Zirconium-Catalyzed Coupling of Propene and α-Picoline

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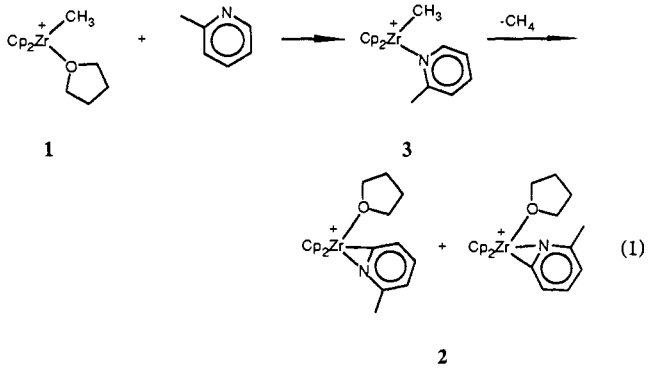
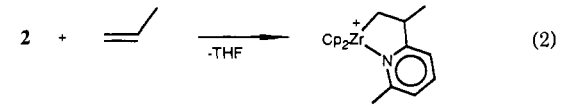
Electrophilic early transition-metal and f-element alkyl complexes undergo a variety of insertion, elimination, C–H activation/abstraction, and hydrogenolysis reactions.[1] The role of these reactions in catalytic olefin polymerization[2] and olefin and alkyne hydrogenation[3] has been elucidated, and an understanding of their mechanisms is emerging.[4,5] A current challenge is to develop other catalytic processes which utilize these key reactions.[6,7] We report that our initial studies in this area with cationic Zr alkyl complexes[8] have led to the discovery of a zirconium-catalyzed process for the coupling of olefins with 2-Me-pyridine (α-picoline) which involves sequential aryl C–H activation (C–H abstraction), olefin insertion, Zr–R bond hydrogenolysis, and ligand exchange steps.

While neutral Cp^*_2MR complexes (M = group III, lanthanide) undergo C–H activation reactions with hydrocarbons,[5a,9] we anticipated that this would be less likely for closely related cationic Zr compounds $[Cp_2Zr(R)(L)][BPh_4]$ due to the presence of the ligand L and the counterion. Accordingly we have focused our attention on potential reactions of ligand C–H bonds. The methyl complex $Cp_2Zr(CH_3)(THF)^+$ (**1**) reacts (<20 min, 20 °C) with α-picoline in CH_2Cl_2 solution to yield CH_4 (0.95 equiv, Toepler pump) and η^2-picolyl complex **2** (two isomers, ca. 1/1, >90% NMR, 84% isolated), eq 1.[10] Analogous complexes are formed in the reactions of Cp^*_2MR (M = Lu, Sc, Y, Ti) complexes with pyridines.[11] ^1H NMR monitoring of the reaction in eq 1 reveals



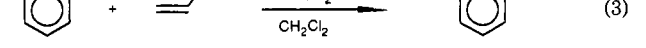
shifts in the resonances of **1** and α-picoline consistent with the formation of intermediate picoline complex **3** prior to aryl C–H activation.

Like the isoelectronic benzyne complexes $Cp_2Zr(\eta^2\text{-}C_6H_4)(L)$ and related compounds,[12] **2** reacts with unsaturated substrates via insertion into the Zr–C bond. For example, reaction with propene (45 min, 23 °C, 1 atm) produces **4** (100% NMR, 90% isolated) which has a chelated structure (eq 2). This reaction is inhibited by THF which suggests that THF dissociation precedes insertion.



We explored several approaches to incorporation of the clean propene/picoline coupling reaction represented by eq 1 and 2 into a catalytic process. Previously we observed that $Cp_2Zr(R)(L)^+$ species in which L is a simple $2e^-$ donor (e.g., PMe_3) react rapidly with H_2 to produce R–H and cationic Zr hydrides.[8f] On this basis we hypothesized that **4** should undergo rapid hydrogenolysis to produce $Cp_2Zr(H)$(6-Me,2-^{i}Pr-pyridine)$^+$ (**5**) and that the catalytic cycle in Scheme I would be completed by subsequent ligand exchange, H_2 elimination (C–H abstraction), and insertion steps.

Coupling of propene and α-picoline is indeed catalyzed by **4** in the presence of H_2 as shown in eq 3. Noteworthy features of



this reaction include moderate catalytic activity (1–2 t.o./h at 23 °C; activity sensitive to $P_{hydrogen}$, $P_{propene}$, and [picoline]), long catalyst lifetime (> 40 t.o.; catalysis proceeds until propene or picoline is consumed), and high selectivity (no other picoline derived products are observed). In a typical reaction 0.19 g (2.2 mmol) of α-picoline and 0.065 g (0.096 mmol) of **4** were dissolved in CH_2Cl_2 under ca. 1.5 atm of propene and ca. 1 atm of H_2. Conversion of picoline to 6-Me,2-^{i}Pr-pyridine was complete (GC) after 25 h at 23 °C.[13]

(1) (a) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1985**, *56*, 1. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (c) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (d) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333.

(2) (a) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337. (b) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (c) Clawson, L.; Soto, J.; Buchwald, S.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

(3) (a) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111. (b) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291.

(4) (a) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134. (b) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670. (c) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

(5) (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Buchwald, S. L.; Nielson, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171. (c) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425. (d) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (e) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. (f) Chamberlain, L. R.; Kerschner, J. L.; Rothwell, A. P.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6471. (g) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979.

(6) Dimerization of alkynes. Reference 5a and (a) Den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053. (b) Aminomethylation of α-olefins: Nugent, W. A.; Ovenall, D. W.; Holmes, S. J. *Organometallics* **1983**, *2*, 161.

(7) For leading references to metal-catalyzed C–H bond functionalization reactions, see: (a) Jones, W. D.; Foster, G. P.; Putinas, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5047. (b) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640. (c) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025. (d) Baudry, D.; Ephritikhine, M.; Felkin, H.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 788.

(8) (a) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (b) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (c) Jordan, R. F. *J. Chem. Ed.* **1988**, *65*, 285. (d) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. (e) Jordan, R. F.; Echols, S. F. *Inorg. Chem.* **1987**, *26*, 383. (f) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041.

(9) (a) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (b) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276.

(10) The counterion in all cases is BPh_4^-.

(11) See ref 5a, 6a, 9b, and (a) Klei, E.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *214*, 53. See also: (b) Erker, G.; Muhlenbernd, T.; Benn, R.; Rufinska, A. *Organometallics* **1986**, *5*, 402. (c) Fanwick, P. E.; Kobriger, L. M.; McMullen, A. K.; Rothwell, I. P. *J. Am. Chem. Soc.* **1986**, *108*, 8095.

(12) (a) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (c) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. (d) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (e) Rausch, M. D.; Mintz, E. A. *J. Organomet. Chem.* **1980**, *190*, 65. (f) McClain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. (g) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

(13) Scheme I is catalytic in H_2, and activity is indeed observed even at very low H_2 pressures. However, best results are obtained with ca. 1 atm of H_2.

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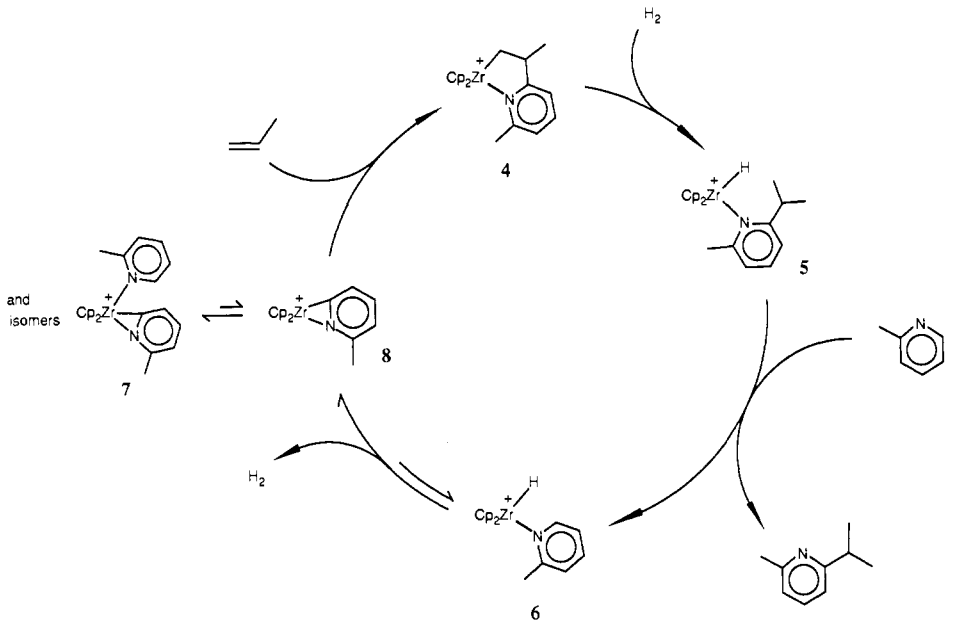
Scheme I



The results of stoichiometric model reactions and NMR monitoring experiments support the essential features of the proposed mechanism in Scheme I. Key observations are as follows. (1) Complex **4** is stable in the presence of excess picoline (i.e., no 6-Me, 2-^{i}Pr-pyridine is evolved), and H_2 is required for catalysis. These results imply that Zr–C bond cleavage in **4** occurs by hydrogenolysis and not by a C–H abstraction reaction of a ring-opened $Cp_2Zr\{CH_2CH(Me)(6\text{-Me-pyrid-2-yl})\}(picoline)^+$ species. (2) Reaction of **4** with H_2 in CH_2Cl_2 (<30 min, 20 °C, 1 atm) produces 6-Me,2-^{i}Pr-pyridine and Cp_2ZrCl_2. Hydrogenolysis of **4** in the presence of ethylene results in rapid formation of polyethylene. These results are consistent with the formation of **5** which contains a highly labile disubstituted pyridine ligand and which thus undergoes rapid reaction with solvent or ethylene.[14] (3) Reaction of **4** with H_2 in the presence of 3 equiv of picoline yields 6-Me,2-^{i}Pr-pyridine and **7** (two isomers, 3/1, 80% NMR). No intermediates are observed when this reaction is monitored by ^{1}H NMR. This is consistent with generation of **5** followed by rapid ligand substitution and H_2 elimination/C–H abstraction. The analogous reaction with D_2 produces 6-Me,2-^{i}Pr-pyridine labeled in the isopropyl methyl position. Catalytic H/D exchange of the ortho and methyl hydrogens of the excess picoline (ca. 5 and 1 t.o./h, respectively at 23 °C) is also observed, indicating that the conversion of **6** to **7** is reversible and that activation of methyl C–H bonds also occurs. (4) Complex **7**, like **2**, inserts propene to yield **4** (100% NMR, <10 min, 23 °C, 1 atm) and 1 equiv of α-picoline. By analogy to eq 2, picoline dissociation to yield **8** likely precedes insertion.[15] (5) Both **4** and **7** are effective catalysts. (6) Minor amounts of propane (ca. 10 mol % vs 6-Me,2-^{i}Pr-pyridine) are formed in the catalytic reactions, consistent with the intermediacy of Zr–H species. (7) ^{1}H NMR monitoring of catalytic reactions reveals that the only significant Zr species present are **4** and/or **7**.[15] This is consistent with the relative rates of the hydrogenolysis (**4** to **5**) and propene insertion (**7** to **4**) reactions (slow) and ligand exchange (**5** to **6**) and H_2 elimination (**6** to **7**) reactions (fast) established above.

(14) (a) In CH_2Cl_2 solution $Cp_2Zr(R)(THF)^+$ complexes and "naked" $Cp_2Zr(R)^+$ complexes decompose to yield $Cp_2Zr(R)Cl$ as initial products and are efficient ethylene polymerization catalysts.[8b] (b) $Cp_2Zr(H)Cl$ undergoes Cl/H exchange with CH_2Cl_2 to yield Cp_2ZrCl_2. Buchwald, S. L.; LaMaire, S. J.; Nielson, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, 3895.

(15) Reaction of **2** with picoline also yields **7**. In this case significant amounts of two additional isomers or oligomers of **7** are also formed. These species are the sole products when **2** is reacted with neat picoline, are minor products in the reaction of **4** with H_2 in the presence of a large excess of picoline, and are observed as minor species in catalytic runs containing high concentrations of α-picoline. These additional isomers/oligomers do not react rapidly with propene.

Further mechanistic studies of the current system and extensions to other substrates are in progress.[16]

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Supplementary Material Available: A listing of characterization data for **2**, **4**, **7**, and 6-Me,2-^{i}Pr-pyridine (4 pages). Ordering information is given on any current masthead page.

(16) Ethylene and 1-butene also are catalytically coupled with picoline. Pyridine is not a suitable substrate due to the formation of an unreactive nonlabile $Cp_2Zr(pyridyl)(pyridine)^+$ species analogous to **7**.

Ramberg–Bäcklund Syntheses and Chemodirected Annulations of Exocyclic Allylsilanes[1]

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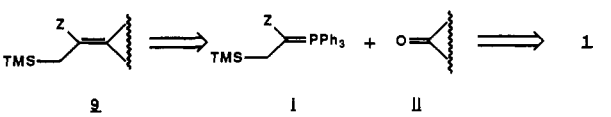
In connection with our synthetic program we required a means to convert an α-sulfonyl anion **1** to a series of vinyl-functionalized allylsilanes **9a–e**.[2] Guided by the observations of Henderickson[3a,b]

(1) Syntheses via Vinyl Sulfones. 36. For a review of this area, see: Fuchs, P. L.; Braish, T. F. *Chem. Rev.* **1986**, *86*, 903.

(2) Although oxidation of α-sulfonyl anion **1** (see: Baudin, J.-B.; Julia, M.; Rolando, C. *Tetrahedron Lett.* **1985**, *26*, 2333) to ketone *i* followed by Wittig reaction with substituted trimethylsilylethyl phosphorane reagents *ii* (the parent reagent Z=H is used in this manner, see: Fleming, I.; Marchi, D., Jr. *Synthesis* **1981**, 560) represented a formal solution for synthesis of **9**, we desired a more general method.



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