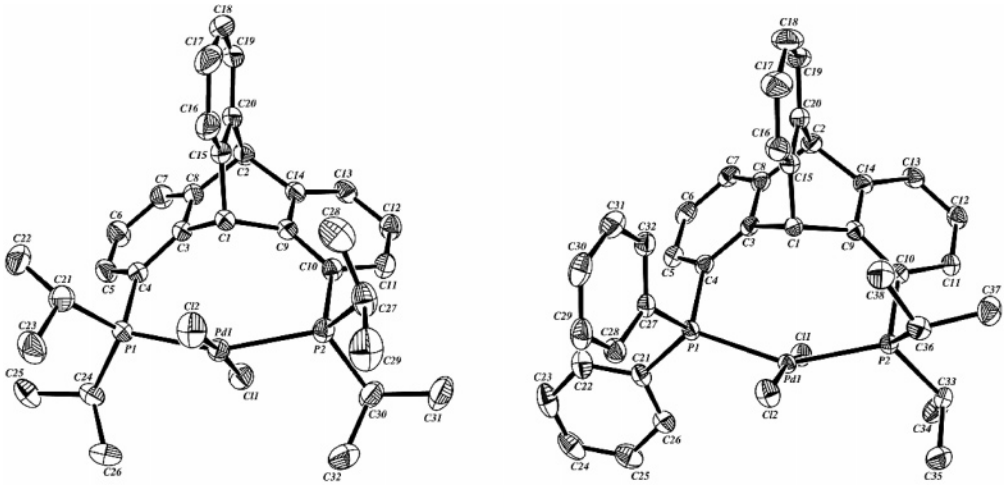

Figure 3. ORTEP drawing (50% probability ellipsoids) of the structures of **4** (left) and **5** (right). Hydrogen atoms and solvent molecules are omitted for clarity.

analysis. The crystallographic parameters are presented in Table 1. We found that palladium centers are strongly distorted from the square-planar geometry toward a butterfly-like environment (the ORTEP illustrations are shown in Figure 3). For example, the observed P(1)−Pd−P(2) and Cl(1)−Pd−Cl(2) angles and P(1)−P(2) intramolecular distance between the two phosphorus groups for **4** are 154.871(17) and 174.90(2)° and 4.549 Å, respectively. The corresponding parameters for **5** are 150.36(2) and 168.94(2)° and 4.502 Å. Although such a strong distortion from the square-planar geometry was previously documented, this arrangement is very rare and atypical for the majority of bidentate ligands. For example, similar parameters have been observed for trans-coordinated Xantphos ligands and some palladium complexes bearing various metalloligands.[23] Clearly, in contrast to earlier precedents, where the distortion originated from the weak palladium−heteroatom or palladium−metal interactions, the butterfly geometry in our compounds arises from a considerable strain in the eight-membered ring along with a certain overcrowding caused by the close proximity of the methine hydrogen to the metal. The positions of the chlorine ligands are almost equally remote from all neighboring atoms and thus avoid a steric congestion.

Remarkably, the Pd−$H_{methine}$ distance was found as short as 2.269 Å in **4** and 2.380 Å in **5**. However, despite this proximity, the insertion of the palladium into the sp^3 carbon−hydrogen bond is unlikely to occur, because of a low acidity of the methine proton. Indeed, our attempts to obtain a palladacycle failed even under very harsh conditions (24 h in DMF at 140 °C).

The P−Pd and Pd−Cl bond lengths lie within the normal range of trans bis-phosphine palladium dichloride complexes (selected data are given in Table 2).

Bimetallic Complexes. Unexpectedly, we found that **2** can behave as a binucleating ligand, resulting in the formation of rare quasi-closed halogen-bridged dipalladium complexes possessing a *nonplanar* Pd_2Cl_4 site. Compound **6** was first isolated as a side product from the reaction described in Scheme 2 and was later prepared in satisfactory yield by reacting **4** with an additional 1 equiv of $PdCl_2(CH_3CN)_2$.

Upon prolonged standing of the chloroform solution of **4**, the formation of new yellow crystalline material was observed.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4 and 5

	4	5
Cl(1)−Pd	2.3230(5)	2.3124(6)
Cl(2)−Pd	2.3176(6)	2.2993(7)
P(1)−Pd	2.3262(5)	2.3335(7)
P(2)−Pd	2.3347(5)	2.3233(7)
Cl(1)−Pd−Cl(2)	174.90(2)	168.94(2)
P(1)−Pd−P(2)	154.871(17)	150.36(2)
Cl(1)−Pd−P(1)	85.699(19)	86.42(2)
Cl(1)−Pd−P(2)	86.104(19)	89.91(2)
Cl(2)−Pd−P(1)	94.57(2)	94.93(2)
Cl(2)−Pd−P(2)	95.67(2)	94.22(2)

The new compound was significantly less soluble in common organic solvents than the parent **5**; however, its solubility in chloroform was still sufficient to record ^1H and ^{31}P NMR spectra. The $^{31}P\{^1H\}$ NMR of the substance showed a new signal that appeared as a deshielded singlet at δ 56.49 ppm, in contrast to that observed at δ 33.93 ppm for **4**. The ^1H NMR spectrum was quite similar to the spectrum of the parent compound, apart from the signal ascribed to the methine hydrogen, which appeared at higher field (8.08 ppm) compared to that for **4** (9.41 ppm). This upfield shift suggested that no simultaneous coordination of phosphorus donors to the same metal center, causing the close proximity of the palladium atom to the methine hydrogen, existed in the new compound. Therefore, initially we proposed the formation of a less soluble dimer. However, the X-ray structure disclosed an unusual coordination mode (Figure 4). Much to our surprise, the structure corresponded to a *nonplanar* diphosphine-bridged $Pd_2(\mu\text{-}Cl)_2$-Cl_2 core.

Although *syn*-$[M_2(\mu\text{-}X)_2X_2L]$ quasi-closed bridged bimetallic complexes have been reported in the literature,[24] very few publications have referred to a dipalladium unit.[25] Moreover, all structurally characterized $[Pd_2(\mu\text{-}X)_2X_2L]$ complexes are planar[25b−d] or only slightly distorted from planarity.[25a] Therefore, the molecular structure of this complex deserves special attention. Unlike **4** and **5**, the environment around each of the palladium atoms is only slightly distorted from the square-planar

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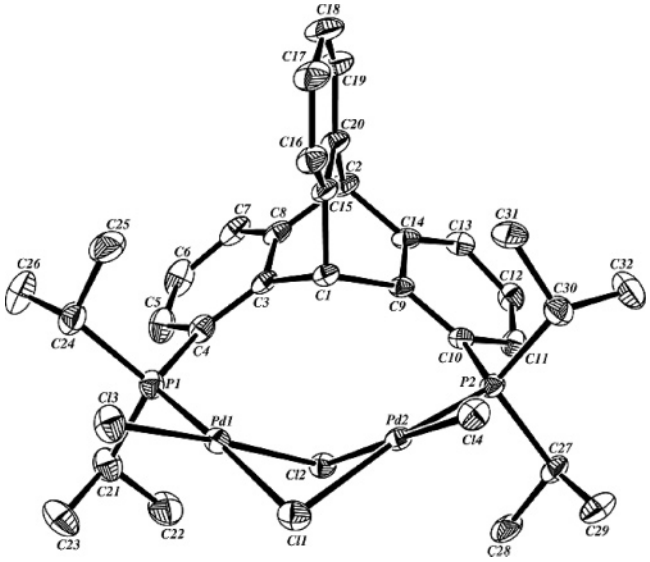


Figure 4. ORTEP drawing (50% probability ellipsoids) of the structure of **6**. Hydrogen atoms and chloroform molecules are omitted for clarity.

geometry, with bond angles ranging within 85.40 and 92.79°. However, the Pd_2Cl_4 core is far from being planar—the Pd(1), Cl(1), Cl(2) and Pd(2), Cl(1), Cl(2) interplanar angle was calculated as 122.32°. Furthermore, as a consequence of this constrained arrangement, the Pd(1)−Pd(2) distance shortens to 3.036 Å, while typically it is an average of ca. 3.45 Å. To the best of our knowledge, such a strong deviation from planarity in halogeno-bridged dipalladium rhombuses has so far never been observed. The most striking example was reported recently by Guzei et al.[26b] The corresponding interplanar angle and palladium−palladium separation were measured as 136.31(5)° and 3.2004(6) Å.

On the other hand, incorporation of a Pd_2Cl_4 unit between the phosphine donors results in a significant increase in P···P distance (5.907 Å in **6** versus 4.549 Å in **4**). This becomes possible due to the drastic deviation of the phosphine groups from the plane of the corresponding aromatic rings (the deviation from planarity averages 0.54 Å).

Terminal chlorine atoms adapt a syn conformation with Pd(1)−Cl(3) and Pd(2)−Cl(4) distances of 2.2853(8) and 2.2882(8) Å, respectively (within the normal range). Pd(1)−Cl(1) and Pd(2)−Cl(1) (trans to phosphine) distances are longer than Pd(1)−Cl(2) and Pd(2)−Cl(2) (trans to chloride), which is in agreement with the trans effect of the phosphorus donors (representative data are tabulated in Table 3).

Later it was found that the reaction between **5** and an equivalent amount of $PdCl_2(CH_3CN)_2$ in chloroform at 50 °C results in the formation of **6** in 49% isolated yield (Scheme 3).

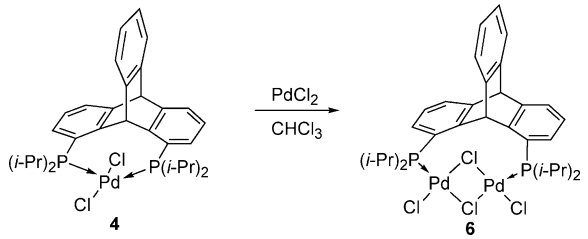
The compound is stable to air and heat in chlorinated solvents (120 °C in $C_2H_4Cl_2$) but readily decomposed in DMSO, producing the parent **4**.

We believe that the difference in solubility between **4** and **6** is the driving force for this transformation. However, the exact pathway by which the ring expansion takes place is not yet clear and we do not yet know the exact factors that govern this unusual binucleating coordination.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4

Pd(1)−P(1)	2.2390(9)	Pd(1)−Cl(3)	2.2853(8)
Pd(2)−P(2)	2.2270(9)	Pd(2)−Cl(1)	2.3941(8)
Pd(1)−Cl(1)	2.3947(8)	Pd(2)−Cl(2)	2.3305(8)
Pd(1)−Cl(2)	2.3224(8)	Pd(2)−Cl(4)	2.2882(8)
P(1)−Pd(1)−Cl(1)	175.64(3)	P(2)−Pd(2)−Cl(1)	173.01(3)
Cl(2)−Pd(1)−Cl(3)	174.85(3)	Cl(4)−Pd(2)−Cl(2)	176.27(3)
P(1)−Pd(1)−Cl(2)	92.04(3)	P(2)−Pd(2)−Cl(4)	92.34(3)
Cl(2)−Pd(1)−Cl(1)	85.56(3)	Cl(4)−Pd(2)−Cl(1)	90.88(3)
Cl(1)−Pd(1)−Cl(3)	91.96(3)	Cl(1)−Pd(2)−Cl(2)	85.40(3)
Cl(3)−Pd(1)−P(1)	89.51(3)	Cl(2)−Pd(2)−P(2)	91.38(3)

Scheme 3. Synthesis of 6



Catalytic Activity. Bulky monophosphines are excellent ligands for many cross-coupling reactions.[27] In contrast, bidentate ligands are generally less effective, even though electron-rich phosphine moieties are installed.[16b,28] In light of these observations, we became interested in exploring the catalytic potential of palladium complexes possessing the new triptycene-based bidentate ligands as catalysts for C−C bond-forming reactions. We found indeed that $PdCl_2$ and $Pd(OAc)_2$ promote in the presence of **2** and **3** the coupling of aryl chlorides with arylboronic acids (Suzuki reaction).

In all cases, the reactions were carried out in dioxane at 70 °C using 1 mol% of the palladium source, 1.5 mol% of the corresponding ligand, 1.3 equiv of the phenylboronic acid, and 2.5 equiv of K_3PO_4 per equivalent of the aryl chloride. These conditions were elaborated after a brief optimization work.

In general, we found that (a) new ligands exhibit excellent catalytic activity in palladium-catalyzed Suzuki cross-coupling of aryl chlorides with phenylboronic acid (Table 4), (b) the dissymmetric **5** was less efficient than its symmetric counterpart **4** (Table 4, entry 1 vs 2), (c) the activity of **4** was virtually similar to that of the complex prepared in situ by premixing $PdCl_2(CH_3CN)_2$ with 1.5 equiv of **2** in dioxane for 25 min (entry 2 vs 3), and (d) $Pd(OAc)_2$/**2** was slightly more reactive than $PdCl_2(CH_3CN)_2$/**2** (entry 3 vs 4). We observed that electron-deficient (entries 5 and 6) and electron-neutral aryl chlorides (entry 7) couple with phenylboronic acid smoothly, forming the desired biphenyls in excellent yield. Reactions with electron-rich aryl chlorides proceed as well, leading to the formation of products in good to excellent yields (entries 8 and 9). Full conversion of the starting material was achieved, and no notable formation of byproducts was detected in almost all cases. A

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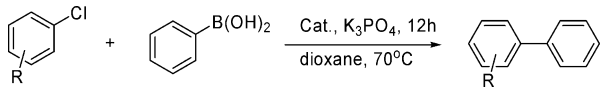
Table 4. Suzuki Cross-Coupling of Aryl Chlorides with Phenylboronic Acid[a]



entry	cat.	atarting material	product	conversn (%)[b]	yield (%)[c]
1	**5**	1-chloronaphthalene	1-phenylnaphthalene	60	58
2	**4**	1-chloronaphthalene	1-phenylnaphthalene	93	91
3	**2**/$PdCl_2(CH_3CN)_2$	1-chloronaphthalene	1-phenylnaphthalene	90	86
4	**2**/$Pd(OAc)_2$	1-chloronaphthalene	1-phenylnaphthalene	99	97
5	**2**/$Pd(OAc)_2$	2-chlorobenzonitrile	2-cyanobiphenyl	99	97
6	**2**/$Pd(OAc)_2$	2-chlorobenzaldehyde	biphenyl-2-carboxaldehyde	99	93
7	**2**/$Pd(OAc)_2$	2-chlorotoluene	2-methylbiphenyl	99	97
8	**2**/$Pd(OAc)_2$	2-chlorophenol	2-hydroxybiphenyl	99	92
9	**2**/$Pd(OAc)_2$	2-chloroanisole	2-methoxybiphenyl	99[d]	89

[a] Conditions: aryl chloride (1 mmol), phenylboronic acid (1.3 mmol), [Pd] (0.01 mmol), **2** (0.015 mmol), K_3PO_4 (2.5 mmol), dioxane (3 mL), 70 °C for 12 h. [b] By GC (dodecane as an internal standard). [c] Isolated yield (average of two runs). [d] The reaction reaches full conversion after 24 h (not optimized).

blank experiment in the absence of **2** was carried out to confirm the catalytic effect of the ligand.

These results clearly indicate that, apart from intriguing coordination chemistry, new triptycene-based ligands have a potential in catalysis, and therefore, further studies on their catalytic activity will be undertaken.

Conclusion

We have demonstrated that new strongly bent triptycene-based diphosphines are versatile bidentate ligands for the synthesis of trans-spanned palladium complexes and display diverse chelating modes. The new ligands and the corresponding palladium complexes are air stable and exhibit high catalytic activity in Suzuki cross-coupling reactions of aryl chlorides. In addition, we found that **2** can form uncommon quasi-closed halo-bridged dipalladium complexes possessing a very short intermetallic distance. Further investigation of the new mono- and bimetallic compounds, as well as attempts to obtain **3** in enantiopure form, are in progress.

Experimental Section

All manipulations were performed using standard Schlenk techniques under an atmosphere of dry N_2. Anhydrous solvents, palladium chloride, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, *n*-butyllithium (1.6 M in hexane), diisopropylchlorophosphine, diphenylchlorophosphine, and all the chemicals used in the catalytic experiments were purchased from Aldrich and used without further purification. 1,8-Dibromoanthracene and 1,8-dibromotriptycene were prepared from commercially available starting materials (Aldrich) by following published procedures.[19a,32] NMR spectra were recorded on a Bruker instrument operating at 400 MHz for proton, 100 MHz for carbon, and 121 MHz for phosphorus. Diffraction data were collected with a Bruker APEX CCD instrument (Mo Kα radiation ($\lambda = 0.710\ 73$ Å)). Crystals were mounted onto glass fibers using epoxy. Single-crystal reflection data were collected on a Bruker APEX CCD X-ray diffraction system controlled by a Pentium-based PC running the SMART software package.[29] The integration of data frames and refinement of cell structure were done by the SAINT+ program package.[30] Refinement of the structure on F^2 was carried out by the SHELXTL software package.[31] Further information may be found within CIF files, provided as Supporting Information.

1,8-Dibromotriptycene (1). 1,8-Dichloroanthraquinone (40 g, 0.145 mol) was treated with KBr (90.0 g, 0.75 mol), $CuCl_2$ (2.5 g, 18 mmol), and 85% H_3PO_4 (11 mL) in nitrobenzene (350 mL). Water was distilled from the reaction mixture until the temperature reached 200 °C, and then the mixture was stirred at reflux for 24 h. Water was added after cooling to dissolve all inorganic components. The product was extracted with DCM. The DCM was evaporated, and methanol was added to precipitate the crude product. Conversion of ca. 75% is usually achieved at this stage. The procedure is repeated one more time, using the mixture as a starting material (no chromatographic separation is required). Conversion is 95−99%. The isolated yield of 1,8-dibromoanthraquinone is 68−75% (no purification is required: the product is >95% pure). 1,8-Dibromoanthracene[32] and 1,8-dibromotriptycene (**1**)[19a] were obtained as described previously.

1,8-Bis(diisopropylphosphino)triptycene (2). To a cold stirred solution (−78 °C) of **1** (3 g, 7.28 mmol) and TMEDA (5.5 mL, 5 equiv) in dry THF (35 mL) was added *n*-BuLi (1.6 M, 9.2 mL, 2 equiv) over a period of 30−35 min. The resulting yellow to brown solution was stirred for an additional 15 min, and a diisopropylchlorophosphine (2.3 mL, 14.5 mmol, 2 equiv) solution in THF (3 mL) was added dropwise. The nearly colorless solution was allowed to reach room temperature and then refluxed for 1 h. After this solution was cooled, ethyl acetate (50 mL) was added; the organic phase was successively washed with sodium bicarbonate and water, dried, and evaporated. The crude material was purified by filtration through a pad of silica gel and crystallized from methanol, affording 1.8 g (51% yield) of analytically pure material. ^{1}H NMR (THF-d_8): δ 7.51 (t, $J = 5$ Hz, 1H), 7.35−7.30 (m, 4H), 7.12 (d, $J = 7.5$ Hz, 2H), 6.94 (t, $J = 7.5$ Hz, 2 Hz), 6.90−6.87 (m, 2H), 5.44 (s, 1H), 2.23−2.18 (m, 2H), 2.07−2.01 (m, 2H), 1.21 (dd, $J = 7$ Hz, $J = 7$ Hz, 6H), 1.06 (dd, $J = 8$ Hz, $J = 8$ Hz, 6H), 0.92 (dd, $J = 7$ Hz, $J = 7$ Hz, 6H), 0.75 (dd, $J = 7$ Hz, $J = 3$ Hz, 6H). ^{31}P NMR (THF-d_8): δ 4.75. Anal. Calcd for $C_{32}H_{40}P_2$: C 78.98; H 8.29. Found: C 79.26; H 8.22.

1-(Diisopropylphosphino)-8-(diphenylphosphino)triptycene (3). To a cold stirred solution (−78 °C) of **1** (3 g, 7.28 mmol) and TMEDA (2.8 mL, 2.5 equiv) in dry THF (35 mL) was added *n*-BuLi (1.6 M, 4.6 mL, 1 equiv) over a period of 30−35 min. The resulting yellow to brown solution was stirred for an additional 15 min, and a diisopropylchlorophosphine (1.6 mL, 7.28 mmol, 1 equiv) solution in THF (3 mL) was added dropwise. The nearly colorless solution was warmed to room temperature and refluxed for 1 h. The crude material was isolated as described previously. The monosubstituted triptycene derivative was ca. 90% pure at this stage. After being dried under reduced pressure, the crude monophosphine was

(29) SMART-NT, version 5.6; Bruker AXS GMBH, Karlsruhe, Germany, 2002.

(30) SAINT-NT, version 5.0; Bruker AXS GMBH, Karlsruhe, Germany, 2002.

(31) SHELXTL-NT, version 6.1; Bruker AXS GMBH, Karlsruhe, Germany, 2002.

(32) Haenel, M. W.; Jakubik, D.; Krueger, C.; Betz, P. *Chem. Ber.* **1991**, *124*, 333.

redissolved in dry THF (35 mL), lithiated, and treated with diphenylchlorophosphine (1.3 mL, 7.28 mmol, 1 equiv) at −78 °C. The nearly colorless solution was warmed to reach room temperature and then refluxed for 1 h. After this solution was cooled, ethyl acetate (50 mL) was added; the organic phase was successively washed with sodium bicarbonate and water, dried, and evaporated. The crude material was purified by filtration through a pad of silica gel and crystallized from methanol, affording 1.9 g (47 %) of analytically pure material. ^{1}H NMR (THF-d_8): δ. 7.33 (t, J = 7 Hz, 2H), 7.29−7.22 (m, 12H), 7.11 (d, J = 4 Hz, 1H), 6.94 (t, J = 8 Hz, 1H), 6.85−6.81 (m, 2H), 6.73 (t, J = 7 Hz, 1H), 6.67 (d, 4 Hz, 1H), 6.55−6.52 (m, 1H), 5.46 (s, 1H), 2.17−2.12 (m, 1H), 2.04−1.99 (m, 1H), 1.19 (dd, J = 7 Hz, J = 7 Hz, 3H), 1.02 (dd, J = 7 Hz, J = 7 Hz, 3H), 0.80 (dd, J = 7 Hz, J = 7 Hz, 3H), 0.71 (dd, J = 7 Hz, J = 4 Hz, 3 H). ^{31}P NMR (THF-d_8): δ −9.26 (d, J = 21 Hz), −18.05 (d, J = 21 Hz). Anal. Calcd for $C_{38}H_{36}P_2$: C, 82.29; H, 6.54. Found: C, 82.33; H, 6.47.

[PdCl$_2$(2)] (4). A solution of **2** (200 mg, 0.411 mmol) and $PdCl_2(CH_3CN)_2$ (106.5 mg, 0.411 mmol) in dichloromethane (4 mL) was stirred for 10 min at room temperature. All volatiles were evaporated under reduced pressure. The residue was rinsed with pentane and dried in vacuo, affording **4** as a yellow powder (251 mg, 94%). ^{1}H NMR ($CDCl_3$): δ 9.42 (s, 1H), 7.47−7.40 (m, 4H), 7.12−6.99 (m, 6H), 5.50 (s, 1H), 2.77−2.70 (m, 4H), 1.58−1.46 (m, 18H), 1.18 (dd, 6H, J = 7 Hz, J = 7 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 150.83 (t, J = 8 Hz), 147.05, 146.25 (t, J = 4 Hz), 143.91, 128.60 (t, J = 19 Hz), 128.04, 126.01, 125.81, 125.49, 124.81, 124.09 (t, J = 3 Hz), 123.07, 56.54 (t, J = 6 Hz), 55.27, 24.97 (t, J = 11 Hz), 24.38 (t, J = 11 Hz), 21.81 (t, J = 2 Hz), 22.36, 18.66 (t, 3 Hz), 17.05. ^{31}P NMR ($CDCl_3$): δ 33.93. Anal. Calcd for $C_{32}H_{40}Cl_2P_2Pd$: C, 57.89; H, 6.07. Found: C, 57.59; H, 5.94.

[PdCl$_2$(3)] (5). A solution of **3** (200 mg, 0.361 mmol) and $PdCl_2(CH_3CN)_2$ (93.5 g, 0.361 mmol) in dichloromethane (4 mL) was stirred for 10 min at room temperature. All volatiles were evaporated under reduced pressure. The residue was rinsed with pentane and dried in vacuo, affording **5** as a yellow powder (231 mg, 88%). ^{1}H NMR ($CDCl_3$): δ 9.13 (s, 1H), 7.97−7.93 (m, 2H), 7.54−7.43 (m, 6H), 7.31−7.28 (m, 2H), 7.16−7.11 (m, 6H), 6.98 (t, J = 7 Hz, 1H), 6.91 (t, J = 7 Hz, 1H), 6.68 (t, J = 8 Hz, 1H), 5.59 (s, 1H), 2.81−2.71 (m, 2H), 1.63−1.53 (m, 6H), 1.32 (dd, J = 7 Hz, J = 7 Hz, 10 Hz, 3H), 1.11 (dd, J = 7 Hz, J = 6 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 150.58, 149.48. 146.49 (t, J = 10 Hz), 146.34, 143.47, 136.71 (d, J = 10 Hz), 134.05 (d, J = 10 Hz), 131.49, 131.17, 129.77, 129.50, 129.28, 129.08, 128.79, 128.69 (d, J = 10 Hz), 128.57, 128.00, 127.71 (d, J = 10 Hz), 127.61, 126.29, 125.96, 125.76 (d, J = 6 Hz), 125.00, 124.72 (d, J = 6 Hz), 124.24 (d, J = 6 Hz), 123.13, 56.12 (t, J = 7 Hz), 55.07, 25.42 (d, J = 20 Hz), 24.75, 21.86, 20.10, 18.75, 16.93. ^{31}P NMR ($CDCl_3$): δ 38.06 (d, J = 577 Hz), 14.47 (d, J = 577 Hz). Anal. Calcd for $C_{38}H_{36}Cl_2P_2Pd$: C, 62.35; H, 4.96. Found: C, 62.07; H, 5.11.

[Pd$_2$Cl$_4$(2)] (6). A solution of **4** (200 mg, 0.301 mmol) and $PdCl_2(CH_3CN)_2$ (78 mg, 0.301 mmol) in chloroform (6 mL) was stirred at room temperature for 24 h. The yellow precipitate that formed was filtered and washed with two portions (2−3 mL) of the same solvent and redissolved in ca. 30−50 mL of chloroform. Analytically pure **6** was obtained by slow diffusion of pentane into a saturated chloroform solution (125 mg, 49%). ^{1}H NMR ($CDCl_3$): δ 8.08 (d, 1H, J = 7 Hz), 7.85 (s, 1H), 7.61 (d, 2H, J = 5 Hz), 7.46 (d, 1H, J = 7 Hz), 7.14−7.07 (m, 6H), 5.58 (s, 1H), 3.38−3.33 (m, 2H), 2.53−2.46 (m, 2H), 1.70 (dd, 6H, J = 7 Hz, J = 11 Hz), 1.38 (dd, 6H, J = 7 Hz, J = 11 Hz), 0.54 (dd, 6H, J = 7 Hz, J = 13 Hz), 0.44 (dd, 6H, J = 7 Hz, J = 8 Hz). ^{31}P NMR ($CDCl_3$): δ 56.49. Anal. Calcd for $C_{32}H_{40}Cl_4P_2Pd_2$: C, 45.69; H, 4.79. Found: C, 45.41; H, 4.95.

General Catalytic Procedure. An oven-dried screw-capped reaction tube was charged with $Pd(OAc)_2$ (0.01 mmol), ligand (0.015 mmol), boronic acid (1.3 mmol), and K_3PO_4 (2.5 mmol). The reaction vessel was evacuated and back-filled with N_2 (two times). Through a rubber septum, aryl chloride (1 mmol) in dioxane (3.0 mL) was added to the reaction tube. The resulting mixture was heated at 70 °C for 12 h before being cooled to ambient temperature for analysis. Conversions were calculated from crude GC using dodecane as an internal standard, and isolated yields were obtained after a standard workup and purification by flash chromatography.

Acknowledgment. We acknowledge Grant No. 034.9043 601 for support and Dr. Shmuel Cohen for solving X-ray structures.

Supporting Information Available: X-ray crystallographic files in CIF format for all structures and text giving spectroscopic data for compounds listed in Table 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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