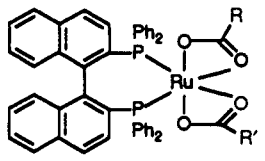
Kinetics and Mechanism of Catalysis of the Asymmetric Hydrogenation of α,β-Unsaturated Carboxylic Acids by Bis(carboxylato){2,2′-bis(diphenylphosphino)-1,1′-binaphthyl}-ruthenium(II), [Ru^{II}(BINAP)(O_2CR)$_2$]

Michael T. Ashby and Jack Halpern*

Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. *Received June 25, 1990*

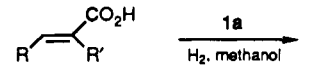
Abstract: The rate law for the hydrogenation of α,β-unsaturated carboxylic acids in methanol, catalyzed by bis(carboxylato){(*R*)- or (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl}ruthenium(II) ([Ru^{II}(BINAP)(O_2CR)$_2$]), at near ambient conditions and in the absence of added product, has the following form: rate = k_{obs}[Ru]$_T$[substrate][H_2]/[substrate]$_0$. The rate law and the results of labeling studies support the conclusion that the catalytically active species in the turnover-limiting step of the reaction is a substrate-containing bis(carboxylato)ruthenium complex that splits H_2 heterolytically to form a metal hydride. Subsequent insertion of the C=C bond of the coordinated substrate yields a five-membered heterometallacyclic species; protonolysis of the resulting Ru–C bond gives the final product. The catalytic rate is very sensitive to the presence of strong acid; slightly more than 1 equiv (with respect to catalyst) of triflic acid inhibits hydrogenation completely. In contrast, the rate of hydrogenation is unaffected by base. The enantiomeric excess, greater than 90% when the substrate is tiglic acid, is unaffected by addition of acid or base.

Following the demonstration that rhodium complexes containing chiral diphosphine ligands can catalyze the hydrogenation of prochiral α-(acylamino)acrylic acid derivatives with enantiomeric excesses (ee's) approaching 100%,[1] the field of asymmetric catalysis has attracted intense attention and many other such asymmetric catalytic reactions have been identified.[2] Yet the original system remains the only asymmetric hydrogenation reaction whose kinetics and mechanism have been elucidated in any detail.[3] More recently, Noyori has reported another asymmetric hydrogenation catalyst, derived from the precursor bis(carboxylato){(*R*)- or (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl}-ruthenium(II) ([Ru^{II}(BINAP)(OAc)$_2$], **1a**).[4] This catalyst yields high ee's for a considerably wider range of substrates including



1a: R = R′ = CH_3
b: R = R′ = $C(CH_3)=CHCH_3$
c: R = R′ = $CH(CH_3)CH_2CH_3$
d: R = CH_3; R′ = $C(CH_3)=CHCH_3$
e: R = $C(CH_3)=CHCH_3$; R′ = $CH(CH_3)CH_2CH_3$

α,β-unsaturated carboxylic acids, for example, 2-(6-methoxy-2-naphthyl)acrylic acid (**2c**), whose hydrogenation yields the anti-inflammatory drug (*S*)-naproxen (**3c**).[4] We report here a study of the kinetics and mechanism of this class of hydrogenation reactions (eq 1), notably of tiglic acid (**2b**).



(1)

2a: R = H; R′ = CH_3
b: R = R′ = CH_3
c: R = H; R′ = 6-MeO-2-$C_{10}H_6$

3a: R = H; R′ = CH_3
b: R = R′ = CH_3
c: R = H; R′ = 6-MeO-2-$C_{10}H_6$

Results

Kinetics of Catalytic Hydrogenation. The catalytic hydrogenation of **2a–c** begins immediately upon addition of the catalyst precursor **1a** to a methanol solution of the former under 1 atm of H_2. The kinetics of catalytic hydrogenation were investigated at near-ambient conditions. The rate of catalytic hydrogenation, monitored by measuring the consumption of H_2 at constant pressure, was found to be pseudo first order in the olefin until the latter was consumed (Figure 1). The pseudo-first-order rate constants (k_{obs}), defined by eq 2, where [S] is the concentration of unreacted substrate, are listed in Table I. k_{obs} was found to

$$k_{obs} = -\mathrm{d}\ \ln\ [S]/\mathrm{d}t \qquad (2)$$

be first order in the initial concentration of the catalyst precursor **1a** and in H_2 but to depend inversely on the initial concentration of substrate **2b** and on the sum of the initial concentrations of substrate **2b** and product **3b** (Figures 1 and 2).

Determination of the Equilibrium Constants *K*. To determine the relative extents of binding to the catalyst of the different carboxylates present in the reaction mixture, the equilibrium constants[5] were determined for the equilibria of eqs 3 and 4, where HA and HB are pairwise combinations of the carboxylic acids

$$Ru(A)_2 + HB = Ru(A)(B) + HA \qquad (K) \qquad (3)$$

$$Ru(A)(B) + HB = Ru(B)_2 + HA \qquad (K') \qquad (4)$$

present in solution during the hydrogenation of the substrate **2b**: acetic acid (from the catalyst precursor **1a**), tiglic acid (**2b**), and 2-methylbutyric acid (**3b**). The results, listed in Table II, reveal that the binding of the second carboxylate is nearly independent of the nature of the first carboxylate ligand (i.e. $K/K' \cong 4$). If HA and HB compete equally well for the binding sites, then statistically K should be 2 and K' should be 0.5; i.e., Ru-

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(2) (a) Noyori, R. *Science* **1990**, *248*, 1194. (b) Ojima, I. *Pure Appl. Chem.* **1984**, *56*, 99. (c) Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: Oxford, 1982; Vol 8, pp 463–498. (d) *Asymmetric Catalysis*; Bosnich, B., Ed.; NATO ASI Ser. E, No. 103; Martinus Nijhoff: Dordrecht, 1986.

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(5) K and K' are the apparent relative binding constants, related to the actual relative binding constants for the equilibria $RuA_2 + B^- = RuAB + A^-$ and $RuAB + B^- = RuB_2 + A^-$ by the ratio of the acid ionization constants of HA and HB. For the purpose of our kinetic analysis, the former equilibrium constants (i.e. those defined by eqs 3 and 4) are the relevant ones.

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Table I. Kinetic Data for the Hydrogenation of Tiglic Acid (**2b**) by Ru(BINAP)$(O_2CR)_2$ (**1**)

$[Ru]_T$, M	$[S]_0$, M	$[P]_0$, M	P_{H_2}, atm	$10^3[H_2]$,[a] M	$[H^+]$, M	$[OR^-]$, M	temp, °C	k_{obs}, s^{-1}	k, $M^{-1}\,s^{-1}$
20.0×10^{-5}	5.00×10^{-2}	0	1.00	3.69	0	0	21.3	5.10×10^{-3}	172
10.0×10^{-5}	5.00×10^{-2}	0	1.00	3.69	0	0	20.9	2.48×10^{-3}	168
5.00×10^{-5}	5.00×10^{-2}	0	1.00	3.69	0	0	21.0	1.24×10^{-3} [b]	168
2.50×10^{-5}	5.00×10^{-2}	0	1.00	3.69	0	0	20.8	0.63×10^{-3}	170
5.00×10^{-5}	10.0×10^{-2}	0	1.00	3.69	0	0	20.9	0.73×10^{-3}	197
5.00×10^{-5}	2.50×10^{-2}	0	1.00	3.69	0	0	21.2	2.62×10^{-3}	177
5.00×10^{-5}	1.25×10^{-2}	0	1.00	3.69	0	0	21.5	4.82×10^{-3}	163
5.00×10^{-5}	2.50×10^{-2}	1.25×10^{-2}	1.00	3.69	0	0	20.8	1.73×10^{-3}	175
5.00×10^{-5}	2.50×10^{-2}	3.15×10^{-2}	1.00	3.69	0	0	20.5	1.12×10^{-3}	171
5.00×10^{-5}	2.50×10^{-2}	5.90×10^{-2}	1.00	3.69	0	0	20.7	0.71×10^{-3}	161
5.00×10^{-5}	2.50×10^{-2}	0	1.50	5.53	0	0	21.5	3.91×10^{-3}	176
5.00×10^{-5}	2.50×10^{-2}	0	0.67	2.47	0	0	20.7	1.60×10^{-3}	161
5.00×10^{-5}	2.50×10^{-2}	0	0.44	1.62	0	0	21.0	0.98×10^{-3}	151
5.00×10^{-5}	2.50×10^{-2}	0	1.00	3.69	2.50×10^{-5}	0	20.8	1.36×10^{-3}	
5.00×10^{-5}	2.50×10^{-2}	0	1.00	3.69	5.00×10^{-5}	0	21.2	0.30×10^{-3} [c]	
5.00×10^{-5}	2.50×10^{-2}	0	1.00	3.69	10.0×10^{-5}	0	20.5	0	
5.00×10^{-5}	2.50×10^{-2}	0	1.00	3.69	0	1.25×10^{-3}	20.5	2.75×10^{-3}	
5.00×10^{-5}	2.50×10^{-2}	0	1.00	3.69	0	2.50×10^{-3}	21.0	2.80×10^{-3} [d]	
5.00×10^{-5}	2.50×10^{-2}	0	1.00	3.69	0	3.75×10^{-3}	21.8	2.85×10^{-3}	
5.00×10^{-5}	2.50×10^{-2}	0	1.00	3.69	0	5.00×10^{-3}	21.0	2.73×10^{-3}	
							av = 21.0 ± 0.4		av = 170 ± 11

[a] Solubility of H_2 is 3.69×10^{-3} M atm^{-1}. [b] % ee = 100(R - S)/(R + S) = 92%. [c] % ee = 94%. [d] ee = 93%.

Table II. Equilibrium Constants for the Binding of α,β-Unsaturated Carboxylic Acids by Ru(BINAP)$(O_2CR)_2$

HA	HB	$K = \frac{[RuAB][A]}{[RuA_2][B]}$	$K' = \frac{[RuAB_2][A]}{[RuAB][B]}$	K/K'
acetic acid	**2b**	5.0 (9)[a]	1.1 (2)[a]	4.5
2b	**3b**	1.6	0.4	4.0

[a] An average of six measurements for which K ranged from 4.2 to 6.8 and K' ranged from 0.9 to 1.4. The standard deviation of the least significant digit is shown in parentheses.

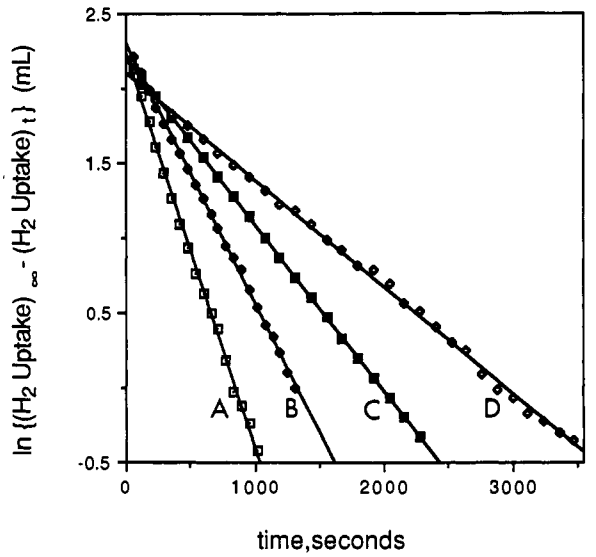


Figure 1. First-order plots of H_2 uptake vs time for the Ru(BINAP)$(O_2CR)_2$-catalyzed hydrogenation of tiglic acid (**2b**) at 21 °C: $[\mathbf{1a}]_0 = 5.0 \times 10^{-5}$ M; $[\mathbf{2b}]_0 = 2.5 \times 10^{-2}$ M; H_2 pressure = 1.0 atm; V = 20 mL. The initial concentrations of added product were the following: A, $[\mathbf{3b}]_0 = 0$ M ($k_{obs} = 2.62 \times 10^{-3}\ s^{-1}$); B, $[\mathbf{3b}]_0 = 1.25 \times 10^{-2}$ M ($k_{obs} = 1.73 \times 10^{-3}\ s^{-1}$); C, $[\mathbf{3b}]_0 = 3.15 \times 10^{-2}$ M ($k_{obs} = 1.12 \times 10^{-3}\ s^{-1}$); D, $[\mathbf{3b}]_0 = 5.95 \times 10^{-2}$ M ($k_{obs} = 0.71 \times 10^{-3}\ s^{-1}$).

$(A)_2$:Ru(A)(B):Ru$(B)_2$ = 1:2:1 when the concentrations of HA and HB are equal. The actual values of $K = 1.6$ and $K' = 0.4$ ($K/K' = 4.0$) reflect a slight preference for the binding of the anion of **2b** over **3b**. Furthermore, at equal concentration of **2b** and HOAc, a significant preference for the binding of tiglate over acetate was found ($K = 1.1$, $K' = 5.0$, $K/K' = 4.5$).

Influence of Acid and Base on the Kinetics of Catalytic Hydrogenation. The kinetic data reported here were obtained in a quartz reaction vessel. The decision to use a quartz vessel was dictated by the results of earlier experiments that were plagued with reproducibility problems when Pyrex glassware was used. We found it impossible to obtain reliable kinetic data unless the Pyrex glassware was "silated" with chlorotrimethylsilane (TMSCl). Typically, a Pyrex reaction vessel was flame dried while connected to a vacuum line, treated with TMSCl, and the volatiles were removed under high vacuum with heating. Kinetic data obtained in a reaction vessel constructed of Pyrex treated with TMSCl were identical, within experimental error, with those obtained with use of the quartz reaction vessel not treated with TMSCl. These observations prompted us to investigate the influence of strong acids and bases on the kinetics of hydrogenation of **2b** catalyzed by **1**.[6] The results are listed in Table I and summarized in Figure 3. Trifluoromethanesulfonic acid was chosen to investigate the influence of H^+ on the kinetics of hydrogenation. In a control experiment, it was determined that trifluoromethanesulfonate had no effect on the rate. Tetrabutylammonium hydroxide was chosen to investigate the effect of base. The latter, being a stronger base, presumably deprotonates the substrate **2b**, i.e., $RCOOH + OH^- \rightarrow RCOO^- + H_2O$. Figure 3 reveals that base has no effect on

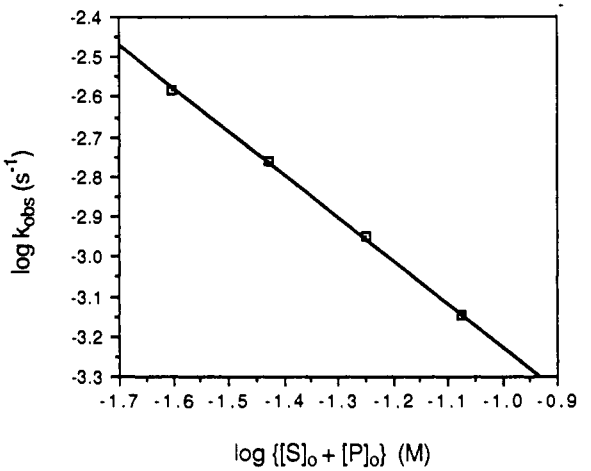


Figure 2. Dependence of the rate of the Ru(BINAP)$(O_2CR)_2$-catalyzed hydrogenation of tiglic acid (**2b**) on the sum of the initial substrate and product concentrations; $[\mathbf{2b}]_0 = 2.50 \times 10^{-2}$ M; slope = 1.08.

(6) Carboxylic acids are weak acids in methanol; e.g., the pK_a of HOAc in methanol is 9.5: Meites, L. In *Handbook of Analytical Chemistry*; McGraw-Hill: New York, 1963; pp 1-35.

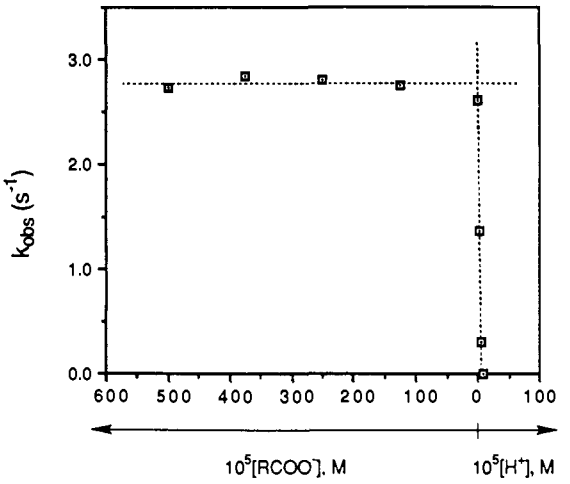


Figure 3. Dependence of the rate of the Ru(BINAP)(O_2CR)$_2$-catalyzed hydrogenation of tiglic acid (**2b**) on the concentrations of added acid and base; $[\mathbf{1a}]_0 = 5.0 \times 10^{-5}$ M, $[\mathbf{2b}]_0 = 2.5 \times 10^{-2}$ M.

the rate. In contrast, acid affects the rate markedly. *In the presence of little more than 1 equiv of acid, with respect to the catalyst concentration, reaction is completely suppressed.* The inhibition by acid can be reversed by adding base. We note that these results are apparently at variance with a report that addition of 2 equiv of tetrafluoroboric acid has no influence on the product or the optical yields obtained for the **1a**-catalyzed hydrogenation of **2b**.[4] Perhaps the higher catalyst concentration, lower substrate concentration, higher H_2 pressure, and longer reaction times of the latter experiment compensate for the presence of acid.

The acid may serve to protonate **1** to give cationic species which, apparently, are not active catalysts for the hydrogenation of **2b**. Consistent with this, addition of trifluoromethanesulfonic acid or tetrafluoroboric acid to a methanol solution of **1a** results in the formation of four new unidentified species, as indicated by the ^{31}P NMR spectrum of the reaction mixture (see Experimental Section). Addition of tetrabutylammonium acetate to the latter solution results in re-formation of **1a**.

With respect to the original impetus for investigating the influence of acids and bases on the kinetics of hydrogenation of **2b** by **1a**, the apparent inhibition of the rate by Pyrex glass, we note that it has previously been reported that anhydrous methanol reacts with Pyrex and other borasilicate glasses to give methylborates.[7] The borates may serve as Lewis acids.

Molecular Structure of 1 in Methanol. The ^{1}H and ^{31}P NMR spectra of **1a** and **1b** indicate that at room temperature the carboxylate ligands and the two phosphorus atoms of the BINAP ligand are magnetically equivalent on the NMR time scale (see Experimental Section). However, when methanol was employed as the solvent, the NMR spectra proved to be dynamic at low temperatures. Static ^{1}H and ^{31}P NMR spectra obtained at −80 °C reveal that neither the acetate ligands nor the phosphorus atoms of the BINAP ligand of **1a** are magnetically equivalent: ^{1}H NMR (CD_3OD, −80 °C), δ 1.65 (s, 3 H, $OCCH_3$), 1.73 (s, 3 H, $OCCH_3$), 6.1–8.0 (m, aromatic protons); $^{31}P\{^1H\}$ (CD_3OD, −80 °C) δ 65.63, 65.18 (AB at 80.96 MHz, $^2J_{PP}$ = 46 Hz). The spectra obtained at −80 °C indicate that the molecular symmetry of **1a** in methanol solutions is lower than that (C_2) found for the pivalate derivative in the solid state.[8] In CD_2Cl_2 solution, the acetate ligands and the phosphorus atoms of the BINAP ligand of **1a** remained magnetically equivalent to −90 °C. Thus, the solvent affects the molecular structure of **1a** in solution, perhaps by serving as a ligand. In support of this, acetonitrile reacts with **1a** to give a 1:1 adduct, which is stable enough to isolate: ^{1}H NMR (CD_3OD, 20 °C), δ 1.56 (s, 3 H, $OCCH_3$), 1.71 (d, 3 H, $^3J_{N-H}$ = 4 Hz, $^{15}NCCH_3$), 1.88 (s, 3 H, $OCCH_3$), 6.4–7.9 (m, aromatic protons); $^{31}P\{^1H\}$ (CD_3OD, −50 °C) δ 63.1 (dd, $^3J_{P-P'}$ = 40.5 Hz, $^3J_{^{15}N-P}$ = 2.9 Hz), 57.1 (dd, $^3J_{N-P'}$ = 3.7 Hz). The molecular structure of **1b** in methanol apparently is similar to that of **1a**: $^{31}P\{^1H\}$ (CD_3OD, −80 °C) δ 66.18, 65.70 (AB at 80.96 MHz, $^2J_{PP}$ = 46 Hz). Most significantly, *no NMR evidence was found to suggest that the C=C bond of* **1b** *coordinates to the metal.*

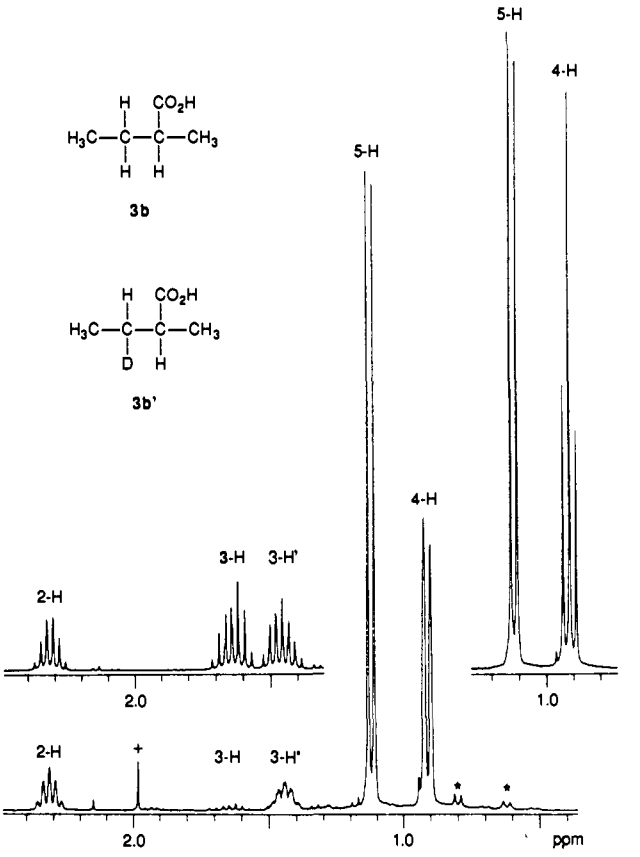
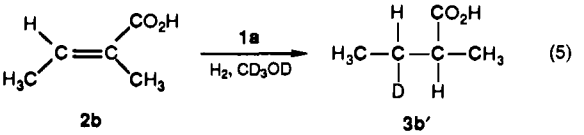


Figure 4. NMR spectra of **3b** (top) and **3b'** (bottom): (+) AcOH, (*) **1c**. Note (1) the near absence of the 3-H signal in **3b'** and (2) that the 4-H proton signals of **3b** and **3b'** appear as a triplet and a (broadened) doublet, respectively, as a result of splitting by the adjacent CH_2 and CHD groups.

Reactions of 1 in Methanol d_4. Substrate **2b** was catalytically hydrogenated with **1a** in CD_3OD to determine whether and where deuterium was incorporated into the product. As depicted by eq 5, deuterium incorporation was found to be both regio- and stereoselective (Figure 4). Incorporation of deuterium was largely



(5)

confined to *one* of the diastereotopic β-positions of the product, whereas incorporation into the α-position and the other β-position was minor. *The lack of significant deuterium incorporation into the α-position of the product rules out substantial H/D exchange between H_2 and the solvent prior to reaction with the substrate and also implies the H/D exchange between the Ru–H intermediate and the solvent, prior to insertion of the C=C bond, must be comparatively slow.* Finally, bearing on this theme is our finding that, whereas reaction of H_2 with **1a** did not result in accumulation of a detectable amount of a Ru–H complex, **1a** did catalyze the H/D exchange between H_2 and CD_3OD (see Experimental Section).

Discussion

Kinetics, Mechanism, and Rate Law for the Hydrogenation of 2b Catalyzed by 1. The mechanism depicted in Figure 5 encom-

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(8) Ohta, T.; Takaya, H.; Noyori, R. *Inorg. Chem.* **1988**, *27*, 566.

passes the essential features of the results described above: (1) rapid equilibrium between **1** and the substrate, (2) heterolytic splitting of H_2 to give a ruthenium dicarboxylate monohydride species, (3) insertion of the C=C bond of the substrate into the Ru–H bond to give a five-membered heterometallacyclic species, and (4) protonolysis (deuteronolysis) of the Ru–C bond to regenerate the ruthenium–dicarboxylate adduct. Assuming the carboxylate substitution equilibrium step of Figure 5 to be rapid and subsequent addition of H_2 to be turnover limiting, only these two steps need to be considered in deriving the rate law. Acetate and the conjugate bases of both the substrate **2b** and product **3b** bind to the ruthenium with comparable binding constants. Since the concentration of the catalyst precursor **1a** and, thus, the concentration of acetate are low compared to the initial concentration of the substrate, it may be assumed that the catalyst precursor is, in effect, **1b**. Therefore, the equilibrium of Figure 5 is between **1b**, **2c**, and **1e** (hereafter, for the purpose of derivation of the rate equation, referred to as RuS_2, RuSP, and RuP_2, respectively). The position of this equilibrium is determined by the concentrations of the substrate **2b** and product **3b**, which vary during the course of the hydrogenation reaction. Assuming RuS_2 to be twice as active as RuSP (a statistical factor) the rate law is given by eq 6. If, as indicated by the NMR spectra, most of

$$-d[S]/dt = k([RuSP] + 2[RuS_2])[H_2] \quad (6)$$

the ruthenium-containing species are bis(carboxylates) (**1**), then $[Ru]_T = [RuS_2] + [RuSP] + [RuP_2]$. Accordingly, we can express $[RuS_2]$ and [RuSP] in terms of $[Ru]_T$:

$$K = \frac{[RuSP][S]}{[RuS_2][P]};\ [RuSP] = K\frac{[RuS_2][P]}{[S]} \quad (7)$$

$$K' = \frac{[RuP_2][S]}{[RuSP][P]};\ [RuP_2] = K'\frac{[RuSP][P]}{[S]} = KK'\frac{[RuS_2][P]^2}{[S]^2} \quad (8)$$

$$[Ru]_T = [RuS_2] + K[RuS_2]\frac{[P]}{[S]} + KK'[RuS_2]\frac{[P]^2}{[S]^2} \quad (9)$$

The concentrations of the active species RuS_2 and RuSP now can be defined in terms of $[Ru]_T$:

$$[RuS_2] = \frac{[Ru]_T}{1 + K\frac{[P]}{[S]} + \frac{KK'[P]^2}{[S]^2}} = \frac{[Ru]_T[S]^2}{[S]^2 + K[S][P] + KK'[P]^2} \quad (10)$$

$$[RuSP] = \frac{K[Ru]_T[S][P]}{[S]^2 + K[S][P] + KK'[P]^2} \quad (11)$$

Therefore, the rate law, in terms of $[Ru]_T$, is given by

$$\frac{-d[S]}{dt} = k\left(\frac{K[Ru]_T[S][P] + 2[Ru]_T[S]^2}{[S]^2 + K[S][P] + KK'[P]^2}\right)[H_2] \quad (12)$$

Introducing the approximation that $K = 2$ and $K' = {}^1/_2$, the rate law reduces to

$$\frac{-d[S]}{dt} = 2k\left(\frac{[Ru]_T[S]}{[S] + [P]}\right)[H_2] = 2k\left(\frac{[Ru]_T[S]}{[S]_0 + [P]_0}\right)[H_2] \quad (13)$$

In the absence of added product, eq 13 reduces to

$$\frac{-d[S]}{dt} = 2k\left(\frac{[Ru]_T[S]}{[S]_0}\right)[H_2] \quad (14)$$

Comparison of eq 13 with eq 2 yields

$$k_{obs} = \frac{2k[Ru]_T[H_2]}{[S]_0 + [P]_0} \quad (15)$$

or, in the absence of added product

$$k_{obs} = 2k[Ru]_T[H_2]/[S]_0 \quad (16)$$

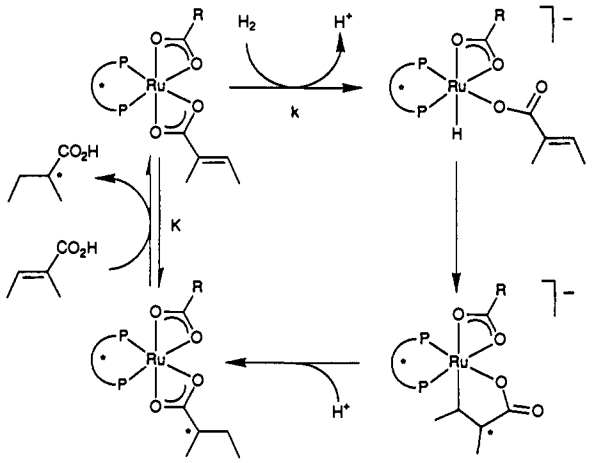

Figure 5. Mechanistic scheme for the the $Ru(BINAP)(O_2CR)_2$-catalyzed hydrogenation of tiglic acid (**2b**). When starting with the catalyst precursor $Ru(BINAP)(OAc)_2$ entry with the catalytic cycle is effected by the rapid displacement of the acetate ligand by tiglate.

Table III. Kinetic Data for the Hydrogenation of α,β-Unsaturated Carboxylic Acids by $Ru(BINAP)(O_2CR)_2$

substrate	$[Ru]_T$, M	$[S]_0$, M	k_{obs}, s^{-1}	k, M^{-1} s^{-1}
2a	5.00×10^{-5}	5.00×10^{-2}	1.12×10^{-3}	151
2b	5.00×10^{-5}	2.50×10^{-2}	2.62×10^{-3}	177
2c	1.25×10^{-5}	2.50×10^{-2}	3.28×10^{-3}	887

Values of k_{obs}, derived from the pseudo-first-order rate plots, such as those in Figure 1, are listed in Table I, together with the corresponding values of k calculated with eq 15. At 20 ± 0.4 °C, $k = 170 \pm 11$ M^{-1} s^{-1}.

Further evidence for the first step of the catalytic cycle of Figure 5, reaction of a bis(carboxylato)ruthenium species with H_2, is provided by the observation of $Ru(BINAP)(OAc)_2$-catalyzed H/D exchange between H_2 and CD_3OD. In the absence of a C=C bond to insert into the Ru—H, the reaction of **1** with H_2 apparently proceeds reversibly. The equilibrium of this step must lie far to the left since the hydride does not accummulate in sufficiently high concentration to be detected. A direct parallel is to be found in the previously reported heterolytic splitting of H_2 by ruthenium chloride complexes.[9]

Other α,β-Unsaturated Carboxylic Acids. The rates of hydrogenation of substrates **2a** and **2c** also were measured. Approximate first-order kinetics were observed in both cases, yielding the pseudo-first-order rate constants listed in Table III. The experiment that employed **2a** was complicated in that **2a** readily polymerizes in the absence of radical inhibitors. Therefore, it was not possible to store stock solutions of **2a** for more than a day or two. However, good results were obtained with freshly distilled samples of **2a**. It may be seen that the values of k for **2a** and **2b** are similar; however, **2c** is significantly more reactive. In view of the similar reactivities of **2a** and **2b**, the greater reactivity of **2c** cannot be attributed to the β substituent. More sterically demanding substrates generally react more slowly. Since the naphthyl moiety of **2c** is significantly more sterically demanding than a methyl group, it appears likely that the enhanced reactivity of **2c** is due to electronic factors. Clarification of this point calls for examination of a broader range of substrates.

In conclusion, attention is directed to formal parallels between the system described in this paper and the following: (1) the hyydrogenation of unsaturated carboxylic acids in aqueous solutions catalyzed by $Ru^{II}Cl_n$ complexes, the first characterized homogeneous catalytic hydrogenation of an olefin;[9] and (2) the catalysis of the hydrogenation (including asymmetric hydrogenation) of α-(acetylamino)acrylic acid esters by Rh^I(diphosphine) complexes, the mechanism of which also involves reaction of H_2

(9) Halpern, J.; Harrod, J. F.; James, B. R. *J. Am. Chem. Soc.* **1966**, *88*, 5150.

with a metal–substrate adduct (albeit by oxidative addition rather than heterolytic splitting) to give a five-membered heterometallic intermediate.[3] An important difference, however, is that whereas coordination of the substrate to the metal in both of the above catalyst–substrate adducts is through the C=C bond, coordination of the substrate in **1b** and **1e** appears to be entirely through the carboxyl groups. The absence of any significant contribution from C=C bond coordination in these adducts is supported by the similarities of the NMR spectra of **1a–e** and by the similar binding constants (K and K') of **2b** and **3b**. While the presence of small amounts of (C=C)-coordinated isomers of **1b** and **1e** cannot be excluded, the high values of k make it unlikely that the reactions of **1b** and **1e** with H_2 are due to such minor species. Also arguing against such a possibility are the insensitivity of k to steric influences associated with variation of the substituents on the C=C bond (Table III) and the fact that the ratio of the rate constants for the reactions of **1b** and **1e** with H_2 is close to the statistical factor of 2. If coordination of the C=C bond to Ru is, as generally believed, a prerequisite to insertion, then such coordination must occur *after* reaction with H_2.

Finally, it is noteworthy that our observation of inhibition of the catalytic activity of **1** by acids contrasts with reports on related, although not identical, systems that claim rate enhancements in the presence of acids.[10] The significance of this is unclear. However, in view of our difficulties in obtaining reproducible results in Pyrex glass, caution should be exerted in comparing our observations with other reports in the literature.

Experimental Section

Reagents. Ultra-high purity grade hydrogen (Linde Corp.) was used without further purification. Tiglic acid (Aldrich) was dried over P_2O_5 and sublimed under vacuum. Methacrylic acid (Aldrich) and (±)-2-methylbutyric acid (Aldrich) were dried over $CaCl_2$ and vacuum distilled just before use. Spectroscopic grade methanol was dried by successive distillation from sodium under argon. Trifluoromethanesulfonic (triflic) acid (Aldrich) was received in an ampule, which was opened and stored in an inert atmosphere glovebox. Tetrafluoroboric acid–diethyl etherate (Aldrich) was used as received. Tetrabutylammonium hydroxide was obtained from Aldrich as a 1 M solution in methanol. (*R*)-(+)-α-Methylbenzylamine (Aldrich) and (*S*)-(+)-2-methylbutyric acid (Aldrich) were used as received. Bis(acetato){(*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl}ruthenium(II) (**1a**) was synthesized according to the published procedure.[8] (*R*)-(+)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) and 2-(6-methoxy-2-naphthyl)acrylic acid were gifts from the Hoffmann-La Roche and Monsanto companies, respectively, and were used as received.

Preparation of 1b. A solution of **1a** (100 mg) and tiglic acid (50 mg) in 5 mL of methanol was allowed to evaporate in a glovebox until its volume had been reduced by ca. 50%, during which time well-formed yellow crystals of **1b** grew. The solute was removed with a pipet and the crystals were washed with methanol (ca. 0.5 mL). The isolated yield of **1b** was not determined. No NMR signals other than those assignable to **1b** were detected: ^{1}H NMR ($CDCl_3$) δ 1.58–1.59 (m, $O_2C(CH_3)$=C(H)(CH_3)), 6.4–7.8 (m, vinylic and aromatic protons); ^{31}P{^{1}H} ($CDCl_3$) δ 64.7 (s).

Reaction of 1b with H_2. A CD_2Cl_2 solution of **1b** in a PTFE high-vacuum stopcock-equipped NMR tube was freeze–pump–thawed on a vacuum line, 500 Torr of H_2 was introduced, and the tube was flame sealed. The tiglate ligands were slowly hydrogenated to give **1c**: ^{1}H NMR (CD_2Cl_2) δ 0.72 (t, $^3J_{HH}$ = 7.2 Hz, $OC(CH_3)(H)C(H)_2(CH_3)$), 0.98 (d, $^3J_{HH}$ = 6.4 Hz, $OC(CH_3)(H)C(H)_2(CH_3)$), 1.29, 1.50 (dq, $OC(CH_3)(H)C(H)_2(CH_3)$), 2.08 (q, $OC(CH_3)(H)C(H)_2(CH_3)$), 6.5–7.9 (m, aromatic protons); ^{31}P{^{1}H} ($CDCl_3$) δ 65.1 (s).

Measurements of the Catalytic Hydrogenation Rates by H_2 Uptake at Constant Pressure. The rate of uptake of H_2 was measured with an apparatus consisting of a magnetically stirred reaction vessel, a pressure reference bulb, an oil manometer configured to indicate the reaction vessel pressure relative to the reference bulb, a calibrated gas piston, and a mercury manometer. The reaction vessel was constructed of quartz and was connected via a gradient seal to two high-vacuum PTFE stopcocks. One of the stopcocks opened to an O-ring joint that was used to attach the vessel to the apparatus; the other stopcock opened to a septum port. The reaction vessel was flame dried on a vacuum line and fitted with a rubber septum. For subambient pressure experiments it was necessary to pack the septum port with Krytox fluorinated grease to prevent air from contaminating the reaction vessel when the septum was punctured. Methanol solutions containing all the reaction components less the catalysts precursor **1a** were loaded into the reaction vessel in an inert atmosphere glovebox with use of Hamilton gas-tight syringes. The vessel was sealed with the high-vacuum valves, removed from the glovebox, and connected to a vacuum line, where the reaction solution was freeze–pumped–thawed twice. The vessel was moved to the gas uptake apparatus and was submerged in a constant temperature water bath. After the apparatus had been purged several times with H_2, the high-vacuum valve of the vessel was opened, and the reaction vessel was filled with a measured pressure of H_2. The reaction vessel and gas uptake apparatus were allowed to equilibrate for 1 h. Following equilibration, a methanol solution of the catalyst **1a** was added to the reaction vessel via the septum port. The resulting reaction mixture was allowed to equilibrate for 1 min and the reference bulb was isolated from the reaction vessel by closing an interconnecting valve. H_2 uptake, as indicated by displacement of the oil manometer level, was compensated for by lowering the reaction vessel volume through compression of the calibrated piston. The piston volume displacement required to maintain constant pressure was determined at measured intervals of time. Data were collected until at least 90% of the substrate had been converted to product. First-order rate plots of the data were typically found to be linear over 95% conversion of the substrates to their hydrogenated products (Figure 1). Product conversions were routinely checked by ^{1}H NMR.

Measurement of the Enantiomeric Excesses of 2-Methylbutyric Acid (3b). Samples for the analysis were obtained directly from the reaction solutions used for the H_2 uptake experiments. The solvent was removed with a rotary evaporator and the resulting residue was taken up in a minimum amount of $CDCl_3$ (ca. 0.4 mL). The chiral solvating agent (CSA) (*R*)-(+)-α-methylbenzylamine (ca. 0.1 mL) was added and the ^{13}C NMR spectrum was recorded. A pair of peaks at ca. 17 ppm corresponding to the 2-methyl carbons of the adducts of the product **3b** with the CSA were integrated and the optical yields calculated as percentages with the following formula: % ee = 100(R-S)/(R+S). The 2-methyl ^{13}C resonance of the (*R*)-(−)-2-methylbutyric acid adduct of the CSA is located downfield with respect to the (*S*)-(+)-2-methylbutyric acid adduct.

Determination of the Equilibrium Constants K and K' for Acetic Acid and Tiglic Acid (2b). To a 0.01 M CD_3OD solution of **1a** in an inert atmosphere glovebox were added successive aliquots of **2b** to give solutions containing equilibrium mixtures of I. The relative concentrations of **1a**, **1b**, **1d**, free acetic acid, and free **2b** were obtained by integration of the ^{1}H NMR spectra. Six equilibrium mixtures were prepared that contained varied amounts of acetic acid and **2b**. For **1a**: ^{1}H NMR (CD_3OD) δ 1.71 (s, 6 H, $OCCH_3$), 6.1–8.0 (m, aromatic protons); ^{31}P-{^{1}H} (CD_3OD) δ 65.4 (s). For **1b**: ^{1}H NMR (CD_3OD), δ 1.56 (s, 6 H, $OC(CH_3)$=C(H)(CH_3)), 1.62 (d, 6 H, $^3J_{HH}$ = 4.5 Hz, $OC(CH_3)$=C(H)(CH_3)), 6.1–8.0 (m, aromatic and vinyl protons); ^{31}P{^{1}H} (CD_3OD) δ 65.4 (s). For **1d**: ^{1}H NMR (CD_3OD) δ 1.59 (s, 3 H, $OC(CH_3)$=C(H)(CH_3)), 1.64 (d, 3 H, $^3J_{HH}$ = 4.2 Hz, $OC(CH_3)$=C(H)(CH_3)), 1.71 (s, 3 H, $OCCH_3$), 6.1–8.0 (m, aromatic and vinyl protons); ^{31}P{^{1}H} (CD_3OD) δ 65.9, 64.9 (AB at 80.96 MHz, $^2J_{PP}$ = 49 Hz). For acetic acid: ^{1}H NMR (CD_3OD) δ 2.01 (s). For **2b**: ^{1}H NMR (CD_3OD) δ 1.82 (d, 3 H, $^3J_{HH}$ = 4.5 Hz, $OC(CH_3)$=C(H)(CH_3)), 1.84 (s, 3 H, $OC(CH_3)$=C(H)(CH_3)), 6.84 (q, 1 H, $OC(CH_3)$=C(H)(CH_3)).

Determination of the Equilibrium Constants K and K' for Tiglic Acid (2b) and 2-Methylbutyric Acid (3b). To a CD_3OD solution of **1b** containing excess tiglic acid in an inert atmosphere glovebox was added (*S*)-(+)-2-methylbutyric acid. An equilibrium mixture of **1b**, **1c**, and **1e** formed. The relative concentrations of **1b**, **1c**, **1e**, **2b**, and **3b** were obtained by integration of the ^{1}H NMR spectrum. Only a portion of the spectrum for each species did not overlap. The resonances at 1.56 ppm (s, 6 H, $OC(CH_3)$=C(H)(CH_3)) for **1b**, 0.77 ppm (d, 6 H, $^3J_{HH}$ = 14.3 Hz, $OC(CH_3)(H)C(H)_2(CH_3)$) for **1c**, 0.75 ppm (d, 3 H, $^3J_{HH}$ = 13.5 Hz, $OC(CH_3)(H)C(H)_2(CH_3)$) for **1e**, 1.82 ppm (d, 3 H, $^3J_{HH}$ = 4.5 Hz, $OC(CH_3)$=C(H)(CH_3)) for **2b**, and 1.12 ppm (d, 3 H, $^3J_{HH}$ = 7.4 Hz, $OC(CH_3)(H)C(H)_2(CH_3)$) for **3b** were used.

Reaction of 1a with H_2 in Methanol-d_4. H_2 (1 atm) was added to a solution containing **1a** (ca. 2 mg) in CD_3OD (0.5 mL) in a NMR tube fitted with a J. Young valve. The tube was shaken and the ^{1}H NMR spectrum quickly determined. The spectrum contained, in addition to the peaks for **1a** and the residual peaks of the solvent, two transient peaks assigned to dissolved H_2 and HD. A ^{1}H NMR spectrum collected a few minutes later showed neither of the latter peaks, indicating the dissolved H_2 had been converted to D_2. In support of the latter conclusion, the residual OH peak of the solvent increased proportionally in intensity. The sequence of shaking the tube and recording the ^{1}H NMR spectrum was repeated several times with similar results. No change in that part of

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the spectrum corresponding to **1a** was observed.

Reaction of 1a with Trifluoromethanesulfonic Acid. To a solution containing **1a** (8 mg) in CD_3OD (0.5 mL) in a NMR tube fitted with a J. Young valve was added trifluoromethanesulfonic acid (2 μL). A complicated ^{31}P NMR spectrum results, which is apparently the result of four phosphorus-containing species (**4a-d**), each of which possess inequivalent BINAP phosphorus atoms: $^{31}P\{^1H\}$ (CD_3OD, -80 °C) δ 82.1 (d, 3%, $J_{PP'}$ = 25 Hz, **4a**), 74.9 (d, 5%, $J_{PP'}$ = 25 Hz, **4a**), 61.9 (d, 27%, $J_{PP'}$ = 44 Hz, **4b**), 61.0 (d, 13%, $J_{PP'}$ = 44 Hz, **4c**), 60.3 (d, 29%, $J_{PP'}$ = 44 Hz, **4b**), 52.3 (d, 13%, $J_{PP'}$ = 42 Hz, **4c**), 52.3 (d, 5%, $J_{PP'}$ = 32 Hz, **4d**), 52.3 (d, 5%, $J_{PP'}$ = 32 Hz, **4d**). The above experiment was repeated three times. The percentages given indicate the relative abundance of **4a-d** for the particular experiment described above. The relative abundance of **4a-d** varied from experiment to experiment; however, **4b** always formed predominantly, followed next by **4c**. Tetrabutylammonium hydroxide and sodium methoxide, in the absence of excess carboxylic acid, react with **4a-d** as they react with **1a**, to give an insoluble orange precipitate. *However, addition of excess tetrabutylammonium acetate converts* ***4a-d*** *to* ***1a***.

Reaction of 1a with Tetrafluoroboric Acid. To a solution containing **1a** (ca. 12 mg) in CD_3OD (0.5 mL) in a NMR tube fitted with a J. Young valve was added tetrafluoroboric acid (5 μL). The resulting ^{31}P NMR spectrum was similar to those obtained when trifluoromethanesulfonic acid was added.

Deuterium Crossover Hydrogenation of Tiglic Acid (2b). A quartz tube fitted with a high-vacuum stopcock and O-ring joint was charged with **1a** (2.0 mg), **2b** (4.5 mg), and CD_3OD (1.5 mL). The resulting solution was freeze-pump-thawed twice on a vacuum line and H_2 (1.5 atm) was introduced to the flask. The solution was stirred *vigorously* with a magnetic stir bar. A 0.5-mL aliquot was removed after 3 h. The ^1H NMR spectrum showed that hydrogenation was complete (Figure 4): ^1H NMR (CD_3OD) δ 2.32 (p, 0.64 H, $^3J_{HH}$ = 6.9 Hz, $OC(CH_3)(H)C(H)_2(CH_3)$), 1.62 (m, 0.12 H, $OC(CH_3)(H)C(H)_2(CH_3)$), 1.44 (m, 0.74 H, $OC(CH_3)(H)C(H)_2(CH_3)$), 1.12 (d, 3.1 H, $^3J_{HH}$ = 6.9 Hz, $OC(CH_3)(H)C(H)_2(CH_3)$), 0.91 (br d, 3.0 H, $^3J_{HH}$ = 6.9 Hz, $OC(CH_3)(H)C(H)_2(CH_3)$).

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Generation, Entrapment, and Spectroscopic Characterization of Radical Cations of α,ω-Diphenyl Polyenes within the Channels of Pentasil Zeolites†

V. Ramamurthy,* Jonathan V. Caspar,* and David R. Corbin

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Abstract: Inclusion of *all-trans*-α,ω-diphenyl polyenes (*trans*-stilbene, 1,4-diphenyl-1,3-butadiene, 1,6-diphenyl-1,3,5-hexatriene, 1,8-diphenyl-1,3,5,7-octatetraene) in thermally activated Na-ZSM-5 zeolite leads to the rapid formation of cation radicals of the polyenes. These cation radicals are stabilized within the zeolite host and are conveniently studied by conventional spectroscopic techniques (ESR, UV-vis-NIR diffuse reflectance, emission) enabling us to determine for the first time the steady state fluorescence spectrum of the 1,6-diphenyl-1,3,5-hexatriene and 1,8-diphenyl-1,3,5,7-octatetraene cation radicals. Our method of generation and stabilization of organic cation radicals appears to be both general in scope and simple in practice. While the mechanism of oxidation remains unclear, it appears that the presence of aluminum in the zeolite is a requirement; as the Si/Al ratio decreases the extent of oxidation increases. Using a series of substituted stilbenes of known redox potential leads to an estimated redox potential of 1.65 ± 0.1 eV vs SCE for the zeolite-based oxidant.

Introduction

Although the first stable crystalline cation radical salts were prepared over a century ago, systematic generation and spectroscopic characterization of organic cation radicals has not been routine.[1-3] Conventional methods of generation involve high-intensity photolyses, pulse radiolysis, and treatment with very strong acids.[4,5] Recently, cation radicals have also been generated in fluid solution as intermediates with short lifetimes via photoinduced electron transfer and electrochemical processes.[6-10] Formation of relatively long lived radical cations from aromatics such as anthracene, perylene, etc. on silica-alumina surfaces and on decationized zeolites has been reported previously.[11-25] Radical cations have been generated from zeolite-included saturated and unsaturated hydrocarbons by subjecting them to either X-ray, γ, or UV radiation.[26-29] A study of particular interest to this investigation is a report by Gessner et al.,[30] wherein a color development, possibly due to radical cations, has been observed when *trans*-stilbene was included within silicalite, a pentasil type of zeolite.

In this paper, we present evidence for the generation of stable radical cations from α,ω-diphenyl polyenes (*trans*-stilbene,

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