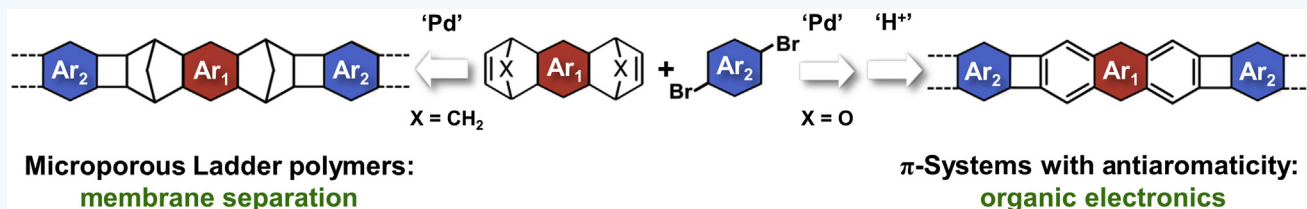


Catalytic Arene (oxa)Norbornene Annulation (CANAL)

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Trends in Chemistry

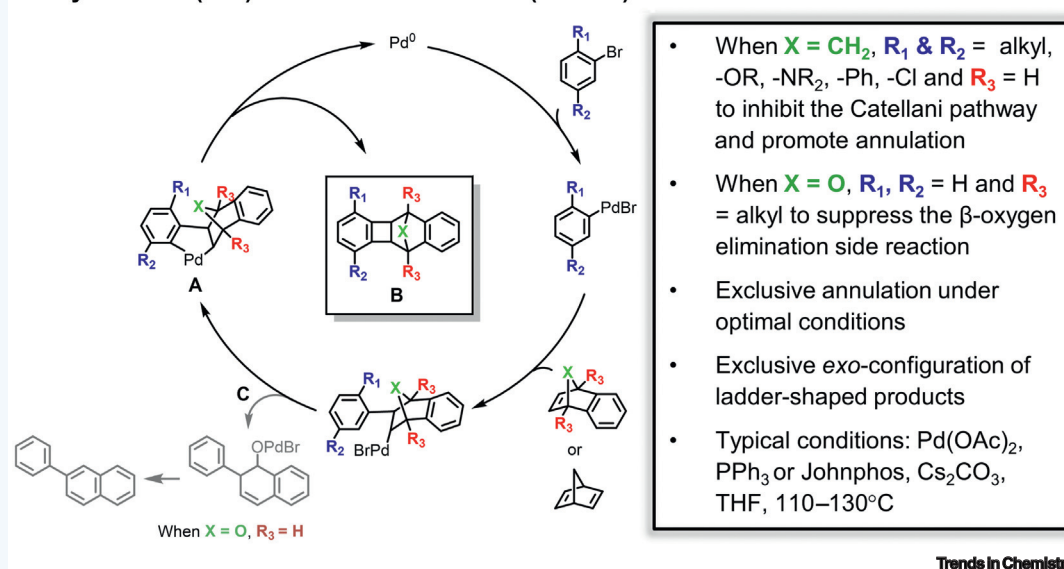
ORIGIN

Conformationally rigid ladder-shaped small molecules and polymers exhibit unusual properties but are usually challenging to synthesize. Inspired by the norbornene-mediated Pd-catalyzed C–H functionalization first developed by Catellani, we repurposed this reaction into efficient and versatile catalytic arene (oxa)norbornene annulation (CANAL) to synthesize two distinct types of ladder-shaped organic materials: rigid contorted ladder polymers and diverse polycyclic conjugated hydrocarbons (PCHs) containing antiaromatic cyclobutadienoids (CBDs).

REACTION MECHANISM

In the classic Catellani reaction, norbornene is used as a mediator to direct a Pd catalyst to activate the ortho C–H bond of an aryl halide (often iodide) and form an aryl-norbornyl-palladacycle **A**, which then reacts with another alkyl or aryl halide to functionalize the ortho position. A largely overlooked side-reaction pathway is reductive elimination of Pd from the palladacycle **A** to form **B** with a four-membered ring. We envisioned this annulation pathway to be extremely useful for developing rare ladder-type polymers as novel materials. The challenge is tuning this side-reaction pathway to be exclusively selective and markedly efficient, requirements for being used in polymerization. We discovered that placing simple substituents at the appropriate positions on aryl bromides is an effective means to inhibit the Catellani pathway and promote annulation. Under relatively simple conditions, using norbornadiene and aryl dibromides, we have synthesized a series of rigid ladder polymers with fused norbornyl benzocyclobutene backbones in different conformations and molecular weights up to a few hundred thousand Daltons. These polymers exhibit high microporosity and exciting performance as membrane materials for gas separations. We also tuned the CANAL chemistry to synthesize conjugated ladder molecules containing antiaromatic CBDs, using oxanorbomenes (X = O) as the substrates, followed by aromatization. Bridge head alkyl substituents R₃ on oxanorbomenes are used to suppress a ring-opening β-oxygen elimination pathway **C** that strongly competes with the CANAL pathway. Using a two-step CANAL-aromatization strategy, we have synthesized many PCHs with varying degrees of antiaromaticity and optoelectronic properties.

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IMPORTANCE

The CANAL reaction enables facile access to two distinct types of unusual organic materials, microporous ladder polymers and conjugated hydrocarbons containing antiaromaticity, using readily available substrates. Tuning of substrate structures and synthetic conditions led to highly efficient and selective annulation. This chemistry demonstrates the critical role of new synthetic methodology and catalysis in driving innovation in organic materials.

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