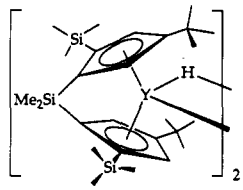
well suited to in situ mechanistic studies. Moreover, the $[Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}CMe_3C_5H_2)_2]$ ligand has been designed to coordinate to yttrium to produce *only* the desired racemic isomer in the synthesis of the chloride precursor.

Addition of $YCl_3(THF)_3$ to $Li_2[Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}CMe_3C_5H_2)_2]$ (Li_2Bp), prepared by the addition of 2 equiv of Me_3SiCl to $Li_2[Me_2Si(3\text{-}CMe_3C_5H_3)_2]$[10] and subsequent deprotonation with 2 equiv of *n*-butyllithium, affords only the C_2-symmetric *ansa*-yttrocene compound, *rac*-$Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}CMe_3C_5H_2)_2Y(\mu\text{-}Cl)_2Li(THF)_2$ ($BpY(\mu\text{-}Cl)_2Li(THF)_2$), in ~48% isolated yield; <2% (^1H NMR) of the C_s meso isomer is detected. The results of a single-crystal X-ray structure determination for $BpY(\mu\text{-}Cl)_2Li(THF)_2$ are published elsewhere.[11] Inspection of the molecular drawing (Figure 1)[12] indicates that the unfavorable steric interactions between the $SiMe_3$ groups in the narrow portion of the Cp–M–Cp wedge are avoided only for the racemic isomer. Even for the favored racemic isomer, the two bulky $SiMe_3$ groups experience crowding from both the Me_2Si bridging unit and the opposite cyclopentadienyl ring.

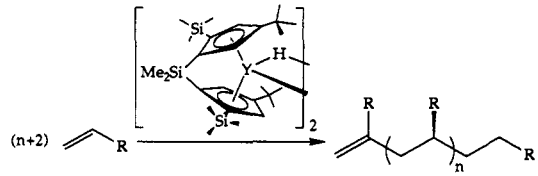
Lithium chloride and THF are conveniently removed by treatment of the lithium dichloroyttrate with the bulky lithium alkyl, $LiCH(Si(CH_3)_3)_2$, followed by hydrogenolysis to yield the colorless, crystalline hydride derivative [*rac*-$Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}CMe_3C_5H_2)_2Y(\mu\text{-}H)]_2$ ([*rac*-BpYH]$_2$) in ~35% isolated yield.



[*rac*-BpY-H]$_2$

[*rac*-BpYH]$_2$ is formulated as a dimer (almost certainly the homochiral *RR* and *SS* enantiomers, considering steric interactions) on the basis of a triplet in the ^1H NMR spectrum assigned to the two bridging hydride ligands (δ 4.87; $^1J_{^{89}Y\text{-}^1H}$ = 31 Hz; ^{89}Y, I = $^1/_2$, 100%). Solutions of [*rac*-BpYH]$_2$ prove to be remarkably unreactive toward PMe_3, and unlike other *ansa*-yttrocene hydride complexes,[13] no ligand redistribution resulting in a [Cp–$SiMe_2$–Cp]-bridged "spanover" dimer is observed after days in C_6D_6 solution (^1H NMR).

Propylene (25% v:v in methylcyclohexane) as well as neat 1-butene, 1-pentene, and 1-hexene are all polymerized, albeit rather slowly over a period of several days at 25 °C to afford modest molecular weight polymers.[14] Preliminary results indicate the following properties for the polymers produced: polypropylene (M_n 4200, PDI 2.32, T_m 157 °C, 97.0% mmmm); poly(1-butene) (M_n 8500, PDI 3.44, T_m 105 °C); poly(1-pentene) (M_n 20 000, PDI 1.99, T_m 73 °C); poly(1-hexene) (M_n 24 000, PDI 1.75, T_m <25 °C). Chain end analysis of the poly(α-olefins) by ^1H and



(R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$)

^{13}C NMR indicate geminally disubstituted olefinic end groups, consistent with chain propagation by 1,2 (primary) addition and termination by β-H elimination.[15] The moderately high melting point for the polypropylene sample as well as the ^{13}C NMR spectra of the polymers at the pentad analysis level shows a remarkably high degree of isotacticity for all polymers.[16] The ^{13}C and ^1H NMR spectra of a poly(1-butene) sample are shown in Figure 2.

rac-[BpYH]$_2$, the first *single-component*, iso-specific Ziegler–Natta catalyst so far as we are aware, is uniquely suited to a study of the subtle steric factors that govern the remarkably high stereospecificities exhibited in the polymerization of α-olefins by this and the related two-component, chiral group 4 catalyst systems. We plan to undertake the synthesis of related catalysts using the successful design feature responsible for the exclusive formation of the racemic isomers of $Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}CMe_3C_5H_2)_2Y(\mu\text{-}Cl)_2Li(THF)_2$ and the catalysts derived therefrom.

Acknowledgment. The work has been supported by the USDOE Office of Basic Energy Sciences (Grant No. DE-FG03-85ER113431) and by Exxon Chemicals Americas. We also wish to thank Drs. Howard W. Turner and Terry J. Burkhardt and Professor Jun Okuda for their insights and assistance.

Supplementary Material Available: Experimental details describing the syntheses of Li_2Bp, $BpY(\mu\text{-}Cl)_2Li(THF)_2$, $BpYCH(SiMe_3)_2$, and $[BpYH]_2$, as well as information regarding α-olefin polymerizations and ^{13}C NMR analyses for the polymers (5 pages). Ordering information is given on any current masthead page.

(10) Bunel, E. E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976.
(11) Marsh, R. E.; Schaefer, W. P.; Coughlin, E. B.; Bercaw, J. E. *Acta Crystallogr.*, in press.
(12) Of the two enantiomers in the unit cell, only the *S* enantiomer is shown.
(13) (a) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9585. (b) Coughlin, E. B.; Bercaw, J. E. Unpublished results.
(14) Hydrogenation of $BpYCH(Si(CH_3)_3)_2$ in neat 1-hexene results in much faster polymer production (>95%, <1 day) with the same high degree of isotacticity.
(15) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025.
(16) Asakura, T.; Demura, M.; Nishiyama, Y. *Macromolecules* **1991**, *24*, 2334.

Observation of a 2-α-Enamine from a 2-(Methoxyphenylmethyl)-3,4-dimethylthiazolium Salt in Water: Implications for Catalysis by Thiamin Diphosphate-Dependent α-Keto Acid Decarboxylases

Gabriel Barletta, W. Phillip Huskey,* and Frank Jordan*

Department of Chemistry
Rutgers, The State University of New Jersey
Newark, New Jersey 07102

Received June 8, 1992

During the past decade, several lines of evidence have suggested the intermediacy of a thiamin diphosphate (ThDP)-bound enamine on the pathway of pyruvate decarboxylase (PDC, EC 4.1.1.1),[1] starting with the observation of a new absorbance with λ_{max} near 440 nm, when the conjugated substrate analogue (*E*)-4-(4-chlorophenyl)-2-oxo-3-butenoic acid was employed.[2] Parallel with the accumulating evidence on PDC thiazolium compounds were synthesized, from which models for such enamines could be generated in nonaqueous media on addition of a strong, nonnucleophilic base. The structures of these enamines were established by UV–vis and NMR spectroscopy.[3a] Later, pK_a's of the con-

(1) For recent reference, see: (a) Kluger, R. *Chem. Rev.* **1987**, *87*, 863–876. (b) Schellenberger, A., Schowen, R. L., Eds. *Thiamin Pyrophosphate Biochemistry*; CRC Press: Boca Raton, FL, 1988; Vol. 1. (c) Bisswanger, H., Ullrich, J., Eds. *Biochemistry and Physiology of Thiamin Diphosphate Enzymes*; Publishers: New York, 1991.
(2) Zeng, X.; Chung, A.; Haran, M.; Jordan, F. *J. Am. Chem. Soc.* **1991**, *113*, 5842–5849 and references therein.
(3) (a) Jordan, F.; Kudzin, Z. H.; Rios, C. B. *J. Am. Chem. Soc.* **1987**, *109*, 4415–4416. (b) Bordwell, F. G.; Satish, A. V.; Rios, C. B.; Chung, A. C.; Jordan, F. *J. Am. Chem. Soc.* **1990**, *112*, 792–797. (c) Barletta, G.; Chung, A. C.; Rios, C. B.; Jordan, F.; Schlegel, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 8144–8149. (d) Jordan, F.; Zeng, X.-P.; Menon-Rudolph, S.; Annan, N.; Barletta, G.; Chung, A. C.; Rios, C. B. In *Biochemistry and Physiology of Thiamin Diphosphate Enzymes*; Bisswanger, H., Ullrich, J., Eds.; VCH Publishers: New York, 1991; pp 34–50.

0002-7863/92/1514-7607$03.00/0

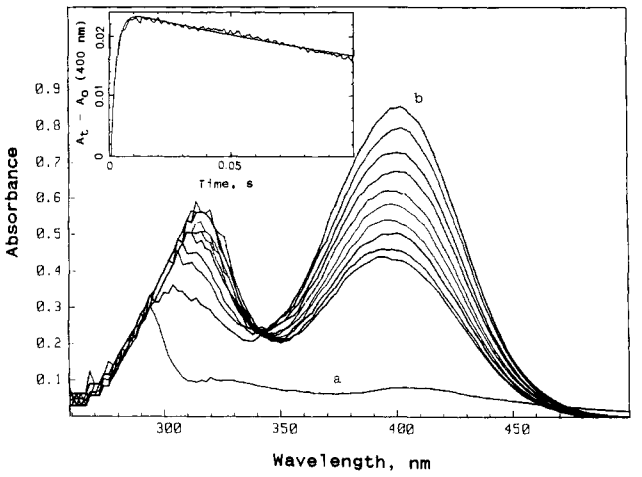
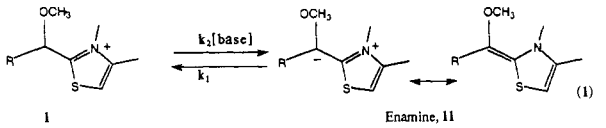
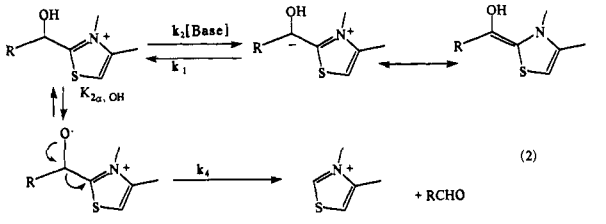


Figure 1. Repetitive-scan stopped-flow spectra recorded (Hi-Tech PQ-SF/SpectraScan instrument) for the reaction of 5.0 mM **Ia** with 0.25 M NaOH. Curve a is the spectrum obtained when the hydroxide solution is replaced by water. Curve b and those progressively less intense are spectra recorded in ca. 90-ms intervals after mixing **Ia** and hydroxide. The inset shows a sample transient at 400 nm (0.15 M NaOH with 1.15 mM **Ia**, T = 25 °C). The zero time refers to the time when the first absorbance was recorded. The curve through the transient is the least-squares fit to the integrated rate expression for the mechanism of eq 3. The extinction coefficient for the enamine in DMSO (17 000 M^{-1} cm^{-1}) was used in the analysis. When **Ia** was replaced with the methyl analog of **I** (R = Me) or with 2-isopropyl-3,4-dimethylthiazolium salts no transient absorbances were seen above 300 nm.

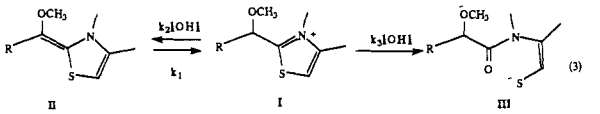
jugate carbon acids (eq 1) in DMSO,[3b] as well as their one-electron oxidation at an electrode[3c] (implicating a thiazolium cation radical intermediate), were reported.



Preliminary kinetic studies on the forward reaction depicted in eq 1 in DMSO showed rapid generation of the enamine.[3d] For R = Me, the formation and disappearance of the enamine according to eq 2 (with the hydroxy group unprotected) could also be monitored in DMSO, indicating that in an aprotic solvent, at least, proton transfer from carbon could successfully compete with elimination of thiazolium ion.[3d] Recently, Stivers and Washabaugh have studied the kinetics of deprotonation at C2α of 2-(1-hydroxyethyl)-3,4-dimethylthiazolium ion (**I** with R = Me and hydroxy in place of methoxy) in water and estimated a pK_a > 20 for this carbon acid.[4]



We report here visible spectroscopic evidence in support of enamine formation according to eq 1 for **Ia** (R = p-$Me_3N^+C_6H_4^-$) in aqueous solutions.[5] Presented in Figure 1 is a rapid-scan stopped-flow spectrum resulting from mixing hydroxide ion with **Ia**. There is evidence of the formation of a new absorbance with λ_{max} near 400 nm (λ_{max} = 400 nm in DMSO) that rapidly decays with time. The inset shows the time development of the absorbance at 400 nm. That the reaction takes place according to eq 3 is supported by the following observations: (a) starting material **I** absorbs below 300 nm and ring-opened form **III** near 300 nm (Figure 1a), whereas the enamine **II** in DMSO (identified according to a variety of spectroscopic criteria) absorbs at 400 nm where the transient absorbance in water is observed; (b) the ^1H NMR spectrum of **III** (formed by addition of NaOD to **I** in D_2O) is consistent with a cis–trans mixture that on acidification reverts to **I**, with no evidence of breakdown products, i.e., the ring opening is reversed at low pH; (c) FT-IR experiments also indicate the presence of a carbonyl in the alkaline reaction mixture at 1585 cm^{-1}.



Transient absorbances at 400 nm were collected at several concentrations of **Ia** over a range of hydroxide concentrations (0.025–0.15 M). Each transient was fit, using a least-squares criterion, to the closed-form, integrated solution of the rate equations corresponding to the mechanism of eq 3 (in which k_2' and k_3' replace k_2[OH] and k_3[OH]). All constants were independent of the concentration of **Ia** over a range of (1.25–5) × 10^{-3} M. The rate constant k_1 (= 498 ± 13 s^{-1}) appeared to be independent of [OH^-]. Plots of k'_2 and k'_3 against hydroxide were linear with near zero intercepts. Least-squares estimates of the slopes of these lines were used to compute second-order rate constants: k_2 = 20.4 ± 0.5 s^{-1} M^{-1}; k_3 = 3.43 ± 0.10 s^{-1} M^{-1}. The rate constants k_1 and k_2, along with K_w for water, can be used to estimate a pK_a of 15.4 for the carbon acid **Ia** in water, 3.0 units above that determined in DMSO for a related compound (R = Ph) by the indicator method.[3b,6]

It is now evident that the enamine can have a significant lifetime in both aqueous and nonaqueous media. The magnitude of the water catalyzed reprotonation rate constant k_1 is of particular interest because it is well below a value expected for a diffusion-controlled process, as might be expected for a highly delocalized carbanion/enamine.[7] In as much as **IIb** (R = Ph) is an analogue of the enamine expected in the benzoylformate decarboxylase reaction, the value of k_1 (1.34 ± 0.26 s^{-1}) from the equilibration of **Ib** and **IIb** can be compared to the turnover number for that enzyme (estimated near 150–300 s^{-1}).[9] Because "spontaneous" protonation by water would be too slow, the enzyme very likely mediates it.[10] Similar conclusions were reached recently for pyruvate decarboxylase[11] based on entirely different experiments.

Acknowledgment. Financial support by the NIH-MBRS, NSF, and the Rutgers Busch Fund is gratefully acknowledged.

(4) Stivers, J. T.; Washabaugh, M. W. *Bioorg. Chem.* **1991**, *19*, 369–383. See references therein for other kinetic estimates of this pK_a.

(5) We have so far been unsuccessful in our attempts to observe the enamine in water from compounds with an unprotected OH group (eq 2).

(6) Many positively charged acids are stronger in DMSO than in water: (a) Koolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23–28 (especially Table VI, column 5). (b) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.

(7) It is known that the "intrinsic barrier" to proton transfer from and to carbon varies enormously with resonance stabilization of the conjugate base.[8] While the carbanion/enamine for the compound studied in ref 4 is resonance stabilized by one group, the one reported here is stabilized by two groups (the absorption maximum of the former is near 300 nm; for the one studied here the maximum is 400 nm in DMSO,[3d] affirming this statement). Therefore, it is difficult to make any comparisons between our results and those in ref 4.

(8) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301–308.

(9) Weiss, P. M.; Garcia, G. A.; Kenyon, G. L.; Cleland, W. W.; Cook, P. F. *Biochemistry* **1988**, *27*, 2197–2205.

(10) The magnitude of the rate constant does not rule out the possibility of a buffer-catalyzed proton transfer in the enzymic reaction.

(11) Ermer, J.; Schellenberger, A.; Hübner, G. *FEBS Lett.* **1992**, *299*, 163–165.