



Diamondoid Phosphines - Selective Phosphorylation of Nanodiamonds

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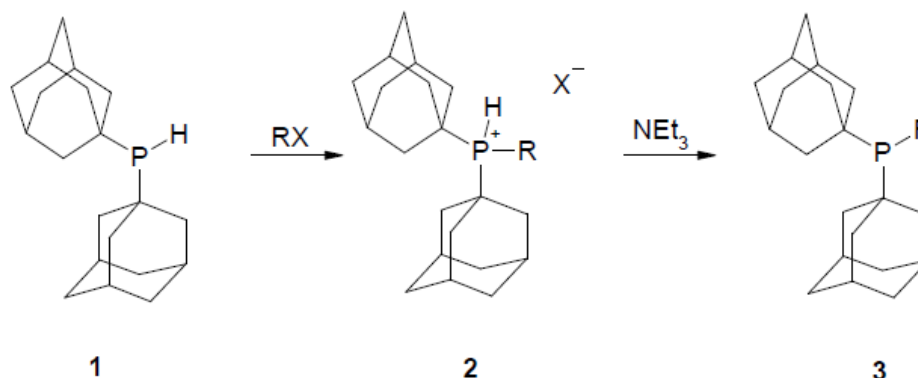
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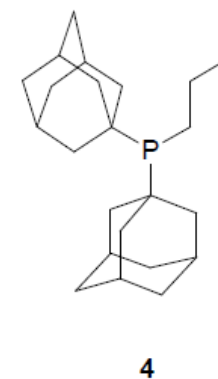


1) Diamondoid Phosphines – new efficient ligands

- 2000 → first use of di(1-adamantyl)alkylphosphines as sterically demanding and electronrich ligands



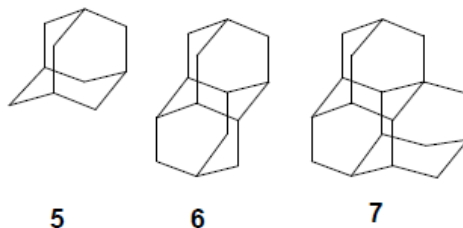
- **4** is an excellent ligand for Heck and Suzuki coupling reactions





1) Diamondoid Phosphines – new efficient ligands

- adamantane is an excellent bulky moiety in phosphine ligands
- diamondoids

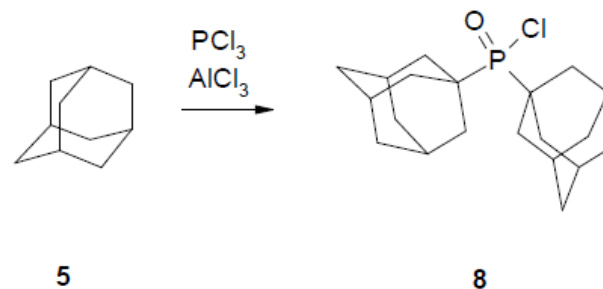


- 2010 → Can higher diamondoids also be phosphorylated and potentially used as ligands?

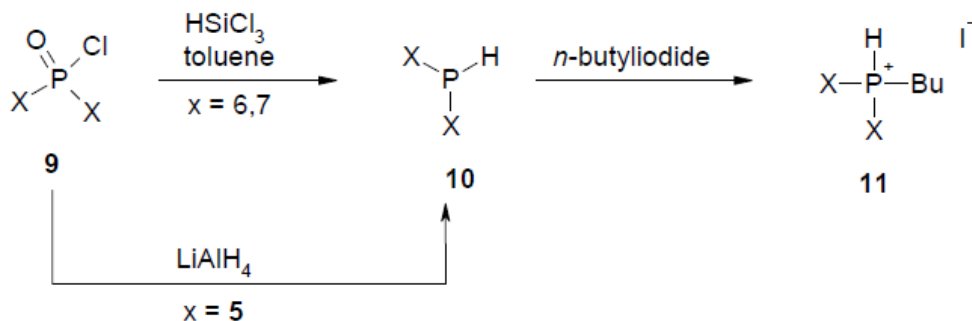


Diamondoid Phosphines – new efficient ligands

- selective conversion of **5**, **6**, **7** into diorganophosphinic acid chlorides under Friedel-Crafts-like conditions



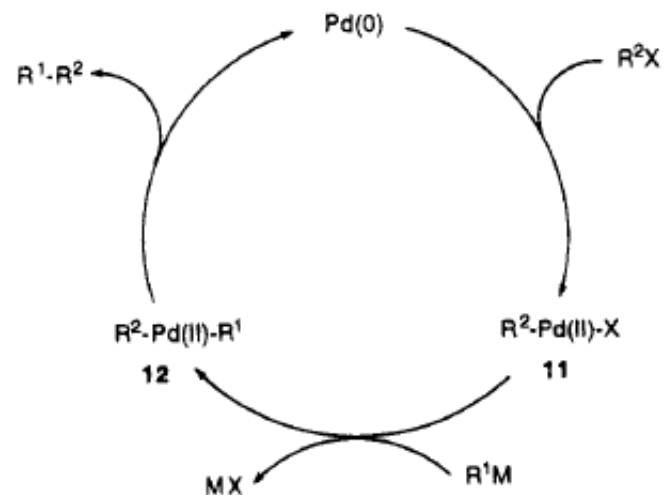
- subsequent reduction and alkylation



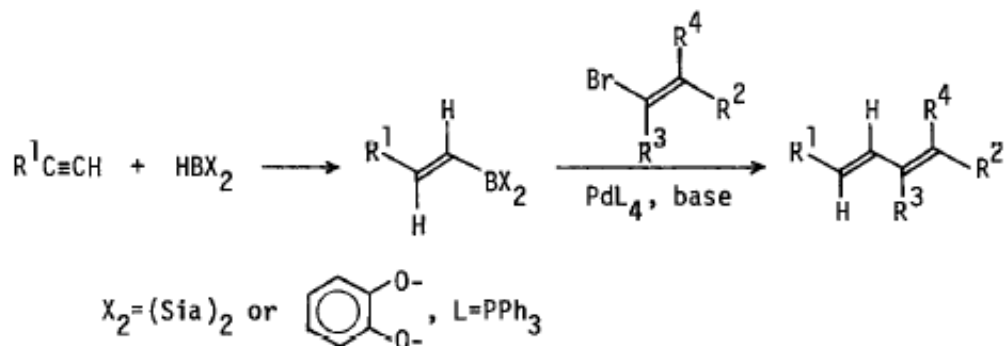


2) Palladium-catalyzed coupling reactions

general catalytic cycle for cross coupling

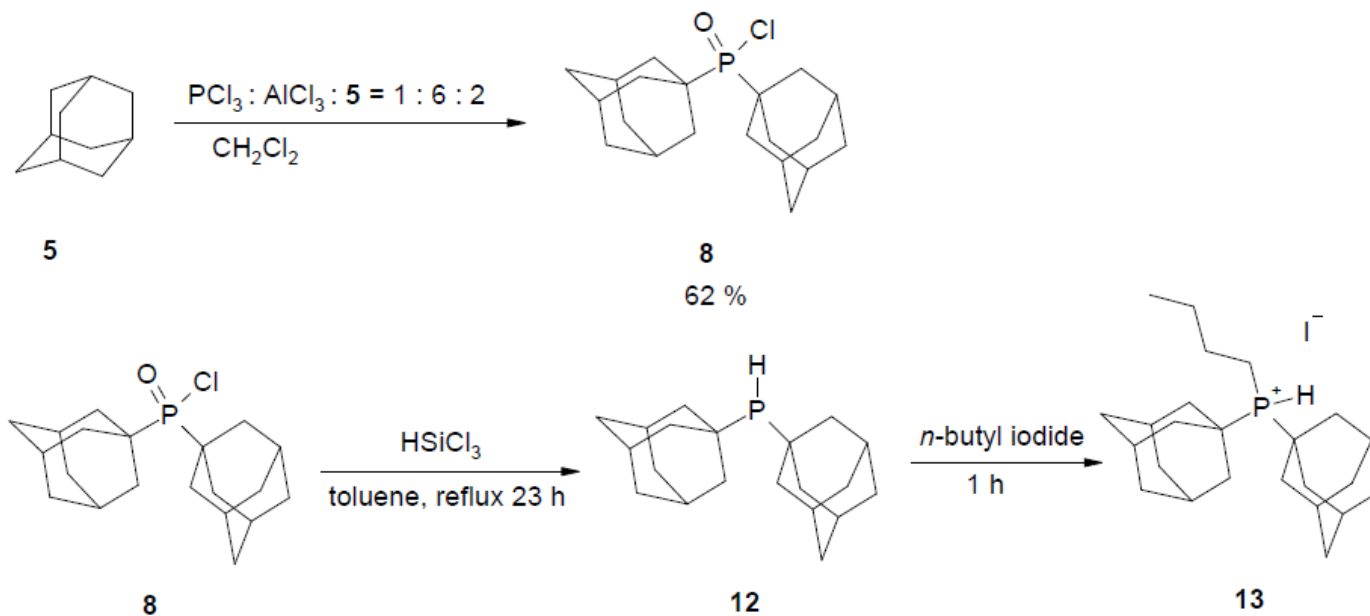


- 1979, novel cross-coupling reaction of 1-alkenylboranes with 1-alkenyl halides



3) Experimental section

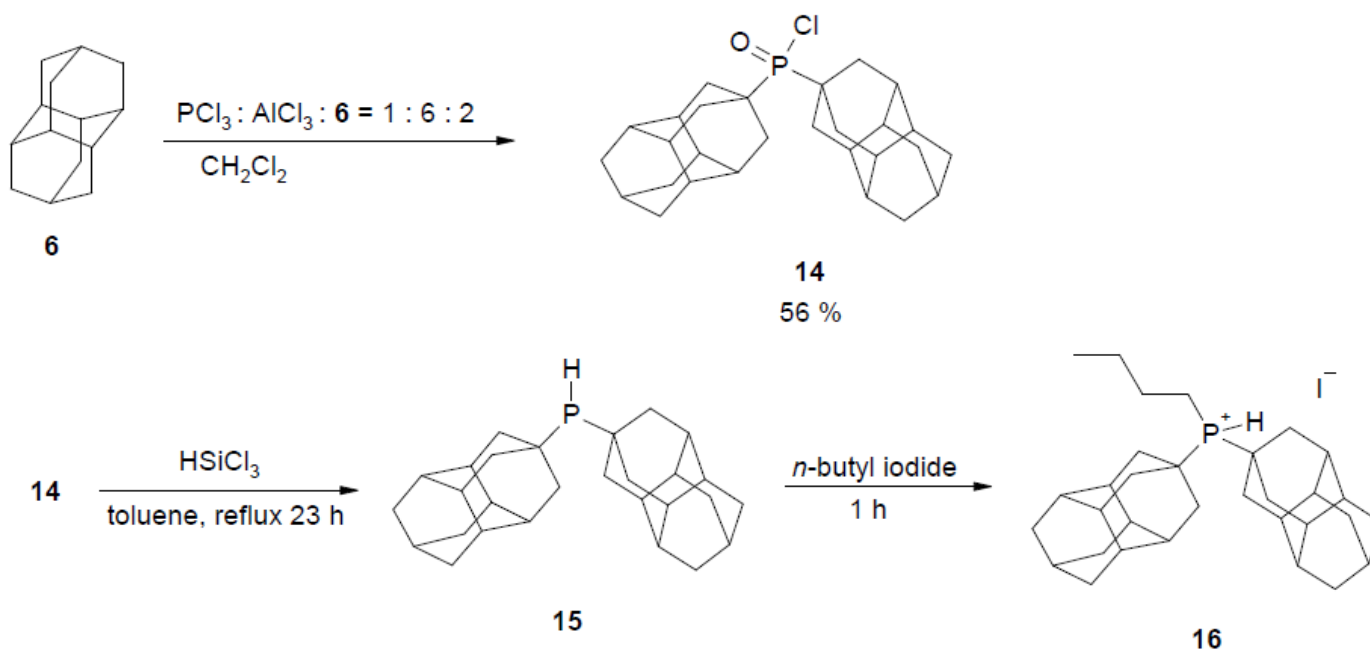
- synthesis of Di-1-adamantyl-*n*-butylphosphonium iodide



→ unsuccessful reduction

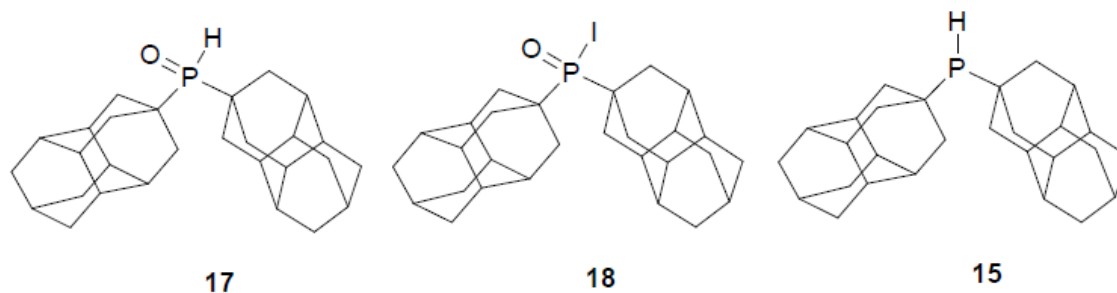
3) Experimental section

- synthesis of Di-4-diamantyl-*n*-butylphosphonium iodide

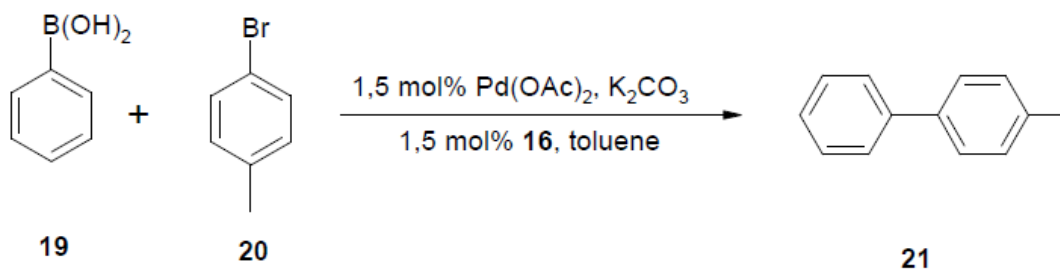


3) Experimental section

- side products



- suzuki coupling with pure **16** and without





4) Results

- GC/MS measurement

	without 16	with 16
retention time <i>p</i> -Bromtoluene [min]	9,77	9,77
abundance	1.100.000	≈ 0
retention time 4-Phenyltoluene [min]	14,70	14,70
abundance	1.900.000	800.000

- no isolate without co-ligand
- with co-ligand: good yield, but contaminated