Bimetallic Pd(III) Complexes in Palladium-Catalysed Carbon-Heteroatom Bond Formation


Wynter Gilson
Literature Presentation
August 7, 2009
Palladium-Catalysed Carbon-Heteroatom Bond Formation

\[
Pd(II)_{d^8} - \text{Square Planar}
\]

\[
Pd(III)_{d^7} - \text{Octahedral}
\]

\[
2 \text{Pd(II)} + 2 \text{OAc} + X + \text{C}_{13}\text{H}_8\text{N}
\]
Pd(III)-Pd(III) Formation Followed by Bimetallic Reductive Elimination

1. AgOAc
   - AgCl

2. 1. AgOAc
   2. AgCl
Bond Distances: Pd(II) vs Pd(III)

1 Pd–Pd 2.84 Å

2 Pd–Pd 2.57 Å
Mechanistic Study

Path 1
1a, Dissociation
1b, Reductive elimination

Path 2
Disproportionation to Pd(II) and Pd(IV)

Path 3
Reductive elimination from cationic Pd(III)

Chemical structures and reactions are depicted in the diagram.
Mechanistic Study

Path 1
1a, Dissociation
1b, Reductive elimination

Path 2
Disproportionation to Pd(II) and Pd(IV)

Path 3
Reductive elimination from cationic Pd(III)

2 + 4 → 3
Mechanistic Study

Path 1
1a, Dissociation
1b, Reductive elimination

Path 2
Disproportionation to Pd(II) and Pd(IV)

Path 3
Reductive elimination from cationic Pd(III)

4 + 3
Mechanistic Study

Path 4
1,2-reductive elimination

Path 5, consistent with data
Concerted 1,1-reductive elimination
Mechanistic Study

Path 4
1,2-reductive elimination

Path 5, consistent with data
Concerted 1,1-reductive elimination
Bridging Acetate Ligand Replaced by Chealating Ligand

\[ \text{Pd} \left( \text{espH}_2 \right)_2 \text{CH}_2\text{Cl}_2, 23^\circ \text{C} \rightarrow \]

\[ \text{Cl} \text{Pd} \left( \text{espH}_2 \right) \text{CH}_2\text{Cl}_2, -30^\circ \text{C} \rightarrow \]

\[ \text{98\% yield from 6} \]

\[ \text{Cl} \text{Pd} \left( \text{espH}_2 \right) \text{CH}_2\text{Cl}_2, 23^\circ \text{C} \rightarrow \]

\[ \text{3} \]
Deuterium Study

1 + XeF₂ → 2. TMSOAc → 9 Pd–Pd 2.57 Å → CH₂Cl₂, 23 °C, 64% → 10

9-\textit{d}_6 \rightleftharpoons 11-\textit{d}_6 \xrightarrow{k_1} \xrightarrow{k_{-1}} 23 °C → 10:10-\textit{d}_3 = 1:1
Palladium-Catalysed Reaction

**Part a:**

25 mol% 1
0.25 equiv. PhlCl₂, CH₂Cl₂

Isolated in 90% yield based on 1

**Part b:**

5 mol% 1 or 2 or 4 or 6 or Pd(OAc)₂

N-chlorosuccinimide, MeCN, 100 °C, 50 h

90 ± 5% yield