Table IV. Total Energies of Model Compounds (−au)

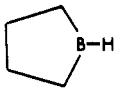
species	6-31G* //6-31G*	6-31G** //6-31G*	MP2(FC) /6-31G* //6-31G*	MP2(FC) /6-31G** //6-31G*
14b (C_s)	180.183 61	180.195 20	180.783 77	180.840 06
15 (C_{2v})	181.383 99	181.398 07	181.974 56	182.047 36
16b (C_s)	193.101 20	193.113 53	193.724 99	193.778 78
17 (C_{2v})	194.288 68	194.303 75	194.906 96	194.976 04
17 (C_2)	194.292 84		194.912 37	

this structure is less than 1 kcal/mol lower than that of **14a**. The "nonbonded" B–C(3) distance in **14b** is 1.821 Å, comparable to the values computed for **1** and **2**, 1.759 and 1.775 Å, respectively (Table II).

It appears that the homoconjugative stabilization favoring C_s borolene is almost completely counteracted by the increase in strain energy, by loss of some hyperconjugative stabilization from its geminal C–H bonds upon folding, and perhaps by other effects as well. Thus reaction 11, in which *both* **2** and **3** are "folded,"

$$\mathbf{2} + \mathbf{15} \rightarrow \mathbf{3} + \mathbf{14b} \qquad \Delta H = 11.4 \qquad (11)$$

has a positive enthalpy change, 11.4 kcal/mol (Tables I and IV). (The geometry of boracyclopentane (**15**) was optimized at HF/6-31G* in C_{2v} symmetry.)

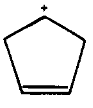


15

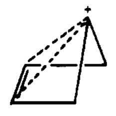
The flat potential energy surface linking **14a** to **14b** is in strong contrast with that of the cyclopenten-4-yl cation, in which the energy of the planar form (**16a**) is 18.9 kcal/mol higher than that of the bridged form (**16b**) at the MP2(FC)/6-31G*//6-31G* level.[18] It is therefore of interest to compare the homoconjugative effects of B and C^+ by means of reaction 12, in which strain energy

$$\mathbf{16b} + \mathbf{15} \rightarrow \mathbf{17} + \mathbf{14b} \qquad \Delta H = 2.1 \qquad (12)$$

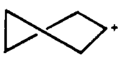
should be approximately balanced. (The cyclopentyl cation (**17**) has C_2 symmetry, a structure ca. 3.4 kcal/mol lower in energy than the C_{2v} form;[19] we find no evidence of energetically significant twisting effects in boracyclopentane.) This reaction, the analogue of reaction 8, has an enthalpy change of ca. 2 kcal/mol. Thus, in the monocyclic case, the homoconjugative stabilization appears to be slightly greater for C^+ than for boron.



16a



16b



17

It is worth noting that in C_s boretane, the transannular interaction of B with C(2) leads to ring puckering and a small barrier, ca. 2.5 kcal/mol, for interconversion of C_s boretanes through a C_{2v} transition state.[20] The same effect is found in the isoelectronic bicyclobutonium ion; however, the barrier to interconversion is much larger, 16.1 kcal/mol.

It would appear, then, that the pronounced stabilizations of **1** and **2** relative to their carbocation analogues are not necessarily found in other systems.

Acknowledgment. We thank Dr. P. J. Fagan for discussions and for informing us of unpublished results. This research was supported, in part, by Grants 668 248, 669 274, and 662 286 of the PSC-CUNY Research Award Program of the City University of New York and a grant of computing time from the City University Committee on Research Computing. In Germany, support was provided by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, the Stiftung Volkswagenwerk, and the Convex Computer Corporation. Generous grants of computer time were provided at KFA, Jülich, and by the Heidelberg Scientific Center of IBM Germany.

---

[18] Schleyer, P. v. R.; Bentley, T. W.; Koch, W.; Kos, A. J.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 6953.

[19] Schleyer, P. v. R.; Carneiro, J. W. de M.; Koch, W.; Raghavachari, K. *J. Am. Chem. Soc.* **1989**, *111*, 5475.

[20] Bühl, M.; Schleyer, P. v. R.; Ibrahim, M. A.; Clark, T. *J. Am. Chem. Soc.* **1991**, *113*, 2466.

Communications to the Editor

Catalysis of H_2–D_2 Equilibration by Platinum–Gold Cluster Compounds

Mark A. Aubart and Louis H. Pignolet*

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received February 14, 1992
Revised Manuscript Received June 8, 1992

The catalysis of H_2–D_2 equilibration ($H_2 + D_2 = 2HD$) has been studied for a series of phosphine-stabilized Pt–Au cluster compounds under homogeneous conditions in the solution phase and under heterogeneous conditions as molecular solids at 30 °C and 760 Torr total pressure. The cluster compounds, **1–4**, shown in Table I are excellent catalysts for this reaction and have turnover frequencies which are orders of magnitude greater than those of most homogeneous catalysts reported to date. Previous homogeneous studies have included monometallic compounds such as *trans*-$IrCl(CO)(PPh_3)_2$,[1] $Pt(O_2)(PPh_3)_2$,[1] $NiI_2(PPh_3)_2$,[2] $RhCl(PPh_3)_3$,[3] $RuH_2(PPh_3)_4$,[4] and $RuHCl(PPh_3)_3$.[4] No cluster compounds have been previously studied. The Pt–Au cluster com-

Table I. H_2–D_2 Equilibration Kinetic Data under Homogeneous Conditions[a]

cluster compound	amount of cluster (μmol)[b]	10^5k at 30 °C (s^{-1})[c]	10^2(turnover freq) (s^{-1})[d]
$[Pt(AuPPh_3)_8](NO_3)_2$ (**1**)	2.5	12.9	6.5 ± 0.5
$[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$ (**2**)	1.5	2.5	2.0 ± 0.1
$[(PPh_3)_2Pt(AuPPh_3)_4](NO_3)_2$ (**3**)	2.2	5.6[e]	3.0 ± 0.1
$[(PPh_3)_2Pt(AuPPh_3)_3](NO_3)$ (**4**)	2.3	8.2	4.6 ± 0.2
$[Au(AuPPh_3)_8](NO_3)_3$ (**5**)	1.3	0[f]	0
$(C_2H_4)Pt(PPh_3)_2$ (**6**)	7.2	6.5	0.11 ± 0.01

[a] The initial gas mixture consisted of ca. 0.5 atm of H_2 and 0.5 atm of D_2. Reactions were typically run for ca. 4 h or until at least 70% equilibrated. [b] Each catalyst was dissolved in 6 mL of nitrobenzene. [c] First-order rate constants were determined by plotting the equation, $\ln\{[HD]_e/([HD]_e - [HD]_t)\} = kt$, where $[HD]_e$ and $[HD]_t$ are the mole fractions of HD at equilibrium and at time t, respectively. $[HD]_e$ was calculated from initial H_2 and D_2 concentrations and $K_e = 3.2$ at 30 °C. [d] Turnover frequency is equal to $k[\text{mol}(H_2 + D_2 + HD)]/(\text{mol cluster})$ where $\text{mol}(H_2 + D_2 + HD) = 1.21 \times 10^{-3}$ for all experiments. [e] Initial rate data reported for the first 75 min where the ln plot was linear. The rate increased nonlinearly after this time due to decomposition (see text). [f] No HD observed after 2 days.

---

[1] Tadros, M. E.; Vaska, L. *J. Colloid Interface Sci.* **1982**, *85*, 389.

[2] Ando, N.; Maruya, K.-I.; Mizoroki, T.; Ozaki, A. *J. Catal.* **1971**, *20*, 299.

0002-7863/92/1514-7901$03.00/0 © 1992 American Chemical Society

pounds have significantly faster turnover frequencies than an analogous gold phosphine cluster compound **5** (gold phosphine compounds and metallic gold mirrors are inactive) or the coordinatively unsaturated monoplatinum phosphine complex **6**. The turnover frequencies show a marked dependence on cluster size and Au/Pt ratio, with $[Pt(AuPPh_3)_8](NO_3)_2$ being the best catalyst. This is important because it is known that the addition of gold to heterogeneous platinum catalysts has beneficial effects on activity and selectivity,[5–8] and Pt–Au cluster compounds can serve as models for such systems. Surprisingly, these bimetallic molecular cluster compounds show catalytic activity for H_2–D_2 equilibration in the solid state with rates comparable to those observed for activated Pt surfaces.

This is the first study of the kinetics of H_2–D_2 equilibration with metal cluster compounds under homogeneous conditions.[9] There have been numerous studies of this reaction under heterogeneous conditions (metal surfaces, supported metals, and activated, supported molecular complexes including clusters)[10–13] where it is difficult to measure specific rates and determine reaction mechanisms. A study under homogeneous conditions offers a significant advantage in determining structure–reactivity relations and reaction mechanism. The homogeneous H_2–D_2 equilibration reaction provides a conveniently studied probe for the activation of H_2, an important process in many industrial catalysts.

The compounds in the table were synthesized by literature methods (**1**,[14] **2**,[15] **3**,[16] **4**,[16] **5**,[17] and **6**[18]) and have been thoroughly characterized by NMR spectroscopy, elemental analysis, and for **1** and **2**, X-ray crystallography. H_2–D_2 equilibration experiments were carried out by measuring the percent of H_2, D_2, and HD as a function of time.[19] The percent of H_2 and D_2 decreased at the same rate, which clearly shows that there is no deuterium exchange with solvent (see the supplementary material). This was confirmed by 3-day experiments with use of only D_2 as the reactant gas. No HD was observed in these experiments, including cases where H_2O was added to the solution. There was also no evidence for deuterium incorporation into the PPh_3 ligands. In addition, nitrobenzene (chosen as the solvent because it is rapidly hydrogenated by *heterogeneous* metal catalysts[20] and is therefore a good internal control) is not hydrogenated to aniline, nor is H_2 taken up in week long control reactions using much higher concentrations of the Pt–Au clusters. Olefins such as 1-hexene, ethylene, and cyclohexene are also *not* hydrogenated by these catalysts. The absence of deuterium exchange and hydrogenation provides good evidence for the *homogeneous* nature of the equilibration as the presence of a heterogeneous platinum impurity would cause these reactions to occur.[13,20–23] Rates were also reproducible for different preparations of cluster compounds. The reactions were checked by ^{31}P NMR and UV–vis spectroscopy, and no decomposition was observed for **1**, **2**, and **4**. Cluster **3** slowly reacted with the gas mixture to produce **2** and unknown side products. Only initial rate data is, therefore, reported for this cluster. All data reported in the table showed first-order kinetics for HD formation (see the supplementary material).

Rate data were determined for **1**, the most effective catalyst, with three different amounts of compound. The reaction was found to be first-order in the amount of cluster compound (see the supplementary material), which demonstrates that the rates are not limited by gas–solvent diffusion. The equilibration reaction is not likely the result of undetectable cluster degradation into small platinum phosphine species because **6**, a highly reactive and unsaturated compound, has a considerably slower turnover frequency. This compound also hydrogenates nitrobenzene to aniline under the conditions of the reaction. Aniline was not produced by any of the Pt–Au clusters in any of the experiments. Other small platinum compounds should be good hydrogenation catalysts for olefins. This reaction does not occur for the cluster compounds studied.

A mechanism for the formation of HD by Pt–Au cluster compounds could involve the reversible addition of H_2 and D_2 to the same cluster core, giving a $PtAu_x(H_2)(D_2)$ type species. Transition metal–gold cluster polyhydrides are known and have H atoms bridging M–Au bonds;[24] however, they have not been synthesized by simple addition of H_2.[25,26] Although a study of the mechanism of the homogeneous equilibration reaction has not been completed and will require detailed kinetic experiments, crystals of **1** and **2** catalyze H_2–D_2 equilibration heterogeneously (gas–solid reaction without solvent) with turnover frequencies (1 and 0.5 s^{-1}, respectively) significantly greater than those of the homogeneous solution reactions and comparable to those observed for activated Pt surfaces.[10–13] These turnover frequencies were determined in the same manner as the homogeneous values (see footnote to the table) and showed a dependence on crystal size. The highest turnover frequencies resulted from finely powdered samples. To our knowledge, this solid-state reaction has not previously been reported for any molecular metal compound with nonvolatile ligands[27] and lends support to the above mechanism. It must of course be considered that the solid-state equilibration is caused by a small amount of solid metal impurity. This is unlikely, however, because the mixture of 5 mg of crystalline **1** with 0.5 atm of D_2 and 0.5 atm of C_2H_4 gave no evidence of deuterium exchange or hydrogenation (GC and MS analysis) after 3 days at 25 °C. Metallic platinum is a good catalyst for deuterium exchange and hydrogenation of ethylene.[20–23] Solutions

---

(3) Strathdee, G.; Given, R. *Can. J. Chem.* **1974**, *52*, 2216 and 2226. Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.

(4) Strathdee, G.; Given, R. *Can. J. Chem.* **1975**, *53*, 106.

(5) Sachdev, A.; Schwank, J. *J. Catal.* **1989**, *120*, 353.

(6) Sermon, P. A.; Thomas, J. M.; Keryou, K.; Millward, G. R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 918.

(7) Yates, R. C.; Somorjai, G. A. *J. Catal.* **1987**, *103*, 208.

(8) Sinfelt, J. H. *Bimetallic Catalysts*; Wiley: New York, 1985.

(9) The only other homogeneous study we could find was on the photoinduced equilibration by $H_4Ru_4(CO)_{12}$, but no rate data were reported: Doi, Y.; Tamura, S.; Koshizuka, K. *J. Mol. Catal.* **1983**, *19*, 213.

(10) See, for example: Jen, H.-W.; Brenner, A. In *Proceedings of the Vth International Symposium on Relations between Homogeneous and Heterogeneous Catalysis*, Novosibirsk, USSR, 1986; Yermakov, Y., Likholobov, V., Eds.; VNU Science Press: Utrecht, The Netherlands, p 865. Tanaka, K.; Watters, K. L.; Howe, R. F.; Andersson, S. L. T. *J. Catal.* **1983**, *79*, 251. Breakspere, R. J.; Eley, D. D.; Norton, P. R. *J. Catal.* **1972**, *27*, 215. Moroz, B. L.; Mudrakovskii, I. L.; Bulgakova, L. I.; Rogov, V. A.; Likholobov, V. A.; Mastikhin, V. M.; Sazonov, L. A.; Yermakov, Y. I. In *Proceedings of the VIth International Symposium on Heterogeneous Catalysis*, Sofia, Bulgaria, 1987; Part 2, p 25.

(11) Burden, A. G.; Grant, J.; Martos, J.; Moyes, R. B.; Wells, P. B. *Faraday Discuss. Chem. Soc.* **1982**, *72*, 95.

(12) Bond, G. C. *Catalysis by Metals*; Academic Press: New York, 1962; Chapter 8.

(13) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, NY, 1981.

(14) Kanters, R. P. F.; Schlebos, P. P. J.; Bour, J. J.; Bosman, W. P.; Behm, H. J.; Steggerda, J. J. *Inorg. Chem.* **1988**, *27*, 4034.

(15) Ito, L. N.; Sweet, J. D.; Mueting, A. M.; Pignolet, L. H.; Schoondergang, M. F. J.; Steggerda, J. J. *Inorg. Chem.* **1989**, *28*, 3696.

(16) Ito, L. N.; Felicissimo, A. M. P.; Pignolet, L. H. *Inorg. Chem.* **1991**, *30*, 387.

(17) Steggerda, J. J.; Bour, J. J.; van der Velden, J. W. A. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 164.

(18) Cook, C. D.; Jauhal, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 1464.

(19) The percents of H_2, D_2, and HD were determined by gas chromatography as described by Yasumori (Yasumori, I.; Ohno, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1302). The reactor consisted of a thermostated, 30-mL glass vessel equipped with a Teflon magnetic stirrer and septum for gas sampling.

(20) (a) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855. (b) Rylander, P. N. *Catalytic Hydrogenation over Platinum Metals*; Academic Press: New York, 1967; Chapter 11. (c) Hudlicky, M. *Reductions in Organic Chemistry*; Halstead Press: New York, 1984; pp 71–76.

(21) Gudkov, B. S. *Russ. Chem. Rev.* **1986**, *55*, 259.

(22) See ref 12, Chapter 11.

(23) Nazario, P.; Brenner, A. *Proc. 9th Int. Congr. Catal.* Phillips, M. J., Ternan, M., Eds. **1988**, 1020. Kemball, C. *J. Chem. Soc.* **1956**, 735.

(24) Alexander, B. D.; Johnson, B. J.; Johnson, S. M.; Casalnouvo, A. L.; Pignolet, L. H. *J. Am. Chem. Soc.* **1986**, *108*, 4409.

(25) Bour, J. J.; Schlebos, P. P. J.; Kanters, R. P. F.; Schoondergang, M. F. J.; Addens, H.; Overweg, A.; Steggerda, J. J. *Inorg. Chim. Acta* **1991**, *181*, 195.

(26) Mueting, A. M.; Bos, W.; Alexander, B. D.; Boyle, P. D.; Casalnuovo, J. A.; Balaban, S.; Ito, L. N.; Johnson, S. M.; Pignolet, L. H. *New J. Chem.* **1988**, *12*, 505.

(27) The only examples of this solid-state reaction we could find are for $Ru_6C(CO)_{17}$ (ref 11) and $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ (Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000).

of these crystals were also inactive for the hydrogenation of olefins or nitrobenzene. A preliminary ^{31}P NMR study also lends support to the above mechanism and shows that H_2 reversibly adds to **1** in CH_2Cl_2 solution at ambient temperature. Under 1 atm of H_2, the original ^{31}P resonance of **1** observed under N_2 (δ 55.0, $J_{(Pt-P)}$ = 497 Hz) is replaced by a new resonance (δ 51.1, $J_{(Pt-P)}$ = 391 Hz). This change is completely reversible as the original spectrum of **1** reappears in about 15 min under an N_2 purge. An investigation into the nature of this new species is underway.

Other studies in progress include homogeneous and heterogeneous H_2–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[16,24-26,28,29] and should provide important structure–reactivity relationships for the activation of H_2.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8818187) and by the University of Minnesota. M.A.A. acknowledges support from the Undergraduate Research Opportunities Program at the University of Minnesota. We also acknowledge other members of the Pignolet research group for helping with compound preparation and Prof. J. J. Steggerda for help with the NMR study. A special thanks goes to Jan Lane for helping with the GC analysis. Jan was a participant in the NSF-supported program. Research Explorations for Secondary Teachers.

Registry No. 1, 110870-04-7; **2**, 107712-38-9; **3**, 131793-14-1; **4**, 131793-10-7; **6**, 12120-15-9; H_2, 1333-74-0; D_2, 7782-39-0.

Supplementary Material Available: Kinetic plots illustrating a typical H_2–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.

(29) Schoondergang, M. F. J.; Bour, J. J.; Schlebos, P. P. J.; Vermeer, A. W. P.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T.; Steggerda, J. J. *Inorg. Chem.* **1991**, *30*, 4704 and references cited therein.

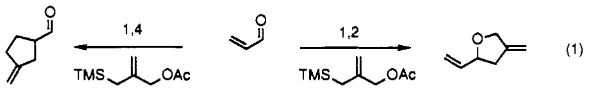
Coordinative Cocatalysis via In^{3+}. A Chemoselectivity Switch for Pd-Catalyzed Cycloadditions

Barry M. Trost,* Sunaina Sharma, and Thomas Schmidt

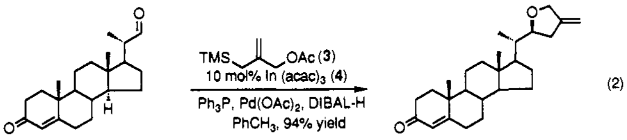
Department of Chemistry, Stanford University
Stanford, California 94305-5080

Received April 27, 1992

Control of 1,2 vs 1,4 addition reactions of nucleophiles with α,β-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.[1] The development of Pd-catalyzed trimethylenemethane (TMM) cycloaddition to give five-membered rings[2] has the characteristics of a conjugate addition followed by cyclization.[3] 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 In^{3+} complexes[4] have on controlling the chemoselectivity of this cycloaddition.

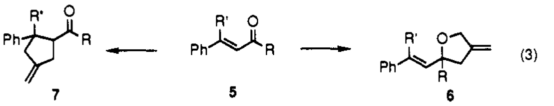


Earlier work in our laboratories established the feasibility of trimethyltin acetate as a cocatalyst to effect cycloaddition of TMM to the carbonyl group of mainly aldehydes.[5] However, it had only a minor effect on the conjugate vs 1,2 competition of cycloaddition to enones. Believing a more electropositive 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).[5a]



1 **2**

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[4b] 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**[6,7] vs **6a**[6]) was a function of ligand, varying from 3:1 to 1:10 to 1:21 to 1:24 on switching from triisopropyl 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 σ-donors than π-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.[7] *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**,[6] 87%, 3:1; **6c**,[6] 83%, >99:<1) or to the methylenecyclopentanes **7** (yield, **7**:**6**) (**7b**,[7] 85%, >99:<1; **7c**,[6] 54%, >99:<1) using TPP in the absence of a cocatalyst and TOAP in the presence of **4**, respectively.



7 **5** **6**

a) R = CH_3, R' = H
b) R = Ph, R' = H
c) R = R' = CH_3

---

(1) For some recent general reviews, see: Lee, V. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 4, Chapter 1.4. Lipshutz, B. H. *Synthesis* **1987**, 325. Taylor, R. J. K. *Synthesis* **1985**, 364. Erdik, E. *Tetrahedron* **1984**, *40*, 641. Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005. Posner, G. H. *Org. React.* **1972**, *19*, 1.

(2) Chan, D. M. T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, Chapter 3.2. Binger, P.; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77. Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.

(3) Trost, B. M.; Miller, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 3687. Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2326.

(4) (a) For coordination in indium complexes, see: Davidson, G. *Coord. Chem. Rev.* **1981**, *34*, 74. Preut, H.; Huber, F. *Z. Anorg. Allg. Chem.* **1979**, *450*, 120. (b) Cf. Matsubara, N.; Kuwamoto, T. *Inorg. Chem.* **1984**, *24*, 2697. Lisoivan, V. I.; Gromilov, S. A. *Russ. J. Inorg. Chem.* **1986**, *31*, 1466. Morgan, G. T.; Drew, H. D. K. *J. Chem. Soc.* **1921**, 1058.

(5) (a) Trost, B. M.; King, S. A.; Schmidt, T. *J. Am. Chem. Soc.* **1989**, *111*, 5902. (b) Trost, B. M.; King, S. A. *J. Am. Chem. Soc.* **1990**, *112*, 408. (c) Trost, B. M.; King, S. A.; Nanninga, T. N. *Chem. Lett.* **1987**, 15.

(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 ealier 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.

0002-7863/92/1514-7903$03.00/0 © 1992 American Chemical Society