

of these crystals were also inactive for the hydrogenation of olefins or nitrobenzene. A preliminary  $^{31}\text{P}$  NMR study also lends support to the above mechanism and shows that  $\text{H}_2$  reversibly adds to **1** in  $\text{CH}_2\text{Cl}_2$  solution at ambient temperature. Under 1 atm of  $\text{H}_2$ , the original  $^{31}\text{P}$  resonance of **1** observed under  $\text{N}_2$  ( $\delta$  55.0,  $J_{\text{Pt-P}} = 497$  Hz) is replaced by a new resonance ( $\delta$  51.1,  $J_{\text{Pt-P}} = 391$  Hz). This change is completely reversible as the original spectrum of **1** reappears in about 15 min under an  $\text{N}_2$  purge. An investigation into the nature of this new species is underway.

Other studies in progress include homogeneous and heterogeneous  $\text{H}_2$ - $\text{D}_2$  equilibration reactions with Pt-Au hydride clusters, other M-Au clusters (M = Pd, Rh, Re, Ru, Ir, and Os), Pt-Au clusters which contain Cu, Ag, Hg, or Sn as a third metal, and a variety of metal carbonyl clusters. A large variety of such M-Au compounds have recently been prepared<sup>16,24-26,28,29</sup> and should provide important structure-reactivity relationships for the activation of  $\text{H}_2$ .

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**Registry No.** **1**, 110870-04-7; **2**, 107712-38-9; **3**, 131793-14-1; **4**, 131793-10-7; **6**, 12120-15-9;  $\text{H}_2$ , 1333-74-0;  $\text{D}_2$ , 7782-39-0.

**Supplementary Material Available:** Kinetic plots illustrating a typical  $\text{H}_2$ - $\text{D}_2$  equilibration reaction for **2** and the concentration dependence on the rate for **1** (3 pages). Ordering information is given on any current masthead page.

(28) Ito, L. N.; Felicissimo, A. M. P.; Pignolet, L. H. *Inorg. Chem.* **1991**, *30*, 988.

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## Coordinative Cocatalysis via $\text{In}^{3+}$ . A Chemoselectivity Switch for Pd-Catalyzed Cycloadditions

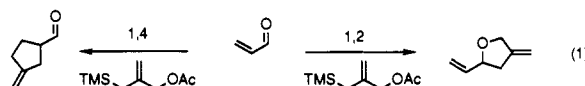
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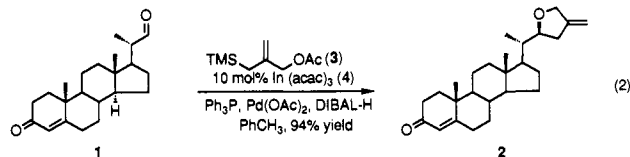
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Control of 1,2 vs 1,4 addition reactions of nucleophiles with  $\alpha,\beta$ -unsaturated aldehydes and ketones represents a general challenge. The tremendous impact of copper in redirecting "hard" nucleophiles from 1,2 to 1,4 addition illustrates the importance of the problem.<sup>1</sup> The development of Pd-catalyzed trimethylenemethane (TMM) cycloaddition to give five-membered rings<sup>2</sup> has the characteristics of a conjugate addition followed by cyclization.<sup>3</sup> To expand the scope of this ring-forming methodology to the formation of heterocycles, we sought to redirect this

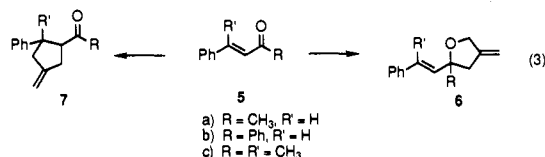
reaction from a 1,4 addition pathway to a 1,2 route with enones (eq 1). We wish to record the remarkable effect that  $\text{In}^{3+}$  complexes<sup>4</sup> have on controlling the chemoselectivity of this cycloaddition.



Earlier work in our laboratories established the feasibility of trimethyltin acetate as a cocatalyst to effect cycloaddition of TMM to the carbonyl group of mainly aldehydes.<sup>5</sup> However, it had only a minor effect on the conjugate vs 1,2 competition of cycloaddition to enones. Believing a more electropositive cocatalyst might be more effective, we turned to tin's neighbor in the periodic table, indium. To establish the feasibility of an indium complex as a cocatalyst to effect carbonyl additions, we explored the addition to the keto aldehyde **1**, which gives methylenetetrahydrofuran **2** with enhanced diastereoselectivity (>19:<1), compared to the use of tin as a cocatalyst (eq 2).<sup>5a</sup>



Enone **5a** was utilized as a test substrate for 1,2 vs 1,4 addition (eq 3). Since both tris(2,4-pentanedionato)indium (**4**) and its hexafluoro analogue<sup>4b</sup> gave similar results, we focused on **4** (10 mol %) for our studies. The palladium(0) catalyst (5 mol %)



was generated by in situ reduction of palladium acetate with DIBAL-H in the presence of the ligand (40 mol %). The ratio of 1,4 vs 1,2 addition (i.e., **7a**<sup>6,7</sup> vs **6a**<sup>6</sup>) was a function of ligand, varying from 3:1 to 1:10 to 1:21 to 1:24 on switching from tris(isopropyl phosphite) (63%) to dppp (73%) to tri-*n*-butylphosphine (59%) to triphenylphosphine (TPP, 82%) in toluene at reflux. This series reveals that ligands which are better  $\sigma$ -donors than  $\pi$ -acceptors promote 1,2 addition. The less polar solvent toluene also promotes 1,2 addition (**7** vs **6** 1:24) more effectively than dioxane (**7** vs **6** 1:9) under comparable conditions. As a control, the same reaction was performed with the same series of ligands in the absence of the cocatalyst with the expected exclusive formation of the 1,4 adduct.<sup>7</sup> So remarkable is the effect of indium that as little as 10 mol % can alter the reaction course from conjugate to 1,2 addition. With a sterically hindered electron-rich ligand such as tri-*o*-anisylphosphine (TOAP), only 1,4 addition occurs even in the presence of indium. Standard conditions for 1,2 additions employ TPP as the ligand. Substrates **5b** and **5c** were converted either to the methylenetetrahydrofurans **6** using the standard conditions (yield, **6**:**7**) (**6b**,<sup>6</sup> 87%, 3:1; **6c**,<sup>6</sup> 83%, >99:<1) or to the methylenecyclopentanes **7** (yield, **7**:**6**) (**7b**,<sup>7</sup> 85%, >99:<1; **7c**,<sup>6</sup> 54%, >99:<1) using TPP in the absence of a cocatalyst and TOAP in the presence of **4**, respectively.

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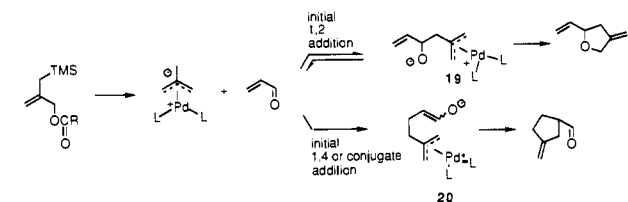
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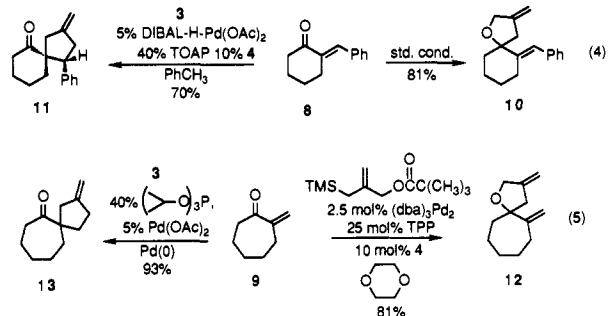
(6) New compounds of the synthetically useful reactions (eq 2-6) have been fully and satisfactorily characterized. The stereochemistry of **11**, **15**, and **17** has been assigned on the basis of analogy to our earlier work (ref 5). In **17**, there is some migration of the exocyclic double bond.

(7) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315.

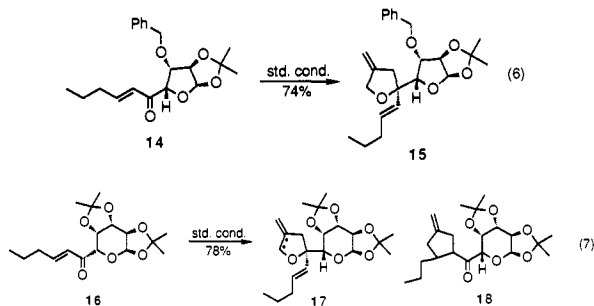
## Scheme I. A Mechanistic Rationale



Enones **8** and **9**, which are particularly prone to conjugate addition, can be diverted from exclusive 1,4 addition (**11**<sup>6</sup> and **13**<sup>6</sup>) to exclusive 1,2 addition (**10**<sup>6</sup> and **12**<sup>6</sup>) (eqs 4 and 5) by the addition of the indium cocatalyst. Carbohydrates that bear many Lewis



basic sites can also lead to good 1,2 selectivity and diastereoselectivity (>20:<1) under our standard conditions in the presence of the indium cocatalyst (**14**<sup>6</sup> → **15**<sup>6</sup>, eq 6; 1,2 vs 1,4 4:1). However, steric hindrance may inhibit 1,2 addition as in the case of the galactopyranose **16**, which gives predominantly the 1,4 adduct (**17**:**18**, 1:4.2) under our standard conditions (eq 7).



A reasonable explanation of the source of the indium effect derives from consideration of both the rate of 1,2 vs 1,4 addition as well as the rate of ring closure (see Scheme I). The absence of any coordinating group to stabilize an oxyanion disfavors 1,2 addition in the usual Pd-catalyzed TMM cycloaddition, thereby precluding formation of zwitterion **19**. On the other hand, the charge delocalization of the zwitterion **20** permits its formation with the ultimate production of the carbocycle. The presence of an oxyanion stabilizing group such as In<sup>3+</sup> promotes attack at the more electrophilic carbonyl carbon to give the In<sup>3+</sup>-stabilized zwitterion **19**. Since the counterion of the oxyanion has also proven to be important in its reaction with ( $\pi$ -allyl)palladium complexes,<sup>8</sup> In<sup>3+</sup> may also promote the collapse of **19** to the methylenetetrahydrofuran. The fact that increasing the reaction temperature by going from THF to dioxane at reflux increases the ratio of 1,2 vs 1,4 addition products suggests that reversal of the 1,2 adduct **19** is competitive with cyclization and that the higher temperatures favor cyclization. While this scheme accounts for all of our current observations, we cannot rule out the involvement of some bimetallic palladium-indium complex as the active entity.<sup>9</sup> This dramatic

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chemoselectivity switch by indium complexes may prove useful in other nucleophilic reactions.<sup>10</sup>

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**Supplementary Material Available:** Listings of characterization data for **6a-c**, **7c**, **10-13**, and **15** (2 pages). Ordering information is given on any current masthead page.

(9) Cf. Yoshida, Y.; Shinohara, H.; Hanari, I. *Jpn. Kokai Tokyo Koho* 8000328; *Chem. Abstr.* **1980**, *92*, 129610c.

(10) Subsequent to initiation of our work on indium, several reports of its potential in other aspects of synthesis have appeared. Catalysis: Mukaiyama, T.; Ohno, T.; Nishimura, T.; Han, J. S.; Kobayashi, S. *Chem. Lett.* **1990**, 2239. Stoichiometric: Nomura, R.; Miyazaki, S.; Matsuda, H. *J. Am. Chem. Soc.* **1992**, *114*, 2738. Li, C. J.; Chan, T. H. *Tetrahedron Lett.* **1991**, *32*, 7017. Araki, S.; Butsugan, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 727. Araki, S.; Katsumura, N.; Butsugan, Y. *J. Organomet. Chem.* **1991**, *415*, 7. Araki, S.; Ito, H.; Katsumura, N.; Butsugan, Y. *J. Organomet. Chem.* **1989**, *369*, 291. Araki, S.; Ito, H.; Butsugan, Y. *J. Org. Chem.* **1988**, *53*, 1831.

## How Crystalline Environment Can Provide Outstanding Stability and Chemistry for Arylnitrenes

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Elucidation of the chemical behavior of reactive intermediates in the solid state ought to give mechanistic information which is important in controlling topochemical reactivities.<sup>1</sup> Continuous interest in one-centered diradicals, such as carbenes or nitrenes,<sup>2</sup> as reactive intermediates prompts us to study the chemical reactivity and/or magnetic interaction of these species in the solid state. As an extension of our effort on diarylcarbenes along this line,<sup>3</sup> here we describe how the crystalline environment provides outstanding stability and reactivity for aryl nitrenes, especially for (4-carboxyphenyl)nitrene, when they are generated in host crystals of aryl azides.<sup>4</sup>

UV photolysis on powdered crystals of aryl azides **1a-c** afforded aryl nitrenes **2a-c** at cryogenic temperatures. The temperature dependence of the triplet ESR signals<sup>5</sup> of nitrenes was carefully

<sup>†</sup> On leave from Ecole Polytechnique, France.

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(2) Chemical behavior of carbenes and nitrenes in the gas phase or in solution is extensively investigated. See: (a) *Tetrahedron Symposia-in-Print*; Platz, M., Guest Ed.; *Tetrahedron* **1985**, *41*, 1423-1612. (b) Wentrup, C. *Tetrahedron Lett.* **1974**, *30*, 1301. (c) Lehman, P. A.; Berry, R. S. *J. Am. Chem. Soc.* **1973**, *95*, 8614. (d) Drzica, P. S.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 3443. (e) Costantino, J. P.; Richter, H. W.; Lee Go, C. H.; Waddell, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 1744. (f) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5229. (g) Morgan, S.; Jackson, J. E.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 2782.

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(4) A fortuitous finding was reported on a remarkably stable nitrene generated by photolysis of crystals of cyanuric triazide. See: Moriarty, R. M.; Rahman, M.; King, G. J. *J. Am. Chem. Soc.* **1966**, *88*, 842.

(5) The triplet signal carries a hyperfine coupling of  $a_N = 1.8$  mT.