# Quick-reference Guide to Pd/Phosphine Catalysts in Suzuki Couplings

| **#** | **Common identification** | **Hits** |
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| 1 | **Pd(PPh₃)₄** (tetrakis-triphenyl-phosphine Pd(0)) | **8 955** |
| 2 | **PdCl₂(PPh₃)₂** | **1 651** |
| 3 | **Pd(0) / Pd black** | **206** |
| 4 | **Pd(Pᵗᴮᵘ₃)₂** | **113** |
| 5 | **PdCl₂** | **81** |
| 6 | Pd(PPh₂H)₄-like | **57** |
| 7 | **PdCl₂[P(o-tolyl)₃]₂** | **45** |

This guide summarizes when chemists in the USPTO 2010‑2016 dataset (11 177 reactions with an explicit \*catalyst1\* entry) choose one of four common Pd/phosphine systems.  
  
Key descriptors that differentiate catalyst choice include:  
• Leaving‑group identity (Cl < Br < I reactivity)  
• Ortho‑substitution on the aryl halide and the organoboron partner  
• Organoboron class (boronic acid vs. boronic ester)  
  
Use the table below to select a starting catalyst, then escalate ligand bulk/electronics when substrates become more sterically hindered or electronically deactivated.

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| Catalyst (pre‑catalyst) | When it is usually chosen | Leaving‑group bias | Ortho congestion tolerance (aryl halide / boronate) | Predominant organoboron class | Practical tips |
| Pd(PPh₃)₄ | Default workhorse for uncomplicated couplings; economical, bench‑stable Pd(0) source | Br ≈ 56 % Cl ≈ 27 % I ≈ 12 % | Single‑ortho common; double‑ortho only 6 % / 2 % | Boronic acids ≈ 65 % | Aqueous carbonate/phosphate bases in DMF, EtOH, or mixed protic media at 60–100 °C |
| PdCl₂(PPh₃)₂ | Slightly tougher electrophiles with more chlorides or steric hindrance | Br ≈ 56 % Cl ≈ 32 % | Similar to Pd(PPh₃)₄ (double‑ortho 6 % / 1 %) | Boronic acids ≈ 65 % | Requires in‑situ reduction; conditions otherwise mimic Pd(PPh₃)₄ |
| Pd(PtBu₃)₂ | Challenging heteroaryl/aryl chlorides and/or bulky boronic esters | Br ≈ 56 % Cl ≈ 37 % | Double‑ortho modest (3 % / 15 %) but overall high steric bias | ≈ 50 % acids / 42 % esters | Strong anhydrous bases (KOtBu, Cs₂CO₃) in toluene, xylene, dioxane at 100–120 °C; keep phosphine:Pd low |
| PdCl₂[P(m‑tolyl)₃]₂ | Severely ortho‑blocked aryl bromides of high MW | Br ≈ 91 % Cl ≈ 6 % | Highest double‑ortho on halide (12 %) but low on boronate (2 %) | Boronic acids ≈ 98 % | Bases like K₃PO₄, NaOtBu in xylene/DME 110–140 °C; niche but invaluable for "brick‑wall" bromides |

How to use:  
1. Start with Pd(PPh₃)₄ or PdCl₂(PPh₃)₂ for routine Br/I couplings or mildly hindered chlorides.  
2. Escalate to Pd(PtBu₃)₂ when either partner is sterically congested or the electrophile is a heteroaryl/aryl chloride.  
3. Reserve PdCl₂[P(m‑tolyl)₃]₂ for high‑MW, double‑ortho aryl bromides that stall under PPh₃ systems.

## Alkyl Substrate Usage

Industrial Suzuki data show that coupling partners bearing sp³ carbon (alkyl halides or alkyl‑boron reagents) are rare overall. When they are present, they appear almost exclusively as the boron component, and primarily with the two PPh₃‑based systems. Bulky PtBu₃ and m‑tolyl ligands are directed toward sterically hindered \*aryl\* substrates, not Csp³ chemistry.

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| Catalyst | Dataset rows | Alkyl halide hits | Alkyl halide % | Alkyl boron hits | Alkyl boron % |
| Pd(PPh₃)₄ | 8955 | 32 | 0.36 % | 497 | 5.6 % |
| PdCl₂(PPh₃)₂ | 1651 | 28 | 1.7 % | 110 | 6.7 % |
| Pd(Pᵗᴮᵘ₃)₂ | 113 | 0 | 0 % | 4 | 3.5 % |
| PdCl₂[P(m‑tolyl)₃]₂ | 45 | 0 | 0 % | 2 | 4.4 % |