Carbon Acidity. 68. Hydrogen Isotope Exchange Kinetics of 1,3-Diphenylindene, Cyclopentadiene, 1,4-Diphenylcyclopentadiene, and 2,7-Di-*tert*-butylfluorene

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Abstract: Second-order rate constants for the hydrogen isotope exchange reactions of 1,3-diphenylindene, cyclopentadiene, 1,4-diphenylcyclopentadiene, and 2,7-di-*tert*-butylfluorene in methanolic sodium methoxide are reported, and these data are compared with the corresponding equilibrium acidities. The comparison reveals that all four compounds adhere to the same Brønsted correlation previously derived for nine other fluorene-type carbon acids. With the addition of the four new compounds, the correlation spans a range of 10 pK_a units with no detectable curvature. Values for the primary isotope effect k_D/k_T for 1,3-diphenylindene and cyclopentadiene are presented and found to be essentially the same as k_D/k_T values found for other fluorene acids. The isotope effect comparison and the linearity of the Brønsted plot suggest that the mechanism of proton transfer and the structure of the transition state remains unchanged over the entire 10 pK_a range of substrate acidity.

The linear free energy relationship often found between equilibrium and kinetic acidities for related groups of compounds is known as the Brønsted equation (eq 1).[1,2] Carbon acids which

$$k_a = G_a(K_a)^\alpha \qquad (1)$$

have been studied with respect to Brønsted relations include ketones and other carbonyl compounds, nitriles, halocarbons, sulfones, and nitroalkanes.[2c,3] Despite their generally low acidity, studies concerning the Brønsted behavior of hydrocarbon acids have also been presented.[4-12] Indeed, several factors make the conjugated hydrocarbon acids particularly attractive substrates for studying Brønsted relations. The pK_a values for a large number of these compounds have been determined in several solvents.[13-17] In addition, the acidic properties of conjugated hydrocarbons are due almost entirely to charge delocalization in the derived carbanions.[18] As a consequence, large changes in acidity can result from rather modest structural perturbations. This allows Brønsted

Table I. Kinetic Acidity of 1,3-Diphenylindene (**1**)[a]

A. In CH₃OH

T (°C)	10^3[NaOMe] (M)	$10^2 k_2^{°D}$	$10^2 k_2^{°T}$	k_D/k_T	k_H/k_D[b]
0.0	12.4	2.82	1.06	2.66	9.91
0.0	15.5	2.37	1.08	2.19	6.28
25.0	5.21	27.9	12.2	2.29	6.97
25.0	2.81	29.5	12.8	2.30	7.05

B. In CH₃OD

T (°C)	10^3[NaOMe] (M)	$10^2 k_2^{°H}$	$10^2 k_2^{°T}$	k_H/k_T	k_H/k_D[b]
0.0	3.13	43.1	2.23	19.4	7.99
0.0	5.22	44.0	2.58	17.1	7.32
25.0	1.01	ND[c]	22.2		
25.0	1.50	ND[c]	25.5		
25.0	1.46	425	26.7	15.9	6.95

[a] Rate constants are given in units of M⁻¹ s⁻¹. [b] Calculated from eq 2, see text. [c] Not determined.

relations to be studied over large ranges of acidity while using a structurally homogeneous group of compounds and avoids the interpretive ambiguities which arise from deviations due to structural factors and the stabilization of carbanions by different electronic mechanisms.

It is well-known that Brønsted relations are valid only over a limited range of rates and pK_a values and that curvature is frequently observed in Brønsted correlations as the range of reactivity is increased. Since the value of the Brønsted exponent α is generally regarded as a measure of the extent of proton transfer at the transition state,[19] a nonlinear Brønsted relation implies a change in transition-state structure along a reaction series. This analysis is consistent with Hammond's postulate[20] regarding transition-state structure as a function of free energy changes. However, it must quickly be added that the discovery[21] of reaction series yielding α values outside the theoretical limits of zero to one has seriously undermined the simple interpretation of α presented above. Moreover, recent publications by Pross,[22] Jencks,[23] Hupe,[24] and others[25] have expressed the view that even

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among reaction series which produce normal (i.e., $0 \leqslant \alpha \leqslant 1$) Brønsted relations, the value of α may not accurately reflect transition-state structure. For example, Hupe and Pohl have shown that a Brønsted plot for the reaction of 4-(4-nitrophenoxy)-2-butanone with oxyanions in aqueous solution exhibits marked curvature,[24a] whereas primary kinetic isotope effect data for the same reactions indicate that no significant change in transition-state structure has occurred.[24b] The curvature in the Brønsted plot was attributed to solvational effects which vary with the basicity of the oxyanion.

Several years ago we reported extensive data concerning the exchange reactivities of fluorene, some 9-substituted and benzo-fluorenes, and indene.[11] A significant result of this work was the demonstration that an excellent linear Brønsted correlation is obtained when rate constants for tritium exchange in methanolic sodium methoxide are compared with cesium ion-pair pK_a values (pK_{CsCHA}) in cyclohexylamine (CHA). Since the time of our original report we have continued these studies with the aim of extending the kinetic measurements to substrates of higher and lower equilibrium acidities. In this paper, isotope exchange kinetic data for 1,3-diphenylindene (1), cyclopentadiene (2), 1,4-diphenylcyclopentadiene (3), and 2,7-di-*tert*-butylfluorene (4) are presented, and the results are discussed in relation to the Brønsted correlation.

Results

1,3-Diphenylindene (1). The pK_{CsCHA} of **1** is 13.6,[14] making it the most acidic substrate for which we have obtained kinetic data. Exchange experiments with **1**-*d,t* were conducted in methanol to obtain rate constants for dedeuteration and detritiation (denoted $k_2^{°D}$ and $k_2^{°T}$, respectively), and experiments with **1**-*t* in methanol-*O-d* provided deprotonation ($k_2^{°H}$) and detritiation rate constants. The experimental methods employed in these studies have been described previously.[11,12] In brief, solutions were prepared by dissolving the appropriately labeled substrate in methanol (or methanol-*O-d*) containing sodium methoxide. Aliquots were withdrawn from the solution periodically, and the substrate was analyzed for tritium content by liquid scintillation counting and/or for deuterium content by mass spectrometry.

The results of several kinetic runs with **1** are summarized in Table I. The rate constants appearing in the table have been extrapolated to zero methoxide concentration by using a "salt effect" equation previously described by us;[11] at the low catalyst concentrations employed in these studies, the correction is quite small. From the data appearing in Table I, the following activation parameters were calculated:[-6] $\Delta H^{\ddagger} = 15.0$ kcal mol^{-1}, $\Delta S^{\ddagger} = -10.6$ eu for deuterium exchange in methanol; $\Delta H^{\ddagger} = 15.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -11.2$ eu for tritium exchange in methanol; $\Delta H^{\ddagger} = 14.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -12.5$ eu for tritium exchange in methanol-*O-d*.

The experimental rate constants were also used to calculate values for the primary isotope effects; these values are shown in Table I. The k_H/k_D values presented in the last column of Table I were calculated from the Swain–Schaad equation (eq 2).[27] Note

$$k_H/k_D = (k_D/k_T)^x = (k_H/k_T)^{x/(x+1)} \qquad (2)$$

$$x = 2.344$$

that the k_H/k_D values are in the high range expected for a transition state in which a substantial degree of proton transfer has occurred. The calculated k_H/k_D values for solvents methanol and methanol-*O-d* are quite similar and show that the solvent isotope effect on the primary isotope effect is small. A solvent isotope effect is revealed in the comparison of detritiation rate constants in protio- and deuteriomethanol.[28] The data give a value

Table II. Kinetic Acidities of Cyclopentadiene (2), 1,4-Diphenylcyclopentadiene (3), and 2,7-Di-*tert*-butylfluorene (4)[a]

substrate	T (°C)	10^2[NaOMe] (M)	$10^3 k_2^{°T}$
2	0.0	50.5	1.03
	25.0	4.85	16.2
	25.0	4.85	38.4[b]
3	0.0	6.01	6.28
	0.0	7.08	6.61
	25.0	4.63	105
	25.0	7.49	106
4	45.0	79.6	0.0964
	45.0	58.0	0.0971

[a] Rate constants are given in units of M^{-1} s^{-1}. [b] For dedeuteration, i.e., $k_2^{°D}$. $k_D/k_T = 2.37$.

of $k_2^{°T}$(MeOD)$/k_2^{°T}$(MeOH) = 2.0 at 25 °C which is close to the value of 2.2 reported for the detritiation of 9-methylfluorene.[11] We attribute the higher rate constants in methanol-*O-d* to the less extensive solvation of methoxide ions in the deuterated solvent.

Cyclopentadiene (2). Although it has long been known that cyclopentadiene readily undergoes hydrogen isotope exchange under suitably basic conditions, few quantitative studies have been presented.[29] This may be due in part to the experimental difficulties arising from the well-known dimerization of **2**. Under the conditions employed in this study, the dimer would be inert toward isotopic exchange.

To determine whether the dimerization reaction occurs to a significant extent over the period of time required for a kinetic run, the rate of dimerization of freshly prepared **2** was monitored by ^{1}H NMR. We found that a dilute (0.3 M) solution of monomeric **2** showed no NMR peaks attributable to the dimer after 9 h at 25 °C and only ca. 3% dimer was detected after 46 h.

Due to the volatility of **2**, analytical problems were encountered which forced us to modify the usual experimental procedure. Preliminary experiments indicated that evaporative losses during the workup of kinetic aliquots resulted in irreproducible isotope analyses. To circumvent this problem, we have employed the novel expedient of trapping the cyclopentadiene directly from each aliquot using 4-phenyl-1,2,4-triazoline-3,5-dione (**5**). Triazoline **5** is a highly reactive dienophile,[30] and the cycloaddition (eq 3) proceeds smoothly to give the readily isolable solid adduct (**6**). With use of this trapping technique, the simultaneous loss of
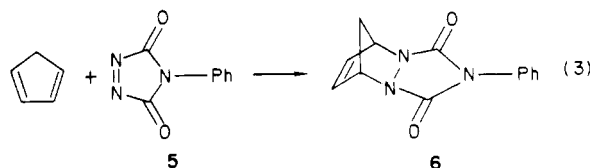
deuterium and tritium from cyclopentadiene-*5-d,t* was monitored at 25 °C. An additional run was performed at 0 °C with use of the singly labeled (tritiated) substrate. The results of these experiments are shown in Table II. The tabulated rate constants have been corrected to account for isotopic scrambling. That is, because of the relatively high value of the primary isotope effect, the equilibrium shown below (eq 4) is established rapidly, and only a fraction of the total amount of substrate is kinetically active.
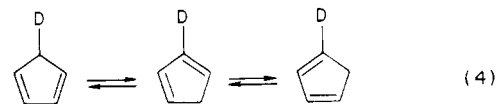
In general, a statistical distribution of the isotopic label among the available sites is not expected due to secondary isotope effects. However, we have determined by NMR (see Experimental Section) that equal amounts of the three isomers exist at equilibrium.[31]

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Carbon Acidity

J. Am. Chem. Soc., Vol. 107, No. 24, 1985 6985

Table III. Summary of Equilibrium and Kinetic Acidities

compd	pK_{CsCHA}[a]	$k_2^{\circ T}$[b]	$-\log k_2^{\circ T}$
1	13.6	0.681	0.167
3	14.3	0.766	0.116
2	16.2	0.108	0.967
4	24.0	9.67×10^{-5}	4.01

[a] Reference 14. [b] At 45 °C, in units of $M^{-1} s^{-1}$.
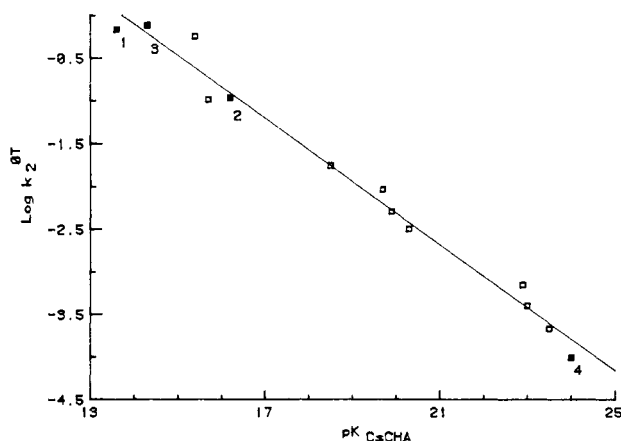
Figure 1. Brønsted correlation of log $k_2^{\circ T}$ (45 °C) with pK_{CsCHA}. This plot combines data from our previous work (ref 11) with the values listed in Table III. The points for the four new compounds are identified by the numbers used in the text. The regression line is given by the following equation: log $k_2^{\circ T}$ = 5.07 − 0.369pK_{CsCHA}.

Thus, the rate constants in Table II were obtained by multiplying the observed second-order rate constants by three.

1,3-Diphenylcyclopentadiene (3) and 2,7-Di-*tert*-butylfluorene (4). The exchange reactivities of these compounds were determined in a straightforward manner by monitoring the decrease in specific activity with time of the tritiated substrates. The results of these experiments are recorded in Table II.

Discussion

In order to facilitate further discussion of the data, it is convenient to present the various rate constants obtained in this study at a common temperature. In Table III, second-order rate constants for detritiation at 45 °C are shown along with the previously reported pK_{CsCHA} assignments made for these compounds.[14] Note that the pK_{CsCHA} values involve the equilibria of ion pairs in the nonpolar solvent CHA while the kinetic acidities refer to the reactions of free carbanions in methanol. We have previously justified a comparison of the two quantities by noting the remarkable insensitivity of the relative equilibrium acidities to solvent effects,[11] and we have recently communicated further data to support this fact.[17]

In previous work on the exchange reactivities of fluorene-type carbon acids, a linear relationship between detritiation rate constants and pK_{CsCHA} values was demonstrated for nine compounds.[11] The four compounds employed in the present study bear a close structural relationship to the florene acids and are expected to belong to the same Brønsted "family". In Figure 1, a plot of pK_{CsCHA} vs. log $k_2^{\circ T}$ values is shown. This plot includes the fluorene acids from our previous study together with the compounds studied herein. It is evident that no loss of linearity in the Brønsted plot is incurred by the inclusion of the four new compounds; the slope of the least-squares line has changed only from −0.367 (r = 0.986, nine points) to −0.369 (r = 0.992, thirteen points). With the addition of compounds 1 and 4 the correlation now covers a range of greater than 10 pK_{CsCHA} units with no detectable curvature. It is particularly interesting that the point for 1,3-diphenylindene fits the correlation. The pK_a of this compound in *methanol* has been measured as 19.8,[32] a value that is

Table IV. Primary Kinetic Isotope Effect for Hydrocarbon Acids

compound	pK_{CsCHA}[a]	k_D/k_T[b]
1	13.6	2.30
9-phenyl-3,4-benzofluorene	15.7	2.48
2	16.2	2.37
9-phenylfluorene	18.5	2.50
fluorene	23.0	2.25
2,3-benzofluorene	23.5	2.45

[a] Reference 14. [b] At 25 °C. Values from this work and ref 11.

approaching the pK_a of methanol in methanol (16.9).[33] Although curvature in Brønsted plots is frequently observed as the pK_a values of the acid and base approach each other,[2] such curvature is not apparent in our correlation.

The linearity of the correlation shown in Figure 1 suggests that the mechanism of proton transfer and the structure of the transition state remain essentially unchanged over the entire range of acidity. An independent probe of transition-state structure is provided by the primary isotope effect. Values of k_D/k_T for many of the compounds included in the Brønsted correlation have been determined and are compared in Table IV. The primary isotope effect for 1,3-diphenylindene, k_D/k_T = 2.30, is nearly unchanged from that of fluorene (k_D/k_T = 2.25) and 2.3-benzofluorene (k_D/k_T = 2.45) despite the fact that the latter two compounds are ten orders of magnitude less acidic than 1. The constancy of the k_D/k_T values over the entire acidity range strongly supports the conclusion regarding transition-state structure arrived at from the Brønsted correlation.

The results described in this study stand in marked contrast to the behavior of several other types of carbon acids for which curved Brønsted plots[2a,b] and substantial variations in primary isotope effect values with changing acidity[34-41] have been observed. Nonlinear Brønsted plots can result from two distinct, though not mutually exclusive, effects. In the first, curvature is the result of a change in the reaction mechanism from rate-limiting proton transfer to diffusion control. This effect is generally restricted to the reactions of oxygen and nitrogen acid–base pairs in aqueous solution, for which the slope of a Brønsted plot typically changes from the limiting values of zero to one over a pK_a range of ca. 6 units.[42] In these cases, the conjugate bases form a hydrogen-bonded network with the solvent in which proton transfer is facilitated.

A different explanation has been proposed to account for systems yielding curved Brønsted plots in which neither the forward nor reverse reaction rates are diffusion controlled. This explanation involves a relationship between curvature and reactivity and has been treated quantitatively by Marcus et al. in a series of papers.[43] In brief, Marcus' theory predicts that systems which encounter large energy barriers toward proton transfer will give rise to linear Brønsted plots over longer pK_a ranges than do systems encountering relatively small energy barriers. For fluorene acids, deprotonation is accompanied by a substantial amount of electronic reorganization to yield a delocalized, aromatic carbanion. This electronic reorganization is undoubtedly responsible for the large energy barrier for equilibrium anion formation[44] and consequently for the long range of linearity of the Brønsted plot.

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6986 *J. Am. Chem. Soc., Vol. 107, No. 24, 1985*

Streitwieser et al.

In the Marcus formalism, the activation energy $\Delta G^{\ddagger}$ for a thermoneutral reaction is termed the intrinsic barrier.[43] Since our data now extend fairly close to the region at which the hydrocarbon acid and basic catalyst have the same pK_a, it is possible to estimate the rate constant for detritiation and the intrinsic barrier at this point. In this calculation, however, allowance must be made for the fact that the fluorene pK_a values are substantially lower in CHA than in methanol. If it is assumed that the difference $pK_{MeOH} - pK_{CHA} = 6.2$ determined for 1.3-diphenylindene is applicable to all of the fluorene acids, then the reaction between acid and methoxide ion is thermoneutral at $pK_{CHA} = 10.7$. From the correlation shown in Figure 1, the rate constant at this pK_{CHA} value is 13.2 M^{-1} s^{-1} which corresponds to $\Delta G^{\ddagger} = 17$ kcal mol^{-1} at 45 °C. This value is typical of the relatively high intrinsic barriers determined for proton-transfer reactions to and from carbon.[2] For example, Marcus has calculated the intrinsic barrier for the protonation of 1,3,5-trimethoxybenzene by carboxylic acids to be 14 kcal mol^{-1}.[43b] In contrast, the intrinsic barriers for reactions involving NH and OH acid–base pairs are known to be much lower (by about 10 kcal mol^{-1}) than for proton-transfer reactions involving carbon.[43b]

It is also notable that the Brønsted exponent $\alpha = 0.37$ determined in this study is significantly lower than the value $\alpha = 0.67$ found for several 2-substituted fluorenes.[45] The latter study included polar ring substituents (NO_2, MeO, Br) and compared rates of tritium exchange in methanolic sodium methoxide with pK_a values determined by the H_- method.[46] The different Brønsted behavior of the ring-substituted fluorenes compared to the hydrocarbon acids clearly results from a difference in electronic effects in the two groups. Anion stabilization in the unsubstituted fluorenes results predominantly from charge delocalization that is only partially developed in the transition structures compared to the equilibrium carbanions. The addition of a polar ring substituent provides an additional ring-charge substituent-dipole interaction that is greater in the transition structure than in the equilibrium carbanion, undoubtedly because much of the charge in the transition-state structure is located in the methoxide group and the fluorenyl-9 position and is effectively closer to the substituent dipole. The net effect is precisely equivalent to the unusual Brønsted behavior of substituted aryl nitroalkanes.[2,3] This analysis also suggests strongly that for conjugated hydrocarbon acids in which such inductive effects play but a minor role, the Brønsted exponent is a valid measure of transition-state structure. That is, for those systems in which charge delocalization is the dominant electronic mechanism, the Brønsted α is a valid measure of the degree of such delocalization at the transition state relative to the fully formed equilibrium anion.

One further aspect of our results deserves attention. It is known that only structurally related groups of compounds will conform to a Brønsted relation.[2] Our studies show that carbon acids containing a cyclopentadiene, indene, or fluorene ring system can all be accommodated by a single correlation. The structural feature common to all of these compounds is the cyclopentadiene moiety. We suggest that the cyclopentadiene nucleus and the aromaticity it imparts upon the derived anions are of primary importance in determining the form of the free energy relationship to which these hydrocarbons adhere. The correlation can then be used to predict the pK_a values of other cyclopentadiene-type acids. For example, Hine and Knight have determined the rate of proton abstraction from 6,6-dimethylfulvene in CH_3O^-/CH_3OH at 35 °C.[47] Using their data and known or estimated values for the activation energy and isotope effect, we estimate tritium exchange in methanol to have $k_2^{\circ T} = 10^{-4}$ M^{-1} s^{-1} at 45 °C, which corresponds to $pK_{CsCHA} = 24.7$.

Experimental Section

Carbon Acids. The hydrocarbon acids used in this study were either commercially available or synthesized by published procedures.[48-50] Isotopically labeled hydrocarbons were prepared by treating a THF solution of the substrate with *n*-butyllithium and then quenching the anion with deuteroacetic acid or tritiated methanol. Each hydrocarbon was purified by either distillation, recrystallization, or vacuum sublimation prior to a kinetic run.

Kinetic Procedures. The kinetic runs involving compounds **1**, **3**, and **4** were performed according to the procedure described previously.[11,12] The exchange reactions with cyclopentadiene differed in some respects, and a typical experiment is described below.

A solution of 0.09 mL of tritiated cyclopentadiene and 0.5 mL of cyclopentadiene-d_1 in 75 mL of dry methanol was placed in a septum-covered flask. The flask was placed under a slight positive pressure of argon and immersed in a well-stirred, thermostated (25.0 ± 0.1 °C) water bath. After allowing 30 min for thermal equilibration, a known amount of 1.03 M methanolic sodium methoxide (also equilibrated to bath temperature) was syringed into the cyclopentadiene solution. Aliquots were removed from the kinetic solution by syringe at measured time intervals. The workup of each aliquot consisted of stopping the exchange reaction by adding cold aqueous hydrochloric acid and extracting the hydrocarbon into hexane. The cyclopentadiene contained in each hexane extract was converted to the cycloadduct **6** by the procedure described below. Weighed amounts of adduct **6** were placed in scintillation vials, diluted with 15.0 mL of scintillation fluid (PPO, POPOP, toluene), and counted on a Searle Mark III scintillation counter. A small portion of the adduct **6** obtained from each aliquot was submitted for low-voltage mass spectral analysis. The relative deuterium content was computed by dividing the sum of the intensities of the M + 1 ($m/z = 242$) and M + 2 peaks by the sum of the intensities of the M, M + 1, and M + 2 peaks. The pseudo-first-order rate constants for dedeuteration and detritiation were obtained from the data with the LSKIN1 program of DeTar and DeTar[51] and converted to second-order rate constants by dividing by the methoxide concentration. This concentration was determined by titrating a portion of the kinetic solution with potassium acid phthalate to a phenolphthalein end point.

Reaction of Cyclopentadiene with 4-Phenyl-1,2,4-triazoline-3,5-dione (5). A solution of cyclopentadiene in hexane was cooled to 0 °C and titrated to a faint pink end point with a saturated ethereal solution of triazoline **5**. The reaction was stirred for 5 min, and 10 mL of 5% aqueous sodium bicarbonate was added. When the pink color of the organic phase had faded (ca. 30 min), the layers were separated. The organic layer was washed with bicarbonate and dried with $MgSO_4$, and the solvent was removed by rotary evaporation to yield adduct **6** as a white solid, mp 142–144 °C (lit.[29] mp 142–144 °C). ^1H NMR ($CDCl_3$): δ 1.91 (q, 1 H, $J = 9$ Hz), 2.23 (q, 1 H, $J = 9$ Hz), 5.12 (m, 2 H), 6.44 (t, 3 H, $J = 1.7$ Hz), 7.37 (m, 5 H).

Cyclopentadiene Dimerization Rate. Monomeric cyclopentadiene was obtained by distilling the dimer at 160–162 °C under nitrogen and collecting the distillate in a receiver cooled to −78 °C. A 0.3 M solution of the fresh distillate in $CDCl_3$ was placed in an NMR tube and the proton spectrum (90 MHz) was examined at periodic time intervals. No peaks due to dimer were detected after 9 h at 25 °C and ca. 3% dimer (δ 5.9 (s), 5.4 (s), 1.0–3.5 (m)) was observed after 46 h.

Determination of Equilibrium Deuterium Distribution in Cyclopentadiene-d_1. Approximately 2 mL of cyclopentadiene-d_1 was placed in a septum-covered flask and allowed to dimerize over a period of 2 weeks. The dimer was then distilled at 160–162 °C. The distillation served both to crack the dimer and to scramble the deuterium label through the facile 1,5-sigmatropic shifts. The distillate was converted to the trapping adduct **6**, and the deuterium site distribution was determined by integration of the proton spectrum using the phenyl hydrogens of the adduct as an internal standard. ^1H NMR ($CDCl_3$): δ 1.95 (s, 0.16 H), 2.28 (s, 0.17 H), 5.15 (s, 0.34 H), 6.46 (s, 0.33 H), 7.44 (m, 5 H).

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