

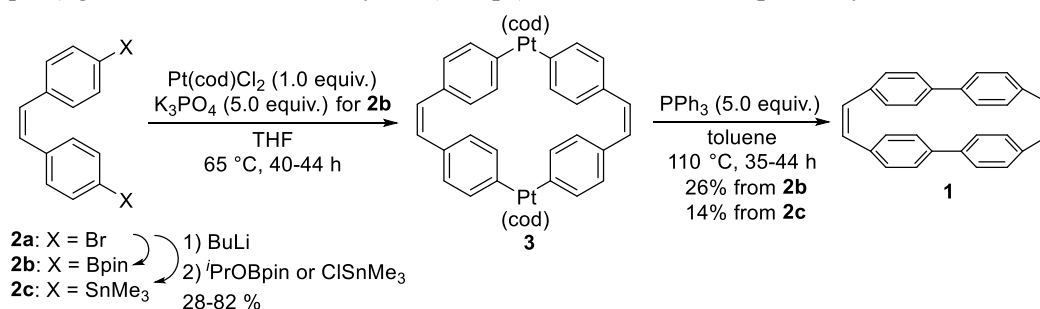
Synthesis of Dehydro[2.2]cyclophanes Using Cyclic Platinum Complex

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[2,2]Cyclophanes ([2,2]CPs), in which aromatic units are linked by two tethers to form a cyclic structure, have attracted significant attention due to unique physical properties, such as through-space conjugation, and the highly strained structures.^{1,2} However, the structural variation has been severely limited due to the lack of an effective and general synthetic method.³ Here we report a new synthetic method of tetrahydro[2,2]paraCP (**1**, Scheme 1),⁴ in which a paraphenylene unit is linked by double ethene-tethers, by extending the synthetic method used for the synthesis of cycloparaphenylenes.⁵

The synthesis started with a 4,4'-dibromo-*cis*-stilbene **2a** (X = Br), and a twofold bromine–borane exchange reaction afforded bis-boronate **2b** (X = Bpin) in 82% yield. Then **2b** reacted with Pt(cod)Cl₂ (cod = 1,5-cyclooctadiene, 1.0 equiv.) in the presence of K₃PO₄ (5.0 equiv.) in THF at 65 °C to afford bis-platinum complex **3**. The platinum-mediated dimerization was also achieved by using a 1:1 mixture of **2c** (X = SnMe₃) and Pt(cod)Cl₂ to give **3**. Subsequent reductive elimination of platinum from **3** in the presence of PPh₃ (5.0 equiv.) gave **1** in 26% and 14% yield (2 steps) from **2b** and **2c** respectively.



Scheme 1. Synthesis of 1.

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