



Noteworthy Chemistry

March 3, 2008

[Increased efficiency of cross-metathesis reactions for hindered olefins](#)

[Anything might be a solar cell: your clothing, your hat, your bag . . .](#)

[Straightforward synthesis of new carbazole-based conductive polymers](#)

[Synthesize and purify polymers in one pot](#)

[A nucleophile - electrophile switch improves diastereomer separation](#)

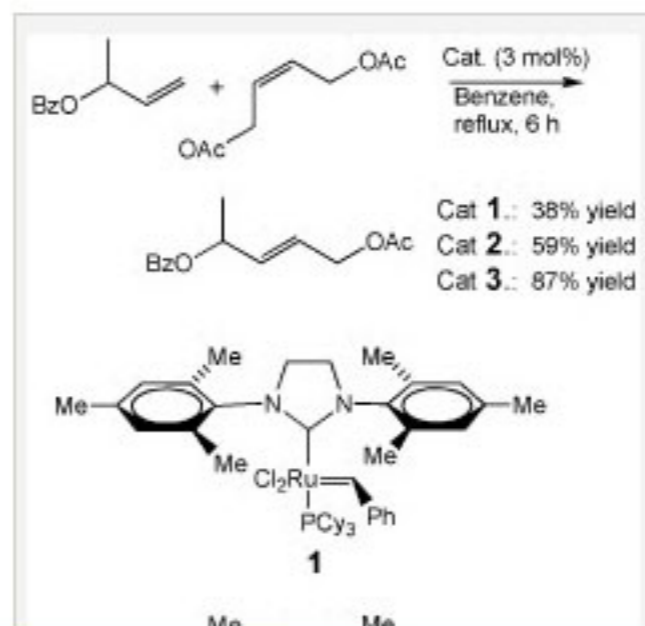
[Temperature-responsive films exhibit asymmetric 3-D shape changes](#)

[Gold nanoparticles initiate photorelease of carboxylic acids](#)

Cross-metathesis reactions show increased efficiency for sterically hindered olefins. I. C. Stewart, D. J. Douglas, and R. H. Grubbs* at Caltech (Pasadena) note that the steric bulk of N-heterocyclic carbene (NHC) ligands of ruthenium-based catalysts significantly affects the efficiency of olefin cross-metathesis (CM) reactions. Whereas NHC ligands establish a general model for selectivity in CM, steric congestion at the site of the reactive olefin moiety is also a limiting condition.

The authors' strategy in this study was to reduce the steric bulk of NHC ligands and assess their efficiency in sterically hindered CM reactions. They investigated the effect of three ruthenium-based metathesis catalysts (**1** - **3**) on olefinic substrates with various allylic substituents. In one experiment, they examined the reaction of 3-buten-2-yl benzoate with *cis*-1,4-diacetoxy-2-butene to form an allylic benzoate as the CM product.

Catalyst **3** produced the desired CM product in an impressive 87% yield; this is consistent with the authors' earlier results with **3** in forming tetrasubstituted olefins by ring-closing metathesis. They subsequently compared catalysts **2** and **3** in several sterically challenging CM reactions,



[Back to Top](#)

Anything might be a solar cell: your clothing, your hat, your bag . . . A "traditional" solar cell is shaped like a plate and uses a transparent electrode such as indium tin oxide (ITO) glass; it requires sophisticated manufacturing equipment and processing. The problems associated with these characteristics—large size, severe angle dependence, mechanical fragility, and high production cost—make it difficult for these devices to be used in microelectronic systems, harsh environments, and commodity products.

A team led by D. Zou at Peking University (Beijing) has made a solar cell with the configuration steel/TiO₂/dye/electrolyte/poly(vinylidene fluoride)/Pt, in which the dye is *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) and the electrolyte is LiI/I₂/3-methyl-2-oxazolidinone/MeCN. The cell is a thin strand that can be very small and almost angle-independent. It uses metal wires as electrodes, circumventing the need for fragile ITO plates. It can be made on the bench in an ordinary laboratory, reducing the production costs associated with vacuum chambers and clean rooms.

In addition, the cells can be woven into products of almost any shape and form because of their strength and flexibility. In civilian life, everything around us could be a solar cell—our clothing, hats, bags, etc. In the military, everything carried and used by soldiers could be power sources: ropes, netting, helmets, tents . . . the possibilities are endless. (*Adv. Mater.* **2008**, *20*, [592 - 595](#); [Ben Zhong Tang](#))

[Back to Top](#)

Here's a straightforward synthesis of new carbazole-based conductive polymers.

T. Michinobu*, H. Osako, and K. Shigehara* at the Tokyo University of Agriculture and Technology prepared alkyne-linked poly(1,8-carbazole) polymers. They functionalized starting material *N*-hexadecylcarbazole (**1**) in the 3- and 6-positions by treating it with *t*-BuCl in the presence of AlCl₃. Treating intermediate **2** with excess *N*-iodosuccinimide (NIS) produced 1,8-diiodo compound **3**.

Trimethylsilylacetylene was then attached at the 1- and 8-positions under Cu-Pd-catalyzed Sonogashira coupling conditions. Intermediate **4** was deprotected with base to remove the trimethylsilyl groups and produce 1,8-diacetylenecarbazole derivative **5**, which was easily polymerized or copolymerized. TMEDA is *N,N,N',N'*-tetramethylethylenediamine.

