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New Palladium Precatalysts
For Cross-Coupling Reactions
by Nicholas C. Bruno and Stephen L. Buchwald

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**Article:**

*New Palladium Precatalysts For Cross-Coupling Reactions* ............................................................................................................. 1-8
By Nicholas C. Bruno and Stephen L. Buchwald

Quick Reference of Buchwald Ligands ................................................................................................................................. 9-11
Quick Reference of Buchwald Precatalysts .................................................................................................................. 12-14
Available Buchwald Ligand Kits ........................................................................................................................................... 15-16
Available Buchwald Precatalyst Kits .................................................................................................................................. 16-17

**Buchwald Precatalysts: From Grams to Kilos. For R&D and Commercial Use** .................. 18-27
Includes technical notes and complete product details.

**Buchwald Ligands: From Grams to Kilos. For R&D and Commercial Use** .................. 28-48
Includes technical notes and complete product details.

**NEW Gold Catalysts Based on Buchwald Ligands** ............................................................................................................. 48-49

References:

******************************************************************************************

**About Our Cover:**
Our booklet cover was inspired by Professor Stephen Buchwald’s cat “Rufus” after whom RuPhos is named. Also shown are TrixiePhos and RockPhos, ligands that were named in honor of two more of his beloved cats, Trixie (who passed away in 2013) and Rocket. Cover illustration by Jim Grenier of Renegade Studios.

******************************************************************************************
New Palladium Precatalysts For Cross-Coupling Reactions
Nicholas C. Bruno and Stephen L. Buchwald
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 02139

Introduction
Palladium-catalyzed cross-coupling reactions have become common tools for C-C and C-X bond formation in academic and industrial settings.1-2 Privileged ligand scaffolds have emerged that can effectively support a vast range of transformations.3 However, as more complex cross-coupling reactions are explored, the method for generation of the catalytically active LnPd(0) species has often proven to be pivotal to the success of a cross-coupling reaction.

Many traditional palladium sources can have significant problems in generating active catalysts. Stable Pd(0) sources such as Pdₙ(dba)₁₈ contain dibenzylideneacetone (dba) ligands that can impede the catalytic cycle.4 These Pd species can also contain varying degrees of free dba and palladium nanoparticles.5 Pd(II) sources such as Pd(OAc)₂ and PdCl₂ need to be reduced to Pd(0) in-situ before entering a Pd(0)-Pd(II) cross-coupling cycle. Other Pd sources such as allyl and [(cinnamyl)PdCl]₂ dimers and Pd(PPh₃)₄ are thermally unstable.

One solution to the issue of palladium activation is through the use of palladium precatalysts.6-7 Precatalysts are generally pre-formed Pd(II) and Pd(0) species such as palladacycles and Pd₀[P(tBu)₃]₂ that exhibit air and moisture stability. Precatalysts activate under general reaction conditions or with external additives to provide the necessary LnPd(0) species to enter the catalytic cycle.

Historical Context
In 1995 Hermann and Beller reported the synthesis and utility of palladacycle 1, generated from the cyclometallation of P(o-tol)₃ with Pd(OAc)₂ at room temperature in toluene for 16 h.8-9 Palladacycle 1 exhibited unprecedented catalytic activity in Heck coupling, achieving TONs as high as 200,000 in some cases (Scheme 1). Employing 1 was markedly more effective than the combination of P(o-tol)₃ and Pd(OAc)₂. This was the first example of developing a palladacycle specifically for catalysis and was the first glimpse of the potential of palladacyclic precatalysts.

Scheme 1. Heck coupling of 4-bromobenzaldehyde and n-butyl acrylate with 1

The work of Hermann and Beller sparked considerable interest in developing palladacycles for catalysis. As a result many palladacyclic precatalysts have emerged since 1995. Some are simply cyclopalladated ligands such as 2,10 and 3,11 which are effective in Heck coupling and C-N cross-coupling, respectively. Others are palladacycles of 2-(dimethylamino)biphenyl 3,12 and N, N-dimethylbenzyl amine 4,13 which could be ligated with various phosphine and N-heterocyclic carbine (NHC) ligands (Figure 1). All of these precatalysts exhibited good reactivity in coupling reactions but required one catalytic cycle, β-hydride elimination, or an exogenous additive to activate.

Figure 1. Representative palladacycles utilized in Pd cross-coupling reactions.
First Generation Precatalysts

In 2007, we isolated a stable, primary amine-bound oxidative addition complex.\textsuperscript{14} Inspired by this discovery and the success of palladacyclic precatalysts, we endeavored to develop a general precatalyst compatible with a broad spectrum of ligands. This led to the development of 6, an intramolecularly amine-coordinated oxidative addition complex that could bear a variety of phosphate ligands.\textsuperscript{15} The success of 6 to generate the desired LPd(0) species was contingent on the deprotonation of the palladium-bound amine, which occurred readily, followed by subsequent reductive elimination to generate LPd(0), indoline, and a salt.

The initial synthesis of 6 is depicted in Scheme 2 and involves the generation of the thermally sensitive (tmeda)PdMe\textsubscript{2}, followed by its reaction with 2-chlorophenethylamine in the presence of ligand. Since the first published synthesis of 6, Vicente and coworkers reported an alternative synthesis that proceeds via C-H activation, utilizing Pd(OAc)\textsubscript{2} and phenethylammonium triflate.\textsuperscript{16}

![Scheme 2. Preparation of palladacyclic precatalysts 6•L and their mode of activation.](image)

Precatalyst 6 in Cross-Coupling Reactions

To evaluate the performance of 6 in cross coupling reactions, its use was compared to traditional palladium sources such as [(allyl)PdCl\textsubscript{2}, Pd\textsubscript{2}(dba)\textsubscript{3}, and Pd(OAc)\textsubscript{2}/PhB(OH)\textsubscript{2} in the arylation of aniline with 4-chloroanisole with \textit{L}\textsubscript{1} as the supporting ligand. BrettPhos, \textit{L}\textsubscript{1}, has been shown to be an effective and selective supporting ligand in the arylation of primary amines. As seen in Figure 1, 6•L\textsubscript{1} provided an extremely active palladium source, reaching full conversion of aryl halide in 35 minutes while none of the other sources provided over 25% conversion. Further exploiting the high reactivity of precatalyst 6•L\textsubscript{1}, aryl chlorides were combined with electron poor anilines, conventionally difficult coupling partners. A range of electron poor anilines were coupled successfully, including the first examples of 2-NO\textsubscript{2}, 2-CO\textsubscript{2}Et, 4-CF\textsubscript{3}, and 4-CN anilines with aryl chlorides.

![Scheme 3. Arylation of aniline with 4-chloroanisole with different Pd sources and \textit{L}\textsubscript{1} as the supporting ligand.](image)

Table 1. Arylation of electron-poor anilines with aryl chlorides by 6•L\textsubscript{1}.

<table>
<thead>
<tr>
<th>Aryl Chloride</th>
<th>Electron-Poor Aniline</th>
<th>Pd Source</th>
<th>Product Yield (%)</th>
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<tr>
<td>4-Cl</td>
<td>PhNH\textsubscript{2}</td>
<td>0.1% Pd/L\textsubscript{1}</td>
<td>86%</td>
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<tr>
<td>4-Cl</td>
<td>PhNH\textsubscript{2}</td>
<td>1% 6•L\textsubscript{1}</td>
<td>99%</td>
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<tr>
<td>n-Pr</td>
<td>PhNH\textsubscript{2}</td>
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<td>4-Cl</td>
<td>4-CN</td>
<td>1% 6•L\textsubscript{1}</td>
<td>90%</td>
</tr>
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</table>

\textit{Note:} All reactions were carried out in dioxane at 80 °C for 35 min.

Table 1. Arylation of electron-poor anilines with aryl chlorides by 6•L\textsubscript{1}.
Precatalysts 6 provide additional benefits in generating LPd(0) compared to traditional palladium sources. They were found to be efficient in arylations of primary and secondary amines, \(^\text{17}\) aminations of unprotected heteroaryl halides, \(^\text{18-19}\) \(\alpha\)-arylations, \(^\text{20}\) and continuous flow chemistry. \(^\text{21-22}\) Additionally, precatalyst activation of 6•L and subsequent oxidative addition of aryl chlorides could occur at temperatures as low as -40 °C with LHMDS. Additionally, the clean generation of LPd(0) with 6 enabled the first Hammett study of the oxidative addition of aryl chlorides with monodentate supporting ligands. \(^\text{15}\)

**Second Generation Precatalysts**

While an improvement from traditional palladium sources, precatalysts 6 still suffered from inherent drawbacks, one of the most significant being their inability to activate with weak base at room temperature. We began investigating alternative precatalyst scaffolds that retained the stability and ease of use of 6 while allowing them to activate at lower temperature. Encouraged by the work of Albert in their development of triphenylphosphine-ligated palladacycles of 2-aminobiphenyl, \(^\text{23-24}\) we hypothesized that using 2-aminobiphenyl as the palladacycle backbone in place of phenethylamine, the NH\(_2\) of the palladium precatalyst would be much more acidic, and thus, a more readily-activated palladium precatalyst. A series of precatalysts bearing biaryl dialkyl phosphines, 7•L, were prepared in a convenient, one-pot procedure from the cyclopalladation of 2-aminobiphenyl by palladium acetate, followed by ion exchange with lithium chloride, and phosphine ligation (Scheme 4). \(^\text{25}\) These precatalysts proved to be much more readily-activated, generating LPd(0) at room temperature with phosphate or carbonate bases.

![Scheme 3. One-pot preparation of precatalysts 7](image-url)

The ready activation of precatalyst 7•L2 and the resulting LPd(0) was utilized in the Suzuki-Miyaura coupling of the polyfluorophenylboronic acids and heteroaryl-2-boronic acids. These boronic acids represent structurally interesting coupling partners for pharmaceutical and agrochemical synthesis as well as in natural product and materials synthesis. However they are prone to rapid protodeboronation, rendering the use of higher temperatures or long reaction times problematic. With 2 – 3 mol % 7•L2, these unstable boronic acids could be coupled to a range of structurally diverse aryl halides in short reaction times (0.5 – 2 h) under mild conditions (ambient temperature – 40 °C) in good to excellent yields. The utilization of 7•L2 was pivotal in the first general method for the Suzuki-Miyaura coupling of these structurally important boronic acids.

![Table 2. Suzuki-Miyaura coupling of unstable boronic acids with 7•L2](image-url)

Precatalysts 7 have found use in a wide array of cross-coupling methodologies. They have been utilized in the first general method for the Suzuki-Miyaura coupling of unprotected, 5-membered heterocycles, \(^\text{26}\) a myriad of Suzuki-Miyuara couplings with aryl- and alkyl-BF\(_3\)K salts, \(^\text{27-29}\) borylations of aryl halides, \(^\text{30}\) alkynylations in continuous flow, \(^\text{31}\) and C-H arylation. \(^\text{32}\)
Third Generation Precatalysts

Generations one and two of our precatalysts were of great use in cross-coupling chemistry. However, the preparation of 6 required Schlenk techniques and the use of unstable intermediates or the use of triflic acid. Precatalyst 7 could not incorporate bulkier biaryl dialkylphosphines, including L1, an important ligand in C-N bond formation. As a result, we developed a third generation precatalyst to address the issues of previous generations. By replacing the chloride ligand in 7 with the non-coordinating and more electron-poor methanesulfonate ligand, a new family of precatalysts was prepared that exhibited the broadest ligand scope to date. Additionally, they were highly soluble and stable in common organic solvents while still retaining the ease of preparation of 7. Precatalysts of type 9 could all be generated from the common intermediate 8. Complex 9 could be prepared with a range of ligands (Table 2) in uniformly high yields. Precatalysts 9 have also been shown to be at least as effective as previous generations of precatalysts in catalysis. Demonstrating the practicality and scalability of this procedure, µ-OMs dimer 8 has been synthesized at a 400 g scale.

![Chemical structures and reactions](image_url)

Table 3. Preparation and representative examples of precatalyst 9

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<tr>
<th>Ligand</th>
<th>Yield (%)</th>
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<tr>
<td>L1</td>
<td>92%</td>
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<tr>
<td>L2</td>
<td>92%</td>
</tr>
<tr>
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</tr>
<tr>
<td>L15</td>
<td>PPh₃ (89%)</td>
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<tr>
<td>L16</td>
<td>P(o-tol)₃ (82%)</td>
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<td>L17</td>
<td>PCy₃ (95%)</td>
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<tr>
<td>L18</td>
<td>P(η₂Bu)₃ (87%)</td>
</tr>
<tr>
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<td>BINAP (93%)</td>
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<tr>
<td>L20</td>
<td>dppf (89%)</td>
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Precatalysts for Bulky Biaryl Di-tert-Butyl Phosphines

Precatalysts 9 were the first to be able to incorporate the extremely bulky biaryl di-tert-butyl phosphine ligands L10-L14. Previous generations of precatalysts could not accommodate these ligands, presumably due to the combination of their steric bulk and the chloride ligands’ inability to dissociate. Prior to the development of 9, preactivation of the ligand and palladium source was necessary through water activation with Pd(OAc)$_2$ or prestirring the ligand with Pd$_2$(dba)$_3$ at elevated temperatures. This was not ideal as these procedures required an additional operation in an ancillary reaction vessel as well as additional equivalents of ligand relative to palladium. The use of 9•L10 – 9•L14 avoid these issues. By employing a palladium source preligated with these ligands, we see good activity in a range of C-N and C-O bond-forming reactions without preactivation or added ligand (Table 4).

![Precatalyst Diagram](image)

**Table 4.** Arylation of amides and alcohols with 9•L10 – 9•L14.

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<th>Entry</th>
<th>ArX</th>
<th>Nu-H</th>
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<th>Pd %</th>
<th>Ligand</th>
<th>Yield</th>
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<td>L10</td>
<td>96%</td>
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<tr>
<td>2</td>
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<td></td>
<td></td>
<td>2%</td>
<td>L10</td>
<td>77%</td>
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<tr>
<td>3</td>
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<td>L12</td>
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<tr>
<td>4</td>
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<td></td>
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<td>92%</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td>1%</td>
<td>L9</td>
<td>92%</td>
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In-Situ Precatalyst Generation

Since precatalysts of type 9 can be formed quickly in a range of solvents and exhibit good solubility, we developed a protocol for generating them in situ for the screening of ligands in a palladium-catalyzed coupling reaction. This in-situ catalyst generation protocol was evaluated in the Suzuki-Miyaura coupling of 4-chloro-3-methylanisole and 2, 6-difluorophenylboronic acid. Vials of palladium source and ligand were aged for 10 minutes in 1 mL of THF and directly added to the reaction mixture, followed by aqueous base. As depicted in Table 3, XPhos was the optimal ligand for this reaction, with µ-OMs dimer 8 showing the highest catalytic activity, even when compared to similar 2-aminobiphenylpalladium dimers. Pd(OAc)$_2$ and Pd$_2$(dba)$_3$ provided little product (Table 4).

Precatalysts in Aromatic Cyanation

Aromatic nitriles are useful synthetic intermediates, pharmaceutical targets, and potential tracers for positron emission topography. We recently reported the cyanation of aryl chlorides and bromides with the non-toxic cyanide source K$_3$[Fe(CN)$_6$]. While there have been previous reports of catalytic processes, they all employ long reaction times, high temperatures, and exhibit limited substrate scopes. Our procedure circumvented these limitations through the employment of precatalyst 8 and the monodentate ligands L$_2$, L$_3$, and L$_9$, which gave much higher yields than the traditional [(allyl)PdCl$_2$, Pd$_2$(dba)$_3$ and Pd(OAc)$_2$ palladium sources. The reaction showed a broad substrate scope, tolerating a range of functional groups, 5-membered heterocycles, and N-H containing heterocycles (Table 5).

Table 5. Aromatic cyanation of aryl halides with 9.
**Table 6.** A brief summary of precatalyst generations developed in our lab and their general mode of activation.

**Conclusion**
In conclusion, the use of preformed palladium precatalysts containing phosphine ligands are an efficient means to generate the desired $L_nPd(0)$ species compared to traditional means of catalyst generation with separate Pd and ligand sources. We have developed three generations of palladacycle precatalysts to address the issues of catalyst activation (Table 6). Our third generation methanesulfonate precatalysts are readily activated, incorporate the broadest range of ligands to date and have a facile preparation that is amenable to large-scale synthesis. Additionally, by generating $LPd(0)$ more efficiently than traditional palladium sources, our palladacycle precatalysts have made possible methodologies that would not otherwise be feasible. We anticipate that the implementation of precatalysts will greatly improve the scope of palladium catalyzed cross-coupling reactions.

**Acknowledgments**
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**References:**
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<td>15-1063</td>
<td>1359986-21-2</td>
<td>250mg 1g 5g</td>
</tr>
</tbody>
</table>
### Buchwald Precatalysts

Bulk quantities available – please inquire

<table>
<thead>
<tr>
<th>Structure</th>
<th>Common Name</th>
<th>Strem Cat. #</th>
<th>CAS Number</th>
<th>Standard Catalog Sizes</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="First Generation" /></td>
<td>BrettPhos Palladacycle (from BrettPhos 15-1152) 1\textsuperscript{st} generation</td>
<td>46-0267</td>
<td>1148148-01-9</td>
<td>500mg 2g 10g 50g</td>
</tr>
<tr>
<td><img src="image2" alt="Second Generation" /></td>
<td>BrettPhos Palladacycle (from BrettPhos 15-1152) 2\textsuperscript{nd} generation</td>
<td>46-0292</td>
<td>1451002-39-3</td>
<td>100mg 500mg 2g</td>
</tr>
<tr>
<td><img src="image3" alt="Third Generation" /></td>
<td>BrettPhos Palladacycle (from BrettPhos 15-1152) 3\textsuperscript{rd} generation</td>
<td>46-0322</td>
<td>1470372-59-8</td>
<td>100mg 500mg 2g 10g</td>
</tr>
<tr>
<td><img src="image4" alt="Third Generation" /></td>
<td>t-butylBrettPhos Palladacycle (from t-butylBrettPhos 15-1164) 3\textsuperscript{rd} generation</td>
<td>46-0325</td>
<td>1445085-87-9</td>
<td>100mg 500mg 2g 10g</td>
</tr>
<tr>
<td><img src="image5" alt="Second Generation" /></td>
<td>DavePhos Palladacycle (from DavePhos 15-1145) 2\textsuperscript{nd} generation</td>
<td>46-0232</td>
<td>1445085-87-9</td>
<td>250mg 1g</td>
</tr>
<tr>
<td><img src="image6" alt="Third Generation" /></td>
<td>DavePhos Palladacycle (from DavePhos 15-1145) 3\textsuperscript{rd} generation</td>
<td>46-0237</td>
<td>1445085-87-9</td>
<td>250mg 1g</td>
</tr>
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<td>Structure</td>
<td>Common Name</td>
<td>Strem Cat. #</td>
<td>CAS Number</td>
<td>Standard Catalog Sizes</td>
</tr>
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<td>-----------</td>
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<td>------------------------</td>
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<tr>
<td><img src="structure1.png" alt="" /></td>
<td>JackiePhos Palladacycle (from JackiePhos 15-1157) 3rd generation</td>
<td>46-0340</td>
<td>100mg 500mg 2g</td>
<td></td>
</tr>
<tr>
<td><img src="structure2.png" alt="" /></td>
<td>RockPhos Palladacycle (from RockPhos 15-1168) 3rd generation</td>
<td>46-0335</td>
<td>100mg 500mg 2g 10g</td>
<td></td>
</tr>
<tr>
<td><img src="structure3.png" alt="" /></td>
<td>RuPhos Palladacycle (from RuPhos 15-1146) 1st generation</td>
<td>46-0266 1028206-60-1</td>
<td>100mg 500mg 2g 10g</td>
<td></td>
</tr>
<tr>
<td><img src="structure4.png" alt="" /></td>
<td>RuPhos Palladacycle (from RuPhos 15-1146) 2nd generation</td>
<td>46-0286 1375325-68-0</td>
<td>250mg 1g 5g</td>
<td></td>
</tr>
<tr>
<td><img src="structure5.png" alt="" /></td>
<td>RuPhos Palladacycle (from RuPhos 15-1146) 3rd generation</td>
<td>46-0314 1445085-77-7</td>
<td>250mg 1g 5g</td>
<td></td>
</tr>
<tr>
<td><img src="structure6.png" alt="" /></td>
<td>SPhos Palladacycle (from SPhos 15-1143) 1st generation</td>
<td>46-0269 1028206-58-7</td>
<td>250mg 1g 5g</td>
<td></td>
</tr>
<tr>
<td><img src="structure7.png" alt="" /></td>
<td>SPhos Palladacycle (from SPhos 15-1143) 2nd generation</td>
<td>46-0283 1375325-64-6</td>
<td>250mg 1g 5g</td>
<td></td>
</tr>
<tr>
<td>Structure</td>
<td>Common Name</td>
<td>Strem Cat. #</td>
<td>CAS Number</td>
<td>Standard Catalog Sizes</td>
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<td>-----------</td>
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<td>------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td><img src="image1.png" alt="Structure" /></td>
<td>SPhos Palladacycle (from SPhos 15-1143) 3rd generation</td>
<td>46-0318</td>
<td>1445085-82-4</td>
<td>250mg 1g 5g 25g</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure" /></td>
<td>XPhos Palladacycle (from XPhos 15-1149) 1st generation</td>
<td>46-0268</td>
<td>1028206-56-5</td>
<td>250mg 1g 5g</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure" /></td>
<td>XPhos Palladacycle (from XPhos 15-1149) 2nd generation</td>
<td>46-0281</td>
<td>1310584-14-5</td>
<td>250mg 1g</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure" /></td>
<td>XPhos Palladacycle (from XPhos 15-1149) 3rd generation</td>
<td>46-0320</td>
<td>1445085-55-1</td>
<td>250mg 1g 5g</td>
</tr>
<tr>
<td><img src="image5.png" alt="Structure" /></td>
<td>t-BuXPhos Palladacycle (from t-BuXPhos 15-1052) 1st generation</td>
<td>46-0264</td>
<td>1142811-12-8</td>
<td>100mg 500mg 2g 10g</td>
</tr>
<tr>
<td><img src="image6.png" alt="Structure" /></td>
<td>t-BuXPhos Palladacycle (from t-BuXPhos 15-1052) 3rd generation</td>
<td>46-0323</td>
<td>1447963-75-8</td>
<td>250mg 1g</td>
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</tbody>
</table>
Buchwald Ligands & Kits (cont.)

Also Available

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Code</th>
<th>New Code</th>
<th>New Code</th>
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<tr>
<td>RockPhos</td>
<td>15-1168</td>
<td>1262046-34-3</td>
<td>15-1063</td>
</tr>
<tr>
<td>CPhos</td>
<td>15-1147</td>
<td>1160556-64-8</td>
<td></td>
</tr>
</tbody>
</table>

Bulk quantities available. Please inquire.

96-5500 Buchwald Biaryl Phosphine Ligand Master Kit
for aromatic carbon-heteroatom bond formation and Suzuki Coupling.

96-5485 Buchwald Biaryl Phosphine Ligand Mini Kit 1
(contains more recently developed ligands)
for aromatic carbon-heteroatom bond formation and Suzuki Coupling.

96-5490 Buchwald Biaryl Phosphine Ligand Mini Kit 2
(contains more mature ligands)
for aromatic carbon-heteroatom bond formation and Suzuki Coupling.

Buchwald Palladacycles & Kits

96-5503 Buchwald Palladacyle Precatalyst Kit 1 (chloro-, 2-aminoethylphenyl- Palladacycles)
Contains the smallest size unit of the following items:

<table>
<thead>
<tr>
<th>Precatalyst Kit 1</th>
<th>Code</th>
<th>New Code</th>
<th>New Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>(from SPhos 15-1143)</td>
<td>46-0269</td>
<td>1028206-58-7</td>
<td></td>
</tr>
<tr>
<td>(from BretPhos 15-1152)</td>
<td>46-0267</td>
<td>1148148-01-9</td>
<td></td>
</tr>
<tr>
<td>(from RuPhos 15-1146)</td>
<td>46-0266</td>
<td>1028206-60-1</td>
<td></td>
</tr>
</tbody>
</table>

| 1st Generation 96-5503 Buchwald Palladacyle Precatalyst Kit 1 |
|-------------------|-------------------|-------------------|
| (from XPhos 15-1149) | 46-0268    | 1028206-56-5      |                   |
| (from t-BuXPhos 15-1052) | 46-0264    | 1142811-12-8      |                   |

Note: Patents:

Components available for individual sale.

Review Article (general uses):

**Buchwald Palladacycles & Kits (cont.)**

**96-5508 Buchwald Palladacycle Precatalyst Kit 3** (Chloro-2'-amino-1,1'-biphenyl-2'-yl Palladacycles)

Contains the smallest units of the following items:

- 250mg
- 1g

(from XPhos 15-1149)
- 250mg
- 1g
- 5g

(from SPhos 15-1143)
- 250mg
- 1g
- 5g

(from RuPhos 15-1146)

Note: Patents:

Components available for individual sale.

**96-5505 Buchwald Palladacycle Precatalyst Kit 2** (Methanesulfonato-Palladacycles)

Contains the smallest unit of the following items:

- 250mg
- 1g
- 5g
- 25g

(from SPhos 15-1143)
- 250mg
- 1g
- 5g
- 2g

(from BrettPhos 15-1152)
- 250mg
- 1g
- 5g

(from RuPhos 15-1146)

Note: Patents: PCT/US2013/030779
US Serial No. 13/799620

Components available for individual sale.
### Buchwald Precatalysts

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
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<tbody>
<tr>
<td>96-5503</td>
<td>Buchwald Palladacycle Precatalyst Kit 1 for Aromatic Carbon-Heteroatom Bond Formation, Suzuki Coupling &amp; Negishi Cross-coupling (chloro-, 2-aminoethylphenyl- Palladacycles)</td>
</tr>
<tr>
<td></td>
<td>See (page 16).</td>
</tr>
<tr>
<td>96-5505</td>
<td>Buchwald Palladacycle Precatalyst Kit 2 (Methanesulfonato- Palladacycles)</td>
</tr>
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<td>See (page 17).</td>
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<tr>
<td>96-5508</td>
<td>Buchwald Palladacycle Precatalyst Kit 3 (Chloro- 2'-amino-1,1'-biphenyl-2-yl Palladacycles)</td>
</tr>
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<td></td>
<td>See (page 17).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
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<tbody>
<tr>
<td>46-0367</td>
<td>Chloro([BrettPhos]2-{2-aminoethylphenyl]palladium(II)})/ [BrettPhos] admixture (molar PdP/P = 1:1)</td>
</tr>
<tr>
<td></td>
<td>white pwdr.</td>
</tr>
<tr>
<td></td>
<td>Technical Note:</td>
</tr>
<tr>
<td>1.</td>
<td>See 46-0267 (page 19).</td>
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<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>46-0364</td>
<td>Chloro([t-butylXPhos][2-aminoethylphenyl)palladium(II)]/ [t-butylXPhos] admixture (molar PdP/P = 1:1)</td>
</tr>
<tr>
<td></td>
<td>white pwdr.</td>
</tr>
<tr>
<td></td>
<td>Note: Patents: US 6,395,916, US 6,307,087</td>
</tr>
<tr>
<td></td>
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<tr>
<td>1.</td>
<td>See 46-0264 (page 18).</td>
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<table>
<thead>
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</thead>
<tbody>
<tr>
<td>46-0264</td>
<td>Chloro(2-di-t-butylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl][2-(2-aminoethyl)phenyl] palladium(II), min. 98% [t-BuXPhos Palladacycle]</td>
</tr>
<tr>
<td></td>
<td>[1142811-12-8]</td>
</tr>
<tr>
<td></td>
<td>C_{37}H_{55}ClNPPd; FW: 686.69; white pwdr.</td>
</tr>
<tr>
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<td>Note: Patents: US 6,395,916, US 6,307,087</td>
</tr>
<tr>
<td></td>
<td>Buchwald Palladacycle Precatalyst Kit 1 component. See (page 16).</td>
</tr>
<tr>
<td></td>
<td>Technical Note:</td>
</tr>
<tr>
<td>1.</td>
<td>See 46-0264 (page 19).</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>46-0283</td>
<td>Chloro(2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl][2-(2-aminoethyl)phenyl] palladium(II) min. 98% [SPhos Palladacycle]</td>
</tr>
<tr>
<td></td>
<td>[1375325-64-6]</td>
</tr>
<tr>
<td></td>
<td>C_{38}H_{45}ClNO_{2}PPd; FW: 720.62; white pwdr.</td>
</tr>
<tr>
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<td>Note: Patents: US 6,395,916, US 6,307,087</td>
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<tr>
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<td>Buchwald Palladacycle Precatalyst Kit 3 component. See (page 17).</td>
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<td>Technical Note:</td>
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<td>1.</td>
<td>See 46-0283 (page 20).</td>
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<table>
<thead>
<tr>
<th>Code</th>
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</thead>
<tbody>
<tr>
<td>46-0269</td>
<td>Chloro(2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl][2-(2-aminoethylphenyl)] palladium(II) methyl-t-butylether adduct, min. 98% [SPhos Palladacycle]</td>
</tr>
<tr>
<td></td>
<td>[1028206-58-7]</td>
</tr>
<tr>
<td></td>
<td>C_{38}H_{45}ClNO_{2}PPd; FW: 672.57; white pwdr.</td>
</tr>
<tr>
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<td>Note: Patents: US 6,395,916, US 6,307,087</td>
</tr>
<tr>
<td></td>
<td>Buchwald Palladacycle Precatalyst Kit 1 component. See (page 16).</td>
</tr>
<tr>
<td></td>
<td>Technical Note:</td>
</tr>
<tr>
<td>1.</td>
<td>See 46-0269 (page 20).</td>
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### Buchwald Precatalysts

<table>
<thead>
<tr>
<th>Code</th>
<th>Formula</th>
<th>Masses</th>
<th>Technical Notes</th>
</tr>
</thead>
</table>
| 46-0292 | **Chloro(2-dicyclohexylphosphino-3,6-dimethoxy-2',4',6'-tri-i-propyl-1,1'-biphenyl)(2'-amino-1,1'-biphenyl-2-yl)palladium(II)**, min. 98%       | 100mg, 500mg, 2g   | 1. Catalyst for cross-coupling reactions using aryl mesylates with electron-deficient anilines.  
2. Catalyst for rapid C-N bond-forming process at low catalyst loading. |
|       | **BrettPhos Palladacycle** [1451002-39-3]                                                                                                    |                     |                                                                                                                                             |
|       | C_{6}H_{8}ClNO_{2}PPd; FW: 846.86; white pwdr.                                                                                               |                     |                                                                                                                                             |
|       | ![Image](image1.png)                                                                                                                         |                     |                                                                                                                                             |

### Technical Note:
1. See 46-0281 (page 20).

| 46-0267 | **Chloro[2-(dicyclohexylphosphino)-3,6-dimethoxy-2',4',6'-tri-i-propyl-1,1'-biphenyl][2-(2-aminoethyl)phenyl]palladium(II)**, min. 98%        | 100mg, 500mg, 2g, 10g | 1. Catalyst for cross-coupling reactions using aryl mesylates with electron-deficient anilines.  
2. Catalyst for rapid C-N bond-forming process at low catalyst loading. |
|         | **BrettPhos Palladacycle** [1148148-01-9]                                                                                                    |                     |                                                                                                                                             |
|         | C_{6}H_{8}ClNO_{2}PPd; FW: 798.81; white pwdr.                                                                                               |                     |                                                                                                                                             |
|         | ![Image](image2.png)                                                                                                                         |                     |                                                                                                                                             |

### Technical Notes:
1. See 46-0281 (page 20).

### References:
From Grams to Kilos. For R&D and Commercial Use.

### Buchwald Precatalysts

<table>
<thead>
<tr>
<th>Code</th>
<th>Formula</th>
<th>Mass (mg)</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>46-0266</td>
<td>Chloro(2-dicyclohexylphosphino-2',6'-di-i-propoxy-1,1'-biphenyl)[2-(2-aminoethylphenyl)] palladium(II), methyl-t-butyloether adduct, min. 98% [RuPhos Palladacycle]</td>
<td>100mg</td>
<td>2g</td>
</tr>
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</table>

**Technical Note:**
1. See 46-0268 (page 20).

<table>
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<th>Formula</th>
<th>Mass (mg)</th>
<th>Mass (g)</th>
</tr>
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<tbody>
<tr>
<td>46-0281</td>
<td>Chloro(2-dicyclohexylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl)(2'-amino-1,1'-biphenyl-2-yl) palladium(II), min. 98% [XPhos Palladacycle]</td>
<td>250mg</td>
<td>1g</td>
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</table>

**Technical Note:**

<table>
<thead>
<tr>
<th>Code</th>
<th>Formula</th>
<th>Mass (mg)</th>
<th>Mass (g)</th>
</tr>
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<tbody>
<tr>
<td>46-0268</td>
<td>Chloro(2-dicyclohexylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl)[2-(2-aminoethylphenyl)] palladium(II) methyl-t-butyloether adduct, min. 98% [XPhos Palladacycle]</td>
<td>250mg</td>
<td>1g</td>
</tr>
</tbody>
</table>

**Technical Notes:**
1. Catalyst for the coupling of aryl chlorides with anilines.
2. Catalyst for the coupling of arenes with dimethylamine.
3. Catalyst for the α-arylation of aldehydes.

Reference:
From Grams to Kilos. For R&D and Commercial Use.

**Buchwald Precatalysts**

46-0268  Choloro[2-dicyclohexylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl][2-(2-aminoethyl)phenyl] palladium(II) methyl-t-butylether adduct, min. 98% [XPhos Palladacycle]  

\[
\text{Cl} \quad + \quad \text{HNMe}_2 \quad \xrightarrow{1 \text{ mol\% catalyst}} \quad \text{THF, r.t.} \quad \text{2 h} \quad \xrightarrow{2 \text{ mol\% catalyst}} \quad \text{Cs}_2\text{CO}_3 \quad \xrightarrow{\text{Dioxane, 24 ppm H}_2\text{O}} \quad \text{80-100 °C} \quad \text{R} \quad \text{NMe}_2 \quad \text{R} \quad \text{CHO} 
\]

References:

Technical Note:
1. See 46-0266 (page 20).

46-0366  Choloro[RuPhos][2-(2-aminoethylphenyl]palladium(II)]/ [RuPhos] admixture (molar Pd/P = 1:1)  

white pwdr.  
Note: Patents: US 6,395,916, US 6,307,087

Technical Note:
1. See 46-0266 (page 20).

46-0369  Choloro[S-Phos][2-(2-aminoethylphenyl]palladium(II)]/ [S-Phos] admixture (molar Pd/P = 1:1)  

white pwdr.  

Technical Note:
1. See 46-0269 (page 18).

46-0368  Choloro[X-Phos][2-(2-aminoethylphenyl]palladium(II)]/ [X-Phos] admixture (molar Pd/P = 1:1)  

white pwdr.  

Technical Note:
1. See 46-0268 (page 20).

46-0340  Methanesulfonato[2-bis(3,5-di(trifluoromethyl) phenyl-phosphino)-3,6-dimethoxy-2',4',6'-tri-i-propyl-1,1'-biphenyl][2'-amino-1,1'-biphenyl-2-yl]palladium(II), min. 98%  

[JackiePhos Palladacycle]  

C\text{32}H\text{38}F\text{12}N\text{O}\text{4}PP\text{d}S; FW: 1150.40; white pwdr.  

Technical Note:
Buchwald Precatalysts

46-0340  Methanesulfonato[2-bis{3,5-di(trifluoromethyl)phenyl-phosphino}-3,6-dimethoxy-2',4',6'-tri-i-propyl-1,1'-biphenyl][2'-amino-1,1'-biphenyl-2-yl]palladium(II), min. 98%

[JackiePhos Palladacycle]

Bu₂NH +  
\[ \text{Pd complex} \] \text{dioxane, 7 h, rt}

Reference:

46-0325  Methanesulfonato(2-(di-t-butylphosphino)-3,6-dimethoxy-2',4',6'-tri-i-propyl-1,1'-biphenyl) (2'-amino-1,1'-biphenyl-2-yl)palladium(II), min. 98% [t-butylBrettPhos Palladacycle]

C₄₄H₆₂NO₅PPdS; FW: 854.43; red-brown pwdr.


Technical Notes:
1. Palladium catalyst used for the arylation of primary amides.
2. Palladium catalyst used for the synthesis of N-aryl carbamates.
3. Palladium catalyst used for the N-monomarylation of amidines.
4. Palladium catalyst used for the cross-coupling of aryl chlorides and triflates with sodium cyanate – a practical synthesis of unsymmetrical ureas.
6. Palladium catalyst used in the N-arylation of 2-aminothiazoles.
7. Palladium catalyst used in the synthesis of diaryl ethers under mild conditions.
From Grams to Kilos. For R&D and Commercial Use.

**Buchwald Precatalysts**

*NEW* 46-0325 Methanesulfonato(2-(di-t-butylphosphino)-3,6-dimethoxy-2',4',6'-tri-i-propyl-1,1'-biphenyl)(2'-amino-1,1'-biphenyl-2-yl)palladium(II), min. 98% [t-butylBrettPhos Palladacycle]

(Cont.)

R\_Z X + NaO CN

```
\text{"Pd complex"} 1 - 2 mol%  \\
\text{without PhOH}  \\
\text{with PhOH}
```

\[
\begin{array}{c}
\text{HN(R\_1)^2}
\end{array}
\]

Tech. Note (4)  
Ref. (4)

R\_Z ZNH + R\_1 R\_1 H2N

```
\text{"Pd complex"}  \\
\text{K3PO}_4 1.5 equiv  \\
t-BuOH, 110\text{°C}
```

51 - 99%

Tech. Note (5)  
Ref. (5)

R\_Z R\_1 M + H2N R\_2 R\_1

```
\text{"Pd complex"}  \\
\text{K2CO}_3 1.4 equiv  \\
t-BuOH, 90-110\text{°C}
```

Tech. Note (6)  
Ref. (6)

R\_1 R\_2 H + ROH

```
\text{"Pd catalyst"}  \\
toluene/DME  \\
K3PO_4 1.5 equiv  \\
16 h
```

Tech. Note (7)  
Ref. (7)

References:

*NEW* 46-0335 Methanesulfonato(2-(di-t-butylphosphino)-3-methoxy-6-methyl-2',4',6'-tri-i-propyl-1,1'-biphenyl)(2'-amino-1,1'-biphenyl-2-yl)palladium(II), min. 98% [RockPhos Palladacycle]

C\text{eH}_{12}\text{NO}_{3}\text{PPdS}; FW: 838.43; brown pwdr.


Technical Notes:
1. Palladium precatalyst used for the arylation of an aliphatic alcohol.
2. Palladium precatalyst used for the synthesis of diaryl ethers under mild conditions.
3. Palladium precatalyst used for the intermolecular C-O bond formation with secondary and primary alcohols.
Buchwald Precatalysts

**46-0335**  Methanesulfonato(2-(di-t-butylphosphino)-3-methoxy-6-methyl-2',4',6'-tri-i-propyl-1,1'-biphenyl)(2'-amino-1,1'-biphenyl-2-yl)palladium(II), min. 98% [RockPhos Palladacycle]

(cont.)

R¹ = alkyl
R² = alkyl, H

References:

**46-0323**  Methanesulfonato(2-di-t-butylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl)(2'-amino-1,1'-biphenyl-2-yl)palladium(II), min. 98% [t-BuXPhos Palladacycle] [1447963-75-8]


References:

References:
### Buchwald Precatalysts

**46-0318**  
**NEW**  
Methanesulfonato(2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl)(2'-amino-1,1'-biphenyl-2-yl)palladium(II) dichloromethane adduct min. 98% [SPhos Palladacycle]  
1445085-82-4

C₃₉H₄₈NO₅PPdS; FW: 780.26; white pwdr.  

**Technical Note:**  
1. Palladium precatalyst for the arylation of amines.

**Reference:**  

**46-0322**  
**NEW**  
Methanesulfonato(2-dicyclohexylphosphino-3,6-dimethoxy-2',4',6'-tri-i-propyl-1,1'-biphenyl)(2'-amino-1,1'-biphenyl-2-yl) palladium(II), min. 98% [BrettPhos Palladacycle]  
1470372-59-8

C₄₈H₆₆NO₅PPdS; FW: 906.50; beige pwdr.  

**Technical Notes:**  
1. Palladium precatalyst for facile C-N cross-coupling reactions.  
2. Palladium precatalyst for the arylation of primary amines.

**References:**  
### Buchwald Precatalysts

<table>
<thead>
<tr>
<th>Code</th>
<th>Formula</th>
<th>Quantity</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>46-0237</td>
<td>Methanesulfonato[2-(dicyclohexylphosphino)-2'-(N,N-dimethylamino)-1,1'-biphenyl] (2'-amino-1,1'-biphenyl-2-yl)palladium(II)</td>
<td>250mg</td>
<td>CH₂Cl₂ adduct, min. 98% [DavePhos Palladacycle] [1445085-87-9]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5g</td>
<td></td>
</tr>
</tbody>
</table>

#### Technical Notes:
1. Palladium precatalyst for facile C-N cross-coupling reactions.
2. Palladium precatalyst for the arylation of secondary amines.

#### References:
From Grams to Kilos. For R&D and Commercial Use.

### Buchwald Precatalysts

<table>
<thead>
<tr>
<th>Code</th>
<th>Name</th>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>46-0320</td>
<td>Methanesulfonato(2-dicyclohexylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl)(2'-amino-1,1'-biphenyl-2-yl)palladium(II), min. 98%</td>
<td>C_{28}H_{37}NO_{3}PPdS; FW: 846.45; white pwd.</td>
<td>Technical Notes: 1. Palladium precatalyst for facile C-N cross-coupling reactions. 2. Palladium precatalyst for the arylation of primary amines.</td>
</tr>
</tbody>
</table>

**Technical Notes:**

1. Palladium precatalyst for facile C-N cross-coupling reactions.
2. Palladium precatalyst for the arylation of primary amines.

**References:**


<table>
<thead>
<tr>
<th>Code</th>
<th>Name</th>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
</table>
| 46-2033 | Palladium(II) acetate/2-dicyclohexylphosphino-2,6-dimethoxy-1,1'-biphenyl (SPhos)/potassium phosphate admixture | [CatKit single-use vials - 1.96 wt% Pd(OAc)_{2}] | Technical Note: Convenient, pre-weighed vial of palladium catalyst-base admixture useful for screening reactions. The vial contains 453mg of admixture, which will deliver 4 mole% of palladium catalyst and 2 equivalents of base, to a reaction using 1 mmole of substrate.

**Contact us for Bulk Quotes or Commercial Use Terms.**
## Buchwald Ligands

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>96-5500</td>
<td>Buchwald Biaryl Phosphine Ligand Master Kit for Aromatic Carbon-Heteroatom Bond Formation, Suzuki Coupling and Negishi Cross-coupling</td>
<td><a href="#">Page 15</a></td>
</tr>
<tr>
<td>96-5485</td>
<td>Buchwald Biaryl Phosphine Ligand Mini Kit 1 for Aromatic Carbon-Heteroatom Bond Formation, Suzuki Coupling and Negishi Cross-coupling (contains more recently developed ligands)</td>
<td><a href="#">Page 15</a></td>
</tr>
<tr>
<td>96-5490</td>
<td>Buchwald Biaryl Phosphine Ligand Mini Kit 2 for Aromatic Carbon-Heteroatom Bond Formation, Suzuki Coupling and Negishi Cross-coupling (contains more mature ligands)</td>
<td><a href="#">Page 15</a></td>
</tr>
</tbody>
</table>

### Technical Notes:
1. Ligand used in the palladium-catalyzed amidation of five-membered heterocycles as electrophiles.
2. Ligand for the palladium-catalyzed monoarylation of ammonia.

### References:

## Additional Ligands

### 15-1138

| 15-1138 | 2-(Di-1-adamantylphosphino)-3,6-dimethoxy-2',4',6'-tri-i-propyl-1,1'-biphenyl, min. 95% | [Page 15](#) |

#### Technical Notes:
1. Ligand used in the palladium-catalyzed amidation of aryl nonaflates and triflates with secondary amides, carbamates, and sulfonamides.
2. Ligand used in the palladium-catalyzed coupling of aryl chlorides with secondary amides, carbamates, and sulfonamides.

### References:
2-Di[3,5-bis(trifluoromethyl)phenylphosphino]-3,6-dimethoxy-2’,4’,6’-tri-i-propyl-1,1’-biphenyl, min. 98% JackiePhos \[1160861-60-8\]

References:

15-1043 racemic-2-Di-t-butylphosphino-1,1’-binaphthyl, 98% TrixiePhos \[255836-67-0\]
C\textsubscript{28}H\textsubscript{31}P; FW: 398.53; white xtl.; m.p. 147-149°
Note: Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15). Buchwald Biaryl Phosphine Ligand Mini Kit 2 component. See (page 15).

Technical Notes:
1. Ligand for the Pd-catalyzed formation of oxygen heterocycles.
2. Ligand for the intermolecular Pd-catalyzed synthesis of aryl ethers.
3. Ligand for the intramolecular Pd-catalyzed synthesis of aryl ethers.
4. Ligand for the synthesis of carbazoles by Pd-catalyzed double N-arylation reaction.
5. Ligand for the Pd-catalyzed cyanation of (hetero)arylchlorides.

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Buchwald Ligands

15-1043 racemic-2-Di-t-butylphosphino-1,1'-binaphthyl, 98% TrixiePhos [255836-67-0] (cont.)

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References:

15-1045 2-(Di-t-butylphosphino)biphenyl, 99% JohnPhos [224311-51-7]

C_{20}H_{27}P; FW: 298.41; colorless xtl.; m.p. 85°

Note: Phosphine Ligand Kit component.

Note: Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15). Buchwald Biaryl Phosphine Ligand Mini Kit 2 component. See (page 15).

Technical Notes:
1. Ligand used in the palladium-catalyzed synthesis of aromatic amines from aryl chlorides, bromides and triflates.
2. Ligand employed in a very active and general catalyst for Suzuki coupling reactions using aryl chlorides, bromides and triflates.
3. Ligand used in palladium-catalyzed synthesis of oxindoles from α-chloroacetanilides.
4. Effective ligand used in palladium-catalyzed arylation of thiazoles.
5. Used in the formation of 2-benzylindolines via sequential palladium-catalyzed N-arylation/cyclization/C-arylation.
7. Ligand used in the palladium-catalyzed vinylation of aryl bromides.
8. Ligand used in the platinum-catalyzed synthesis of indolizines.
9. Ligand used in the palladium-catalyzed diarylation of thiophenes.
10. Ligand used in the amination of vinyl halides by carbazates.
11. Ligand used in the regioselective synthesis of 2,4-disubstituted syloles.
12. Ligand used in the gold-catalyzed hydrophenoxylation of phenols with diphenylacetylene.

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From Grams to Kilos. For R&D and Commercial Use.

**Buchwald Ligands**

**15-1045** 2-(Di-t-butylphosphino)biphenyl, 99% JohnPhos [224311-51-7] (cont.)

ArBr + N\text{CONNHPh} \rightarrow \text{Pd(OAc)}_2, 15-1045, \text{L Cs}_2\text{CO}_3, \text{o-xylene}

R\text{NH}_2 \rightarrow \text{Pd(OAc)}_2, 15-1045, \text{CsF, ArBr}

O\text{PhH, 100 °C, 48h}

Pd(OAc)$_2$, 15-1045, Cs$_2$CO$_3$, toluene

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Buchwald Ligands

15-1045  2-(Di-t-butylphosphino)biphenyl, 99% JohnPhos  [224311-51-7]
(cont.)

References:

15-1164  2-(Di-t-butylphosphino)-3,6-dimethoxy-2',4',6'-tri-i-propyl-1,1'-biphenyl, min. 98% t-butylBrettPhos  [1160861-53-9]
C_{31}H_{49}O_2P; FW: 484.69; white xtl.
Note: Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15). Buchwald Biaryl Phosphine Ligand Mini Kit 1 component. See (page 15).

Technical Notes:
1. Ligand used in the Pd-catalyzed conversion of aryl and vinyl triflates to bromides, chlorides, and fluorides.
2. Ligand used in the Pd-catalyzed cross-coupling of amides and aryl mesylates.
3. Ligand used in the Pd-catalyzed O-arylation of ethyl acetoxyhydroximates.
4. Ligand used in the Pd-catalyzed conversion of aryl chlorides, triflates, and nonaflates to nitroaromatics.
5. Ligand used in the arylation of ureas.
### Buchwald Ligands

<table>
<thead>
<tr>
<th>15-1164</th>
<th>2-(Di-t-butylphosphino)-3,6-dimethoxy-2',4',6'-tri-i-propyl-1',1'-biphenyl, min. 98% t-butylBrettPhos [1160861-53-9]</th>
</tr>
</thead>
</table>

**References:**

**Technical Notes:**
1. Useful ligand for Pd-catalyzed carbon-oxygen bond forming reactions.
2. Ligand used selective Pd-catalyzed arylation of ammonia. Application to the synthesis of dibenzodiazepines.
3. Ligand used for selective Pd-catalyzed silylation of aryl chlorides.

<table>
<thead>
<tr>
<th>15-1048</th>
<th>2-Di-t-butylphosphino-2’-(N,N-dimethylamino) biphenyl, 98% tBuDavePhos [224311-49-3]</th>
</tr>
</thead>
</table>

**Note:** Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15). Buchwald Biaryl Phosphine Ligand Mini Kit 2 component. See (page 15).

**Patents:** US 6,395,916, US 6,307,087.

**References:**
**Buchwald Ligands**

**15-1168**
2-(Di-t-butylphosphino)-3-methoxy-6-methyl-2',4',6'-tri-i-propyl-1,1'-biphenyl, min. 98% RockPhos

\[ \text{C}_{31} \text{H}_{49} \text{OP}; \text{FW: 468.69; white xtl.; m.p. 129-130°} \]

Technical Note:
1. Ligand used in palladium-catalyzed C-O bond forming reactions of secondary and primary alcohols with a range of aryl halides including heterocyclic partners. For the first time, electron-rich aryl halides can be coupled with secondary alcohols.

**Reference:**

**15-1063**
2-Di-t-butylphosphino-4-methoxy-3,5,6-trimethyl-2',4',6'-tri-i-propylbiphenyl, min. 98% [*1:1 mixture with regioisomer, 2-Di-t-butylphosphino-5-methoxy-3,4,6-trimethyl-2',4',6'-tri-i-propylbiphenyl*]

\[ \text{C}_{33} \text{H}_{53} \text{OP}; \text{FW: 496.75; white pwdr.} \]

Technical Note:
1. A surrogate ligand for Me₄tBuXPhos in palladium-catalyzed C-N and C-O bond-forming reactions.

**Reference:**

**15-1049**
2-Di-t-butylphosphino-2'-methylbiphenyl, 99%
tBuMePhos

\[ \text{C}_{21} \text{H}_{29} \text{P}; \text{FW: 312.43; white xtl.} \]

Note: Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15). Buchwald Biaryl Phosphine Ligand Mini Kit 2 component. See (page 15).

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Buchwald Ligands

15-1049  2-Di-t-butylphosphino-2’-methylbiphenyl, 99% tBuMePhos [255837-19-5]  
(cont.)

Technical Notes:
1. Ligand used in the Pd-catalyzed arylation of malonate esters and 1,3-diketones.
2. Ligand used in the Pd-catalyzed formation of t-butyl esters from unactivated aryl halides.
3. Ligand used in the Pd-catalyzed α-arylations of nitroalkanes.

References:

15-1051  2-Di-t-butylphosphino-3,4,5,6-tetramethyl-2’,4’,6’-tri-i-propylbiphenyl, min. 98% Me₄t-butylXPhos [857356-94-6]  
C₃₃H₅₃P; FW: 480.75; white microxtl.; m.p. 166-168°
Note: Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15). Buchwald Biaryl Phosphine Ligand Mini Kit 1 component. See (page 15).

Technical Notes:
1. Ligand for the palladium-catalyzed amidation of aryl chlorides.
2. Ligand for the palladium-catalyzed synthesis of phenols from aryl halides.
3. Ligand for the palladium-catalyzed coupling of aryl halides and secondary alcohols.
4. Ligand for the N 2-Selective Palladium-Catalyzed Arylation of 1,2,3-Triazoles.
5. Ligand for the Gold(I)-catalyzed carbocyclization.

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Buchwald Ligands

15-1051 2-Di-t-butylphosphino-3,4,5,6-tetramethyl-2',4',6'-tri-i-propylbiphenyl, min. 98%
(cont.) Me₄ t-butylXPhos [857356-94-6]

\[
\text{Br} + \text{N} \quad \xrightarrow{[\text{Pd}_2(\text{dba})_3, \text{L}]} \xrightarrow{\text{K}_3\text{PO}_4} \quad \text{N} \quad \xrightarrow{\text{toluene, } 120 \ ^\circ\text{C}} \quad \text{N} \\
\]

Tech. Note (4)
Ref. (4)

References:

15-1052 2-Di-t-butylphosphino-2’,4’,6’-tri-i-propyl-1,1’-biphenyl, min. 98% t-butylXPhos [564483-19-8]

CₙH₄₂P; FW: 424.64; white xtl.; m.p. 147-149°

Note: Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15). Buchwald Biaryl Phosphine Ligand Mini Kit 1 component. See (page 15).


500mg
2g
10g
50g

Technical Notes:
1. Effective ligand for the Pd-catalyzed arylation of pyrazoles, indazoles and amino heterocycles.
2. Ligand used in the Pd-catalyzed synthesis of phenols from aryl halides and KOH.
3. Ligand used in the Pd-catalyzed of benzoic acids from aryl halides and CO₂.
4. Ligand used in the Pd-catalyzed trifluoromethylation of vinyl sulfonates.

R \[ \text{X} \quad \text{HN} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{P} \quad [\text{Cl} \quad \text{CH}_3]_3 \text{Cl} \] 

[Chem. Sci., 2011, 2, 27-50.]

References:
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Buchwald Ligands

15-1140  2-(Dicyclohexylphosphino)biphenyl, 98% CyJohnPhos
[247940-06-3]
C_{12}H_{9}[P(C_6H_{11})_2]; FW: 350.49; white xtl.; m.p. 103°
Note: Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15). Buchwald Biaryl Phosphine Ligand Mini Kit 2 component. See (page 15).

Technical Notes:
1. See 15-1045 (page 30).
2. Ligand used in the palladium-catalyzed synthesis of aromatic amines from aryl chlorides, bromides and triflates.
3. Ligand employed in Suzuki coupling reactions involving aryl chlorides, bromides and triflates.
4. Useful ligand for the Pd-catalyzed oxidation of alcohols in the presence of chlorobenzenes
5. Useful ligand for the Pd-catalyzed amination with ammonia equivalents.
7. Ligand used in the palladium-catalyzed borylation of aryl bromides.
8. Ligand used in the palladium-catalyzed silylation of aryl chlorides.

References:
Buchwald Ligands

15-1143 2-Dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl, min. 98% SPhos [657408-07-6]
C₂₆H₃₅O₂P; FW: 410.53; white xtl.; m.p. 164-166°
Note: Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15). Buchwald Biaryl Phosphine Ligand Mini Kit 1 component. See (page 15).

Technical Notes:
2. Ligand used in the Suzuki cross-coupling of heteroaryl substrates.
3. Ligand used in the Suzuki cross-coupling of aryl potassium trifluoroborates.
4. Effective ligand for the Pd-catalyzed borylation of aryl chlorides.
5. Ligand used in the Pd-catalyzed Kumada-Corriu reaction of functionalized aryl Grignard reagents at low temperature.
6. Allows for the coupling of amino acids derivatives without racemization.

References:
### Buchwald Ligands

#### 15-1142

2'-Dicyclohexylphosphino-2,6-dimethoxy-3-sulfonato-1,1'-biphenyl hydrate sodium salt (water soluble SPhos), min. 98% [870245-75-3]

C₃₆H₄₂NaO₅PS; FW: 512.58; light yellow solid


Technical Note:
1. First general ligand for the Pd-catalyzed Suzuki-Miyaura coupling reaction of aryl chlorides and for the coupling of challenging substrate combinations in water.

![Chemical Structure](image)

**References:**

#### 15-1152

2-(Dicyclohexylphosphino)-3,6-dimethoxy-2',4',6'-tri-i-propyl-1,1'-biphenyl, min. 98% BrettPhos [1070663-78-3]

C₃₅H₅₃O₂P; FW: 536.77; white xtl.; m.p. 191-193°

Note: Buchwald Biaryl Phosphine Ligand Master Kit component. Buchwald Biaryl Phosphine Ligand Mini Kit 1 component. See (page 15).

Technical Notes:
1. Versatile Ligand for the Pd-catalyzed coupling of primary arylamines and alkylamines. a. See also 46-0367 (page 18), 46-0267 (page 19). See reference 7,8.
2. Ligand for palladium-catalyzed cross-coupling reactions using aryl mesylates with electron-deficient anilines.
3. Ligand for palladium-catalyzed cross-coupling of primary arylamines at low catalyst loading.
4. Ligand for palladium-catalyzed cross-coupling of aryl iodides and primary amines.
7. Ligand for the palladium-catalyzed formation of aryl-SCF₃ compounds from aryl bromides.
8. Ligand for the nickel-catalyzed cross-coupling of styrenyl epoxides with boronic acids.

![Chemical Structure](image)
Buchwald Ligands

<table>
<thead>
<tr>
<th>Code</th>
<th>Name</th>
<th>Formula</th>
<th>Notes</th>
</tr>
</thead>
</table>
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Buchwald Ligands

15-1145 2-(Dicyclohexylphosphino)-2'-N,N-dimethylamino)biphenyl, 98% DavePhos [213697-53-1]
(cont.)

2-(Dicyclohexylphosphino)-2'-N,N-dimethylamino)biphenyl, 98% DavePhos [213697-53-1]

(1) Tech. Note (2) Ref. (2)
(2) Tech. Note (3) Ref. (3)
(3) Tech. Note (4) Ref. (4)
(4) Tech. Note (5) Ref. (5)
(5) Tech. Note (6) Ref. (6)
(6) Tech. Note (7) Ref. (7)
(7) Tech. Note (8) Ref. (8)
(8) Tech. Note (9) Ref. (9)
(9) Tech. Note (10) Ref. (10)

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### Buchwald Ligands

**15-1145** 2-(Dicyclohexylphosphino)-2'-{(N,N-dimethylamino)biphenyl, 98% DavePhos** [213697-53-1]**  
(cont.)

References:

**15-1147** 2-Dicyclohexylphosphino-2',6'-dimethylamino-1,1'-biphenyl, min. 98% CPhos** [1160556-64-8]**  
C<sub>28</sub>H<sub>41</sub>N<sub>2</sub>P; FW: 436.61; yellow-orange xtl.; m.p. 111-113°  
Note: Patents: US 6,395,916, US 6,307,087

Technical Notes:
1. Liganad for the Negishi coupling of secondary alkylzinc halides with aryl bromides or chlorides.
2. Preparation of aryl sulfonamides via palladium-catalyzed chlorosulfonylation of arylboronic acids.

**15-1146** 2-Dicyclohexylphosphino-2',6'-di-i-propoxy-1,1'-biphenyl, min. 98% RuPhos** [787618-22-8]**  
C<sub>30</sub>H<sub>43</sub>O<sub>2</sub>P; FW: 466.64; white pwdr.; m.p. 123-124°  

Technical Notes:
   a. See also 46-0266 (page 20), 46-0366 (page 21). See reference 7, 8.
2. Ligand used for the Pd-catalyzed Negishi cross-coupling reaction of (hetero)arylchlorides.
3. Ligand used for the Pd-catalyzed synthesis of N-aryl benzimidazoles.
4. Ligand used for the Pd-catalyzed synthesis of heteroarenes.
5. Versatile ligand used for the Pd-catalyzed C-N coupling reaction of secondary aryl- and alkyl-amines at low temperature with the Pd precatalyst.
**Buchwald Ligands**

15-1146 2-Dicyclohexylphosphino-2',6'-di-i-propoxy-1,1'-biphenyl, min. 98% RuPhos [787618-22-8] (cont.)

References (cont.):
7. Ligand for the palladium-catalyzed trifluoromethylation of hindered aryl chlorides.

References:
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**Buchwald Ligands**

**15-1135**

2'-Dicyclohexylphosphino-2,6-di-i-propyl-4-sulfonato-1,1'-biphenyl hydrate sodium salt (XPhos-SO$_3$Na) [870245-84-4]

C$_{30}$H$_{42}$NaO$_3$PS∙XH$_2$O; FW: 536.68; white solid

Note: Water soluble phosphine. Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15).


**Technical Notes:**
1. Water soluble catalyst for Sonogashira coupling reactions
2. Water soluble catalyst for coupling of benzyl chloride and terminal alkynes.
3. Water soluble ligand for cyanation of aryl chlorides and aryl sulfonates with potassium ferrocyanide.

![Chemical structure of 15-1135](image)

**References:**
2. Synlett., 2006, 18, 2941.

**15-1148**

2-Dicyclohexylphosphino-2'-methylbiphenyl, min. 98% MePhos [251320-86-2]

C$_{25}$H$_{33}$P; FW: 364.51; white xtl.; m.p. 107-110°

Note: Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15). Buchwald Biaryl Phosphine Ligand Mini Kit 2 component. See (page 15).


**Technical Notes:**
1. Ligand used for the Pd-catalyzed formation of a -arylketones.
2. Ligand used for the Pd-catalyzed amination reaction (see 15-1045 page 30).
   a. See (Ref. 5).
3. Ligand used for the Pd-catalyzed hydrazone arylation.
4. Ligand used for the Pd-catalyzed synthesis of 5,5-disubstituted butenolides.
5. Ligand used for the Pd-catalyzed direct arylation of polyfluorinated arenes at room temperature.

![Chemical structures of 15-1148](image)
Buchwald Ligands

15-1148 2-Dicyclohexylphosphino-2'-methylbiphenyl, min. 98% MePhos [251320-86-2] (cont.)

\[
\begin{align*}
\text{R}^1\text{R}^2\text{O} & + \text{X}\text{R}^3 \xrightarrow{\text{Pd, L, K}_2\text{CO}_3} \text{R}^1\text{R}^2\text{O} \\
\text{toluene/t-amyl alcohol (2:1)} & \quad \text{100-110 °C} \\
& \quad \text{68-80%}
\end{align*}
\]

References:

15-1149 2-(Dicyclohexylphosphino)-2',4',6'-tri-i-propyl-1,1'-biphenyl, min. 98% XPhos [564483-18-7]

\[
\begin{align*}
\text{C}_3\text{H}_{13}\text{P} & ; \text{FW: 476.72; white pwdr.; m. p. 185°} \\
\text{Note: Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15). Buchwald Biaryl Phosphine Ligand Mini Kit 1 component. See (page 15).} \\
\text{Patents: US 6,395,916, US 6,307,087.}
\end{align*}
\]

Technical Notes:
1. See also 46-0264 (page 18).
2. Exceptional ligands for Pd-catalyzed amination and amidation of aryl sulfonates. (see Ref. 16).
3. Ligand used for the Pd-catalyzed Suzuki-Miyaura coupling reaction and carbonyl enolate coupling (see Ref. 9).
4. Ligand used for the chemoselective amination of aryl chlorides.
5. Ligand used for the Pd-catalyzed borylation of aryl chlorides.
6. For the formation of trifluoroborates, see also Ref. 11.
7. Ligand used for the Pd-catalyzed amination of vinyl halides and triflates.
8. Ligand used for the Pd-catalyzed three-component synthesis of indoles.
9. Ligand used for the Pt-catalyzed regioselective hydrosilylation of functionalized terminal arylalkynes.
10. Ligand used for the Pd-catalyzed synthesis of carbazoles.
12. Ligand used for the direct arylation of picoline N-oxide.
13. Ligand used for the Negishi coupling of 2-heterocyclic organozinc reagents.
14. Catalyst for a phosphine-catalyzed Heine reaction.
15. Ligand used for the palladium-catalyzed oxidative coupling of indoles and heteroarenes.

\[
\begin{align*}
\text{Bu}^1\text{OSO}_2\text{Ph} & + \text{HNRR'} \xrightarrow{\text{Pd, ligand}} \text{Bu}^1\text{NRR'} \\
\text{Bu}^1 & = \text{n-Butyl; 88%} \\
\text{R, R'} & = \text{H: 88%} \\
\text{R} & = \text{C(O)Me, R'} \quad \text{H: 88%}
\end{align*}
\]

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**Buchwald Ligands**

15-1149  2-(Dicyclohexylphosphino)-2',4',6'-tri-i-propyl-1,1'-biphenyl, min. 98% XPhos \[564483-18-7\] (cont.)

\[
\begin{align*}
\text{Bu}^1\text{O} &= \text{Ts} + (\text{MeO})_2\text{B} \xrightarrow{\text{Pd \ ligand}} \text{Bu}^1\text{O} \\
\text{H}_2\text{N} \text{Cl} + (\text{HO})_2\text{B} \xrightarrow{\text{Pd \ ligand}} \text{H}_2\text{N} \text{Cl} \\
\text{H}_2\text{N} \text{Cl} + (\text{H})_2\text{O} \xrightarrow{\text{Pd \ ligand}} \text{H}_2\text{N} \text{Cl} \\
\text{MeO} \text{Cl} + (\text{B})_2\text{Me} \xrightarrow{\text{Pd \ ligand}} \text{MeO} \text{Cl} \\
\text{NC} \text{H} + (\text{O} \text{Et})_2\text{Me} \xrightarrow{\text{Pd \ ligand}} \text{NC} \text{H} \\
\text{Br} \text{Ph} + \text{NH}_2 + \text{Br} \text{Ph} \xrightarrow{\text{Pd \ ligand}} \text{Br} \text{Ph} \\
\text{R}^1\text{OTf} + \text{R}^2\text{NH}_2 \xrightarrow{1) \text{Pd(OAc)}_2, \text{ligand} \ 2) \text{O}_2, \text{AcOH} \ 2) \text{O}_2, \text{AcOH}} \text{R}^1\text{N} \text{Ph} \\
\text{Br} \text{O} \text{Me} + \text{Cl} \text{B} \xrightarrow{[\text{Si}]-\text{H}, \text{THF}} \text{Br} \text{O} \text{Me} \\
\text{R}^1\text{OTf} + \text{R}^2\text{NH}_2 \xrightarrow{1) \text{Pd(OAc)}_2, \text{ligand} \ 2) \text{O}_2, \text{AcOH} \ 2) \text{O}_2, \text{AcOH}} \text{R}^1\text{N} \text{Ph} \\
\text{Br} \text{O} \text{Me} + \text{Cl} \text{B} \xrightarrow{\text{Pd(OAc)}_2, \text{L} \text{toluene-H}_2\text{O}} \text{Br} \text{O} \text{Me} \\
\end{align*}
\]
### Buchwald Ligands

#### 15-1149

**2-(Dicyclohexylphosphino)-2',4',6'-tri-i-propyl-1,1'-biphenyl, min. 98% XPhos**  
[564483-18-7]

(cont.)

![Chemical structure](image)

- Tech. Note (11)
- Ref. (12)
- Tech. Note (12)
- Ref. (13)
- Tech. Note (13)
- Ref. (14)
- Tech. Note (14)
- Ref. (15)

### References:


#### 15-1745

**2-Diphenylphosphino-2'-(N,N-dimethylamino)biphenyl, 98% PhDavePhos**  
[240417-00-9]

- 500mg
- 2g
- 10g

*C$_2$H$_{24}$NP; FW: 381.46; white pwdr.

Note: Buchwald Biaryl Phosphine Ligand Master Kit component. See (page 15). Buchwald Biaryl Phosphine Ligand Mini Kit 2 component. See (page 15).


### Technical Notes:

1. Useful ligand for sterically hindered substrates in the Pd-catalyzed amination reactions of aryl bromides.
2. Ligand employed in the coupling of enantiomerically pure cis-dimethylpiperazine with bromobenzene. Epimerization was not observed.
3. Ligand employed for the Pd-catalyzed heteroarylation of acetone.
4. Ligand used for the Cu-catalyzed phosphorylation of alcohols.
Buchwald Ligands

15-1745  2-Diphenylphosphino-2′-(N,N-dimethylamino)biphenyl, 98% PhDavePhos [240417-00-9]
(cont.)

\[
\begin{align*}
\text{Br-Ph} & \quad + \quad \text{MeNMe} \quad \xrightarrow{\text{Pd}_2(\text{dba})_3, \text{ligand}} \quad \text{PhN-NPh} \\
\text{NC-Br} & \quad + \quad \text{Bu}_3\text{SnOMe} \quad \xrightarrow{\text{Pd}_2(\text{dba})_3, \text{ligand, toluene, 100 °C}} \quad \text{NC-PhCMe} \\
\text{PhOH} & \quad + \quad \text{OPOPh} \quad \xrightarrow{\text{Cu(OTf)}_2, \text{ligand, Et}_3\text{N, DCM, 20 °C}} \quad \text{OPPOPh} \\
\text{PhCl} & \quad + \quad \text{SPhos-AuNTf}_2 \quad \xrightarrow{\text{Cs}_2\text{CO}_3, \text{toluene, 110 °C}} \quad \text{OPOPh}
\end{align*}
\]

References:

Gold Catalysts Based on Buchwald Ligands

79-0230  Bis(trifluoromethanesulfonyl)imide(2-dicyclohexylphosphino-2′,6′-dimethoxy-1,1′-biphenyl)gold(I), 98% [1121960-90-4]

\[
\begin{align*}
\text{PhO} & \quad + \quad \text{OME} \quad \xrightarrow{2 \text{ mol\% Pd(OPiv)}_2, 4 \text{ mol\% L, Cs}_2\text{CO}_3, \text{toluene, 110 °C}} \quad \text{PhO} \\
\text{PhCl} & \quad + \quad \text{Cu(OTf)}_2 \quad \xrightarrow{\text{ligand, Et}_3\text{N, DCM, 20 °C}} \quad \text{PhO}
\end{align*}
\]

Technical Notes:
1. Highly-efficient and regio-selective catalyst for the selective carbonyl migration in alkynyl-substituted indole-3-carboxamides.
2. Catalyst used in the hydroarylation/aromatization of arene-diynes.
3. Catalyst used in the selective hydration of substituted alkynes at room temperatures.
Gold Catalysts Based on Buchwald Ligands

**79-0230**  Bis(trifluoromethanesulfonylimide(2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl)gold(I), 98% [1121960-90-4]

(Cont.)

![Reaction Diagram]

References:

**79-0225**  Chloro(2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl)gold(I), 98% [854045-95-7]

C_{25}H_{35}AuClO_2P; FW: 642.95; white pwdr.

Technical Note:
1. See 79-0230 (page 48).

**79-0343**  Chloro[2-(dicyclohexylphosphino)-2'-(N,N-dimethylamino)biphenyl]gold(I), 98% [1196707-11-5]

C_{25}H_{35}AuCINP; FW: 625.96; white pwdr.

Technical Note:
1. See 79-0348 (page 49).

**79-0352**  2-(Di-t-butylphosphino)biphenyl(acetonitrile)gold(I) hexafluoroantimonate, 99% [866641-66-9]

C_{22}H_{30}F_6AuNPSb; FW: 772.17; white to off-white pwdr. air sensitive, moisture sensitive

**79-0348**  [2-(Dicyclohexylphosphino)-2'-N,N-dimethylamino)biphenyl][bis(trifluoromethyl)sulfonylimido]gold(I), 98% [1188507-66-5]

C_{28}H_{36}AuF_6N_2O_4PS_2; FW: 870.66; yellow pwdr.

Technical Note:
1. Catalyst used in the formation of a bisenamine from toluidine and phenylacetylene.

Reference:
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