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## Transition Metal Induced Topotactic C-C Bond Formation

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## TRANSITION METAL INDUCED TOPOTACTIC C-C BOND FORMATION

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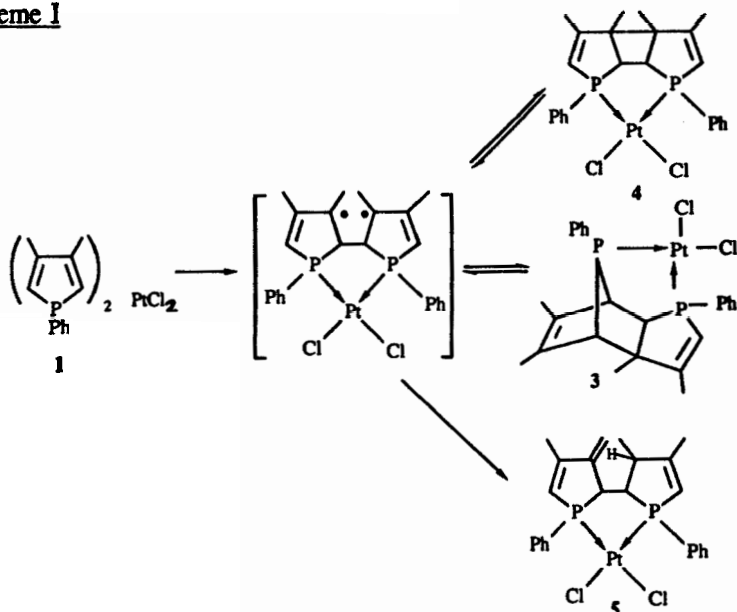
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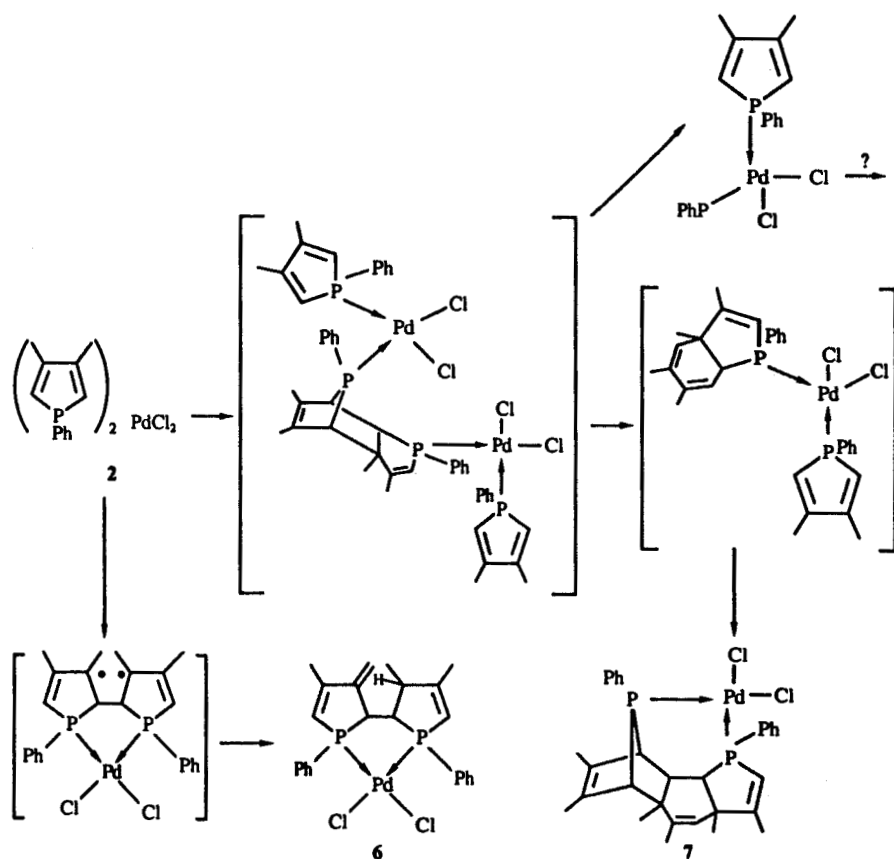
**Abstract** The thermolyses of dichlorobis-(1-phenyl-3,4-dimethylphosphole) platinum (II), **1**, and dichlorobis-(1-phenyl-3,4-dimethylphosphole) palladium (II), **2**, were investigated in 1,1,2,2-tetrachloroethane solutions and in the crystalline state. The solid state reactions show a high degree of topotacticity and probably involve 1,4-biradical intermediates. Three compounds are formed upon thermolysis of **1** in 1,1,2,2-tetrachloroethane at 142°C (scheme I): a [4+2] cycloaddition product, **3**; a [2+2] cycloaddition product, **4**, and a compound, **5**, that results from 1,5-hydrogen migration from a methyl group on one phosphole to the  $\beta$ -carbon of an adjacent phosphole. Only **5** is ultimately formed in quantitative yield from **1** after 24 hours at 150°C in the solid state.

### Scheme I



Under similar conditions **2** is recovered unchanged from 1,1,2,2-tetrachloroethane solution unless **2** is rigorously devoid of any traces of adventitious DMPP. Then both in solution and in the solid state **2** is quantitatively converted to a mixture of **6**, the palladium analog of **5**, an uncharacterized compound and a totally new compound, **7**, that is formed by the sequence (scheme II): a) intermolecular [4+2] cycloaddition, b) phosphinidene elimination, and c) intramolecular [4+2] cycloaddition.

**Scheme II**



Analogs of 3, 4, and 5 and 7 have been characterized by single crystal X-ray crystallography (Figures 1-4).

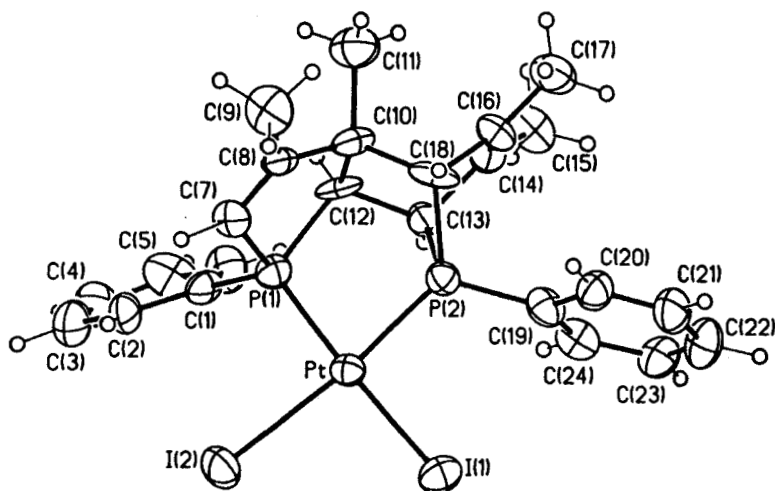


Figure 1 Ortep plot of an analog of 3

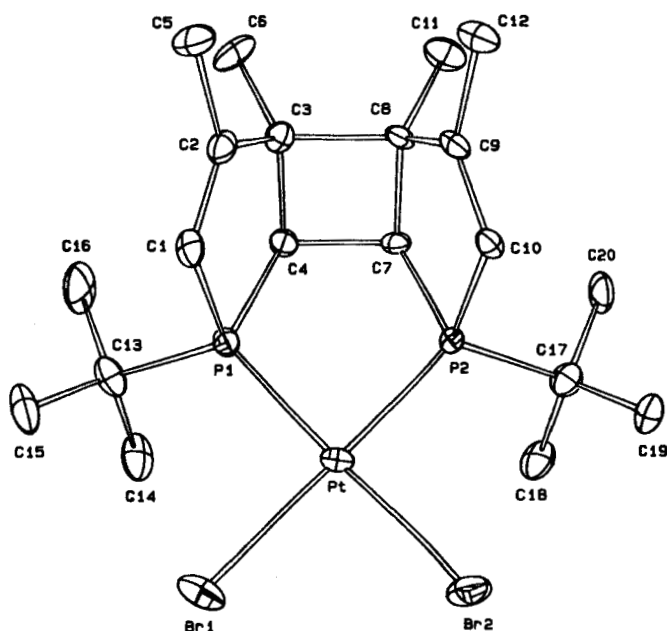


Figure 2 Ortep plot of an analog of 4

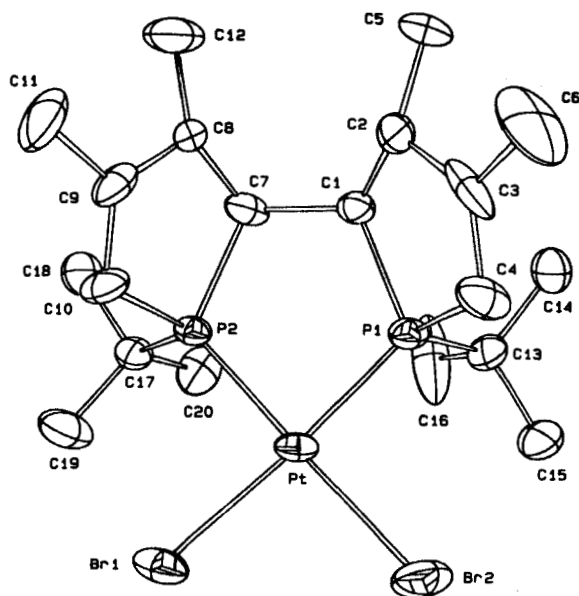


Figure 3 Ortep plot of an analog of 5

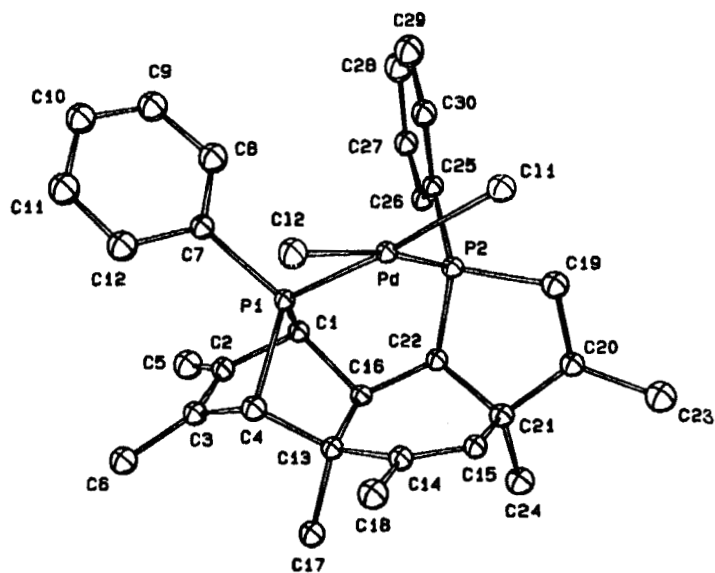


Figure 4 Ortep plot of 7

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