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Valence Isomerization of Quadricyclane Catalyzed by Bis(μ-acetato)-bis(norbornadiene)dirhodium: Evidence for a Rhodocyclobutane Intermediate

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Quadricyclane isomerization is catalyzed by red-orange $[Rh(NBD)(AcO)]_2$ to give norbornadiene (75%) and two endo bis(norbornadienes), **1** (23%) and **2** (2%), at 25 °C. The reaction is characterized by the formation and disappearance of yellow Rh(III) intermediates. In CH_2Cl_2 at 25 °C the rate law $-d[Q]/dt = (0.64\ s^{-1})[Cat]_0$ adequately describes the results of kinetic studies carried out in the presence of large excesses of Q and NBD and with $[Cat]_0 > 10^{-4}$ M. At −50 °C rhodocyclohexane intermediates in the formation of dimers were detected and characterized by ^{1}H and ^{13}C{^{1}H} NMR spectra. The results are consistent with a stepwise mechanism involving insertion of Rh(I) into a cyclopropyl ring to form a rhodocyclobutane intermediate.

Introduction

Transition-metal-catalyzed rearrangements of certain strained-ring organic compounds have been extensively studied[1] since the first report in 1967 by Hogeveen and Volger[2] on the catalytic isomerization of quadricyclane (Q)[3] to norbornadiene (NBD) by transition-metal complexes. Interest in these reactions has recently been reinforced by the possibility of practical applications. Catalyzed isomerization of quadricyclane to norbornadiene is being studied (in conjunction with its reverse photochemical reaction) as a system for solar energy storage.[4,5] Various studies have been carried out to elucidate the catalytic role(s) played by the metal complexes in strained-ring isomerizations, and three different initiating mechanisms have been proposed for the exemplary reaction, the valence isomerization of quadricyclane. These are the concerted mechanism, the oxidative-addition mechanism, and the Lewis acid mechanism. In the concerted mechanism[6] the metal complexes are proposed to remove symmetry constraints (according to the Woodward–Hoffmann rules[7]) against a "thermally forbidden" σ,σ to π,π transformation by injection of an electron pair into the transforming molecule and acceptance of an electron pair in return into a metal-based orbital of different symmetry. The oxidative-addition mechanism[8,9] involves the initial insertion of a metal into a strained carbon–carbon bond to form a metallocyclic intermediate. In the Lewis acid mechanism[10–12] the metal initially functions as an electrophile and a carbon–carbon bond is split heterolytically with the formation of a metallocarbonium ion intermediate.

For Rh(I) complexes, the current evidence,[8] which includes the isolation of a stable acyl–rhodium adduct from the *stoichiometric* reaction of quadricyclane with $[Rh(CO)_2Cl]_2$, strongly favors the oxidative-addition mechanism. A rhodocyclobutane complex has been postulated[8] as an intermediate in the *catalytic* isomerization of quadricyclane by $[Rh(NBD)Cl]_2$.

As a further step toward elucidation of the detailed mechanism, we have chosen to modify the Q → NBD catalyst, $[Rh(NBD)Cl]_2$, previously studied by Halpern and coworkers,[8] by replacing the chloride bridges with various carboxylate bridges, so as to increase electronic and steric control of the reaction. In this work catalysis by $[Rh(NBD)(AcO)]_2$ was subjected to kinetic and spectral studies. X-ray structural studies of the catalyst are reported in an accompanying paper.[13] Catalytic Rh(III) metallocyclic intermediates have been detected, and the oxidative-addition mechanism has been shown to be a principal path for the catalysis.

Experimental Section

Reagent norbornadiene (Aldrich) was distilled from sodium and was stored in an argon atmosphere. Quadricyclane was synthesized by photolysis according to the method of Smith[14] and was purified by fractional distillation at 200 mmHg pressure through a 2-ft. Vigreux column. The quadricyclane thus obtained contained 5% residual norbornadiene. $[Rh(NBD)(AcO)]_2$ was obtained by following literature[15a] procedures for $[Rh(C_8H_{12})(AcO)]_2$. The compound was recrystallized from ethyl acetate to give orange-red crystals (mp 215–218 °C dec., lit.[15b] mp 198–200 °C). Triphenylphosphine was recrystallized twice from ethanol. Methylene chloride (Mallinckrodt), chloroform-*d*, and chloroform (Aldrich) were used as received. Analytical gas chromatography was performed with a Varian Model 3700 (flame-ionization detection). Q, NBD, and bis(norbornadienes) were determined on a 4-m OV-101 column at 60 °C or on a 2-m DEGS column at 50 °C. A known concentration of toluene served as an internal standard. A Cary (Model 14) spectrometer was used to record electronic spectra. A Bruker 270-MHz spectrometer was used for proton NMR spectra, and a Bruker 90-MHz spectrometer with Fourier transform was used for ^{13}C NMR spectra. A pulse delay of 10 s was found adequate to permit excited nuclei to relax. Mass spectra were obtained by means of a GC/Bendix TOF spectrometer combination. Reactions at −50 °C were carried out in a chlorobenzene–dry ice bath, by using syringe techniques to prepare appropriate mixtures directly in NMR tubes in the absence of air.

Kinetic experiments were carried out under a nitrogen atmosphere. In a typical experiment, 10 mL of solution containing 0.1 M Q, 0.8 M NBD, and 0.1 M toluene (as internal reference) in methylene chloride was thermostated at 25 ± 1 °C for 15 min. One milliliter of a millimolar solution of catalyst was then added to initiate the reaction. Samples of solution of 0.5–1.0 mL were taken with a hypodermic syringe at various intervals and injected into test tubes containing 50–100 mg of triphenylphosphine, which quenched the reaction. It was found convenient to then subject the sample to vacuum distillation to separate the rhodium catalyst from the product solution. OV-101 becomes contaminated and useless for analytical chromatography after injection of a few microliters of solution containing rhodium.

Results

Stoichiometry. When a hundredfold excess of quadricyclane is added to a methylene chloride solution of $[Rh(NBD)(AcO)]_2$, the color of the solution changes from red-orange to pale yellow in the time of mixing. At room temperature the red-orange color is restored after a few minutes when isomerization is complete. Electronic spectra show that the disappearance and regeneration of catalyst are quantitative. The process can be repeated by the addition of more Q. Apparently, this is a catalytic reaction in which a yellow intermediate is formed quantitatively during the reaction; furthermore, the spectrum of the yellow intermediate is characteristic of compounds containing Rh(III) rather than Rh(I).

Analysis of the product solutions showed norbornadiene not to be the exclusive product. Two higher boiling products (parent peaks $m/e = 184$) are also formed in lesser quantities;

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Table I. Product Distribution in the Isomerization of Quadricyclane Catalyzed by [Rh(NBD)(AcO)]$_2$[a]

time, min	concentrations, mM					product distribn,[b] mol %		
	[Q]	[NBD]	[1]	[2]	[Q] + [NBD] + 2[1] + 2[2]	1	2	NBD
0	204	11	0	0	215			
9.2[c]	137	56	13	1	221	22	2	76
19.9[c]	12	143	41	3	243	23	2	75
70.0	0	140	41	3	228	24	2	74

[a] At 25 °C, in CH_2Cl_2, $[Cat]_0 = 6.30 \times 10^{-4}$ M. [b] Based on [1] + [2] + [NBD] − $[NBD]_0$. [c] Sample quenched with liquid nitrogen and frozen until GLC analysis; catalyst not removed before analysis.

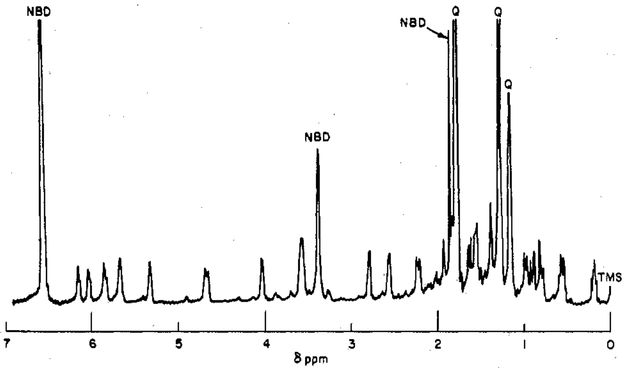
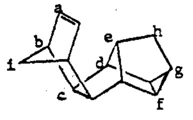


Figure 1. ^1H NMR spectrum of 5 in $CDCl_3$ at −50 °C.

they were identified as isomers of bis(norbornadiene). Four stereo-related isomers of bis(norbornadiene) (1–4) have previously been characterized.[16] The bis(norbornadiene) formed in the catalytic reaction in larger quantity was identified as the endo isomer 1 by its ^1H NMR spectrum.[17] The other minor product has been tentatively assigned as the other endo isomer 2. The net reaction may be described as



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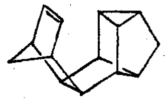

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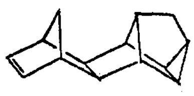

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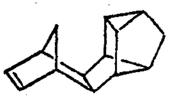

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$$Q \xrightarrow[25\ °C,\ CH_2Cl_2]{Cat} \underset{75\%}{NBD} + \underset{23\%}{1} + \underset{2\%}{2} \qquad (1)$$

Table I summarizes the product distributions. The results clearly indicate that quadricyclane is quantitatively (column 6) converted (within the accuracy of analyses, ~±10%) to norbornadiene and the two dimers in parallel reactions, the distribution of the three products (columns 7–9) remaining practically constant throughout the reaction and for 1 h after the reaction is completed.

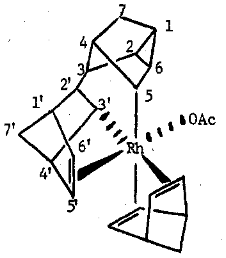
Table II. Proton NMR Spectrum of the Major Yellow Intermediate[a] at −50 °C in $CDCl_3$

δ,[b] mult[c]	rel integrated area[d]	assignt[16–18]
0.30, m	[1]	cyclopropyl
0.65, m	2	
0.87–1.07, σ	4	methylene
1.46, s	e	acetate
1.57–1.73, σ	3	tertiary
2.32, m	1	
2.63, bs	1	
2.83, bs	1	
3.65, bs	2	
4.08, bs	1	
4.75, m	1	olefinic
5.42, m	1	
5.76, m	1	
5.88, m	1	
6.10, m	1	
6.22, m	1	

[a] Solution contains $[Cat]_0 = 0.13$ M, $[Q]_0 = 1.0$ M. [b] Relative to Me_4Si. [c] Multiplicity: s = singlet, m = multiplet, σ = unresolved resonances, bs = broad singlet. [d] The resonance at 0.30 ppm was assigned unit area. [e] Integration of this peak was not attempted because of overlap with one of the strong resonances of excess Q.

NMR Characterization of the Yellow Intermediate(s). When the catalytic isomerization is conducted in chloroform at −50 °C, the catalyst is quantitatively trapped as a yellow intermediate after 15 min and the reaction ceases. The solution is quite stable at this temperature and no significant spectral changes were observed over a period of 20 h. The ^1H NMR spectrum of the intermediate(s) (formed from 0.13 M catalyst and 1.0 M quadricyclane) was recorded in a chloroform-*d* solution (Figure 1). Because the solution contains, in addition to yellow intermediate(s), both unconverted Q and NBD, it was difficult to distinguish the proton resonances of the intermediate(s). Significantly, the ^1H and the $^{13}C\{^1H\}$ NMR spectra (vide infra) of the −50 °C reaction mixture showed that bis(norbornadienes) were not produced at this temperature. By following successive spectral changes as the solution was slowly warmed it was possible to identify resonances of the intermediate(s) as those which disappeared on warming. These resonances fall into two groups; each peak in the second group had integrated area $\leq ^1/_{10}$ of that for a proton in the first group. This suggested the presence of two low-temperature intermediates.

The ^1H NMR spectrum of the major low-temperature intermediate was analyzed as shown in Table II by comparisons with known compounds. The major intermediate at −50 °C is seen to contain a cyclopropyl ring, an acetate group, nine tertiary hydrogens, six olefinic hydrogens, and four methylene hydrogens. A structure that is consistent with these assignments is shown as 5. Two of the resonances appropriate to the six methylene protons called for in 5 are missing; we assume that these two are buried beneath the resonances of Q or NBD. The geometry of 5 is one which could eliminate bis(norbornadiene) 1. The ~10:1 ratio of major to minor



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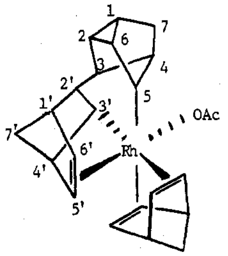

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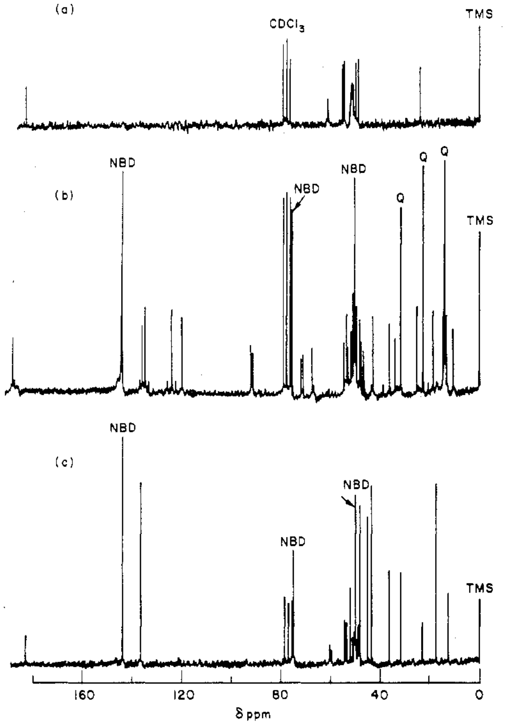


Figure 2. $^{13}C\{^1H\}$ NMR spectrum (in CDCl$_3$ at −50 °C) of (a) [Rh(NBD)(AcO)]$_2$, (b) yellow intermediate solution, and (c) product solution.

intermediate, together with the formation of **1** and **2** in the product solution in the ratio of ~10:1, leads us to suggest that the weaker resonances arise from an intermediate, such as **6**, which eliminates **2** on warming.

To characterize the intermediates in these experiments more fully we recorded the $^{13}C\{^1H\}$ spectra of the catalyst, the intermediates, and the product solution (Figure 2a–c). The seven NBD carbons in [Rh(NBD)(AcO)]$_2$ appear as five doublets (Figure 2a): $\delta = 48.9$ ($J_{Rh-C} = 11.2$ Hz, 2 C, olefinic), $\delta = 50.6$ (two overlapping doublets, $J_{Rh-C} \simeq 7.4$ Hz, 2 C, bridgeheads), $\delta = 54.2$ ($J_{Rh-C} = 11.1$ Hz, 2 C, olefinic), and $\delta = 60.3$ ($J_{Rh-C} = 6.9$ Hz, 1 C, bridging). Note that the transmission of magnetic coupling from rhodium is nearly as effective to the remote carbons of norbornadiene as to those directly bonded. The acetate carbons have resonances at $\delta = 23.7$ (s, methyl) and at $\delta = 181.8$ (s, carboxyl). The spectrum is consistent with the solid-state structure as determined by X-ray study in the accompanying paper.[13] As the temperature of a chloroform-*d* solution of [Rh(NBD)(AcO)]$_2$ is raised from −50 °C, the intensities of the olefinic and bridgehead carbon doublets decrease and collapse (−12 °C), merging into two singlets ($\delta = 51.4$, olefinic; $\delta = 50.6$, bridgehead) at 50 °C. The resonance of the bridging carbon remains as a doublet in this temperature range. This temperature dependence is consistent with coordinated NBD molecules which rotate on their C_{4v} axes with E_a ~7 kcal/mol.

The nine resonances in the product solution (Figure 2c) which are in addition to those attributed to [Rh(NBD)(AcO)]$_2$, NBD, and chloroform may be assigned[19] to compound **1**. Comparison of the spectra in Figure 2a–c also shows that neither the resonances for the catalyst nor those for **1** are present in Figure 2b; all the prominent resonances other than those of NBD, Q, and CDCl$_3$ are listed in Table III and are attributed to intermediate **5**. Nearly all its peaks have relative areas close to the values $^1/_2$ (for doublets), 1, or 2. It is reasonable to conclude that neither the error arising from saturation of nuclei (mitigated by a 10-s pulse delay) nor that arising from the variable nuclear Overhauser effect (mitigated by the size of the molecule) is serious in this system; therefore, the relative integrated areas in Table III have been taken as indicating the carbon numbers corresponding to each resonance.

Table III. $^{13}C\{^1H\}$ NMR Spectrum of the Intermediate **5**

δ,[a] mult[b]	rel integrated area[c]	no. of carbons	assignt, J_{Rh-C}, Hz
10.7, s	0.8	1	
13.7, s	0.9	1	
18.8, s	0.9	1	
23.7, s		1	methyl in acetate, overlapped by Q
25.4, s	1.1	1	
33.9, s	0.65	1[e]	
36.0, s	0.9	1	
42.9, s	2.0	2	
47.2, d	0.41, 0.58	1	$J = 30$
48.9, d	0.58, 0.5[d]	1	$J = 36$
51.1, dd	0.5,[d] 1.0, 0.65	2	$J = 27$
52.2, dd			$J = 28$
53.6, d	0.65, 0.44	1	$J = 20$
66.6, s	1.2	1	
71.3, d	1.0	1	olefinic C, $J = 10.3$
91.3, d	1.0	1	olefinic C, $J = 10.8$
119.3, s	1.0	1	olefinic C
123.4, s	1.0	1	olefinic C
134.0, s	1.0	1	olefinic C
135.0, s	1.0	1	olefinic C
186.6, s	[1.0]	1	carboxyl in acetate

[a] Chemical shift downfield relative to Me$_4$Si, ppm. [b] Multiplicity: s = singlet, d = doublet, dd = overlapped doublets. [c] The carbonyl carbon resonance at 186.6 ppm was assigned unit area. [d] Too close to a large peak to make a meaningful integration; estimated from peak height. [e] Counted as one carbon since no peak is close enough to be counted as the other half of a Rh–^{13}C doublet.

Magnetic coupling between ^{103}Rh and ^{13}C is observed[20] for carbons that are adjacent to rhodium unless the bond has some type of lability. Thus we conclude that the four olefinic carbons which exhibit singlets in the intermediate are coordinated to Rh in some labile manner. This lability might arise, for example, from a flexidentate NBD molecule which functions alternately as an η^2 and η^4 ligand.[24]

The five observed doublets are assigned to the six nonolefinic carbons which are bonded to rhodium by one or two σ bonds. The remaining nine nonolefinic carbons are distant from rhodium by three σ bonds or at least one π bond and are uncoupled. The chemical shifts of the doublets range 47.2–53.6 ppm and their coupling constants range 20–36 Hz. Previous reports of doublets arising from carbons σ-bonded to Rh(III) give coupling constants of 19[21] and 26 Hz.[22] Because three Q or NBD residues are ligated in this intermediate (according to the proton NMR spectrum), a total of 21 nonacetate carbons should be accounted for. Twenty of these are assigned in Table III. It must be assumed that one resonance is buried beneath an NBD or Q or solvent resonance. The structure of intermediate **5** deduced from the proton and ^{13}C NMR spectra are mutually supportive.

In Figure 2b a group of peaks may be discerned, each with an integrated peak area $\leq ^1/_{10}$ of those listed in Table III. We assume that some of these resonances arise from the minor intermediate **6**.

The conversion of the Rh(I) catalyst to Rh(III) intermediates and the low-temperature ^{1}H and ^{13}C NMR spectra of the trapped intermediate **5** strongly support the idea of a six-coordinate Rh(III)-containing metallocycle as an intermediate on the principal path for quadricyclane isomerization by [Rh(NBD)(AcO)]$_2$. Intermediates **5** and **6**, however, yield the bis(norbornadienes) **1** and **2** and do not extrude norbornadiene since at −50 °C the formation of norbornadiene

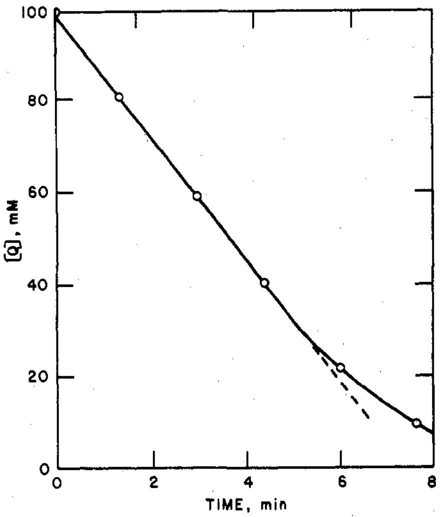
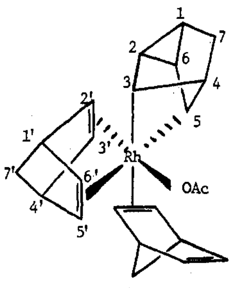


Figure 3. Typical plots of [Q] vs. time for the isomerization of quadricyclane by $[Rh(NBD)(AcO)]_2$. $[Q]_0 = 97$ mM, $[NBD]_0 = 860$ mM, and $[Cat]_0 = 0.301$ mM.

ceases when the intermediates **5** and **6** accumulate. Likely precursor intermediates are **7** and **8**. In these isomers one molecule of Q has opened to form a rhodocyclobutane, and one ligated NBD is monodentate. Intermediates **7** and **8** could subsequently extrude a molecule of NBD or isomerize to **5** and **6**, respectively, e.g., by breaking bonds Rh-3 and Rh-2′,3′ and making bonds 3-2′ and Rh-3′. Owing to stereo constraints, the addition of NBD and Q, both coordinated to the same Rh center, can lead to only endo bis(norbornadienes) **1** and **2**. It is for this reason that **2** is assigned as the minor bis(norbornadiene) product.



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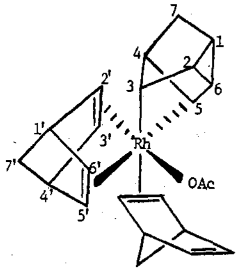

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Kinetic Studies. The kinetics of the rapid isomerization of quadricyclane by $[Rh(NBD)(AcO)]_2$ were studied in methylene chloride solution at 25 °C, usually with Q and NBD in large excess: $[Cat]_0 = 0.19-0.58$ mM, $[Q]_0 = 61-200$ mM, and $[NBD]_0 = 0.45-1.8$ M. Under these conditions, plots of [Q] vs. time are linear for at least 70% of the reaction and then show a slowing of conversion. Figure 3 is typical. The time of onset of curvature depends on the initial concentration of Q and occurs when [Q] drops below 20 mM. The slopes, R, of the linear decrements are listed in Table IV, column 5. The proportionality of R to $[Cat]_0$ over a threefold range demonstrates the reaction to be first order in catalyst; no dependence of rate on $[Q]_0$ or $[NBD]_0$ is seen. These results may be summarized by the rate-law

$$-d[Q]/dt = R = (0.64 \pm 10\%\ s^{-1})[Cat]_0 \quad (2)$$

When isomerization was carried out in the absence of added NBD (experiments, 9, 10), plots of [Q] vs. time show an initially slow reaction which increases in rate and approaches the "normal" rate when [NBD] reaches ~0.3 M. At very low initial catalyst concentrations ($<10^{-4}$ M) the pseudo-zero-order plots curve significantly, and pseudo-first-order plots (ln $([Q]/[Q]_0)$ vs. time) give good straight lines, suggesting that the reaction becomes first order with respect to Q at low catalyst concentrations. These deviant behaviors will be discussed later.

Table IV. Rate Constants for the Isomerization of Quadricyclane in CH_2Cl_2 at 25 °C

expt. no.	$[NBD]_0$, M	$[Q]_0$, mM	$[Cat]_0$, mM	10^4R,[a] M s^{-1}	$R/[Cat]_0$, s^{-1}
1	0.453	61	0.189	1.15	0.61
2	0.910	61	0.189	1.18	0.62
3	1.81	61	0.189	1.13	0.60
4	0.84	187	0.578	3.87	0.67
5	0.84	187	0.578	3.76	0.65
6	0.86	97	0.301	2.16	0.72
7	0.86	97	0.301	2.16[b]	0.72
8	0.84	200	0.193	1.01	0.52
9	0.011	204	0.630	(3.5)[c]	(0.56)[c]
10	0.011	204	0.630	(3.0)[c]	(0.48)[c]
11	0.84	202	0.086	*d*	
12	0.90	201	0.094	*d*	

[a] Zero order with respect to Q for least 70% of the reaction, unless otherwise stated. [b] In air. [c] Zero-order plots exhibit autocatalytic behavior. Parenthesized values are estimated from slopes at the inflection points of the curves. [d] Approximately first order with respect to Q with half-lives of 45 and 41 min in experiments 11 and 12, respectively.

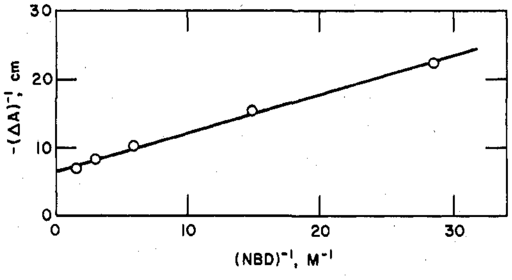

Figure 4. Plot of the adsorption changes at 477 nm accompanying the reaction of $[Rh(NBD)(AcO)]_2$ with NBD, in CH_2Cl_2, at 25 °C and initial concentration of $[Rh(NBD)(AcO)]_2 = 1.4 \times 10^{-4}$ M. In CH_2Cl_2, at 25 °C and initial concentration of $[Rh(NBD)(AcO)]_2 = 1.4 \times 10^{-4}$ M. Slope = 0.59 M cm; intercept = 6 cm.

UV-Vis Studies. Volger and Hogeveen[23] concluded from variable-temperature ^1H NMR studies that $[Rh(NBD)Cl]_2$ reacts with excess NBD to form monomeric $Rh(NBD)_2Cl$. It was desirable to investigate the acetato analogue. To this end a spectral titration of $[Rh(NBD)(AcO)]_2$ with NBD was conducted. A solution of $[Rh(NBD)(AcO)]_2$ in CH_2Cl_2 exhibits an absorption band maximum at 477 nm [ϵ 7070 M^{-1} cm^{-1}] and a minimum at 413 nm [ϵ 1360 M^{-1} cm^{-1}]. Successive additions of NBD cause the absorption of the solution to decrease above and to increase below the isosbestic point at 435 nm. The absorption changes at the band maximum were analyzed and found to be consistent with reaction 3.

$$[Rh(NBD)(AcO)]_2 + NBD \overset{K_3}{\rightleftharpoons} Rh_2(NBD)_3(AcO)_2 \quad (3)$$

Letting ΔA = absorption change per centimeter, $\Delta\epsilon = \epsilon(Rh_2(NBD)_3(AcO)_2) - \epsilon([Rh(NBD)(AcO)]_2)$ and $[Cat]_0$ = initial concentration of $[Rh(NBD)(AcO)]_2$, relation 4 can be

$$-\frac{1}{\Delta A} = \frac{1}{K_3(\Delta\epsilon)[Cat]_0}\,\frac{1}{[NBD]} + \frac{1}{(\Delta\epsilon)[Cat]_0} \quad (4)$$

derived. A plot (Figure 4) of $-(\Delta A)^{-1}$ vs. $[NBD]^{-1}$ is linear; the slope, 0.59 M cm, equals $1/K_3(\Delta\epsilon)[Cat]_0$ and the intercept, 6 cm, equals $1/(\Delta\epsilon)[Cat]_0$. These data yield $K_3 = 10\ M^{-1}$. Other possible reactions, e.g., $[Rh(NBD)(AcO)]_2 + 2NBD \rightleftharpoons 2Rh(NBD)_2(AcO)$, fail to give reasonable agreement with the spectral titration data.

Discussion

A reaction sequence which accommodates the products, the intermediates, and the rate law is given by

$$[\mathrm{Rh(NBD)(AcO)}]_2 + \mathrm{NBD} \overset{K_3}{\rightleftharpoons} \mathrm{Rh_2(NBD)_3(AcO)_2} \qquad (3)$$

$$\mathrm{Rh_2(NBD)_3(AcO)_2} + \mathrm{Q} \xrightarrow{k_5} (\mathbf{7}, \mathbf{8}) + \mathrm{Rh(NBD)(AcO)} \qquad (5)$$

$$\mathbf{7}, \mathbf{8} \xrightarrow{0.75k_6} \mathrm{NBD} + \mathrm{Rh(NBD)_2(AcO)} \qquad (6a)$$

$$\mathbf{7}, \mathbf{8} \xrightarrow{0.25k_6} \mathbf{5}, \mathbf{6} \qquad (6b)$$

$$\mathbf{5} \xrightarrow{k_7} \mathbf{1} + \mathrm{Rh(NBD)(AcO)} \qquad (7a)$$

$$\mathbf{6} \xrightarrow{k_7} \mathbf{2} + \mathrm{Rh(NBD)(AcO)} \qquad (7b)$$

$$2\mathrm{Rh(NBD)(AcO)} \overset{K_8}{\rightleftharpoons} [\mathrm{Rh(NBD)(AcO)}]_2 \qquad (8)$$

$$\mathrm{Rh(NBD)(AcO)} + \mathrm{Rh(NBD)_2(AcO)} \overset{K_9}{\rightleftharpoons} \mathrm{Rh_2(NBD)_3(AcO)_2} \qquad (9)$$

Since the spectral titration data fit eq 3 very well ($K_3 = 10$ M^{-1}), the values K_8 and K_9 must be sufficiently large ($\geq 10^4$) that the monomeric species are negligible in solutions containing $[\mathrm{Cat}]_0 \geq 10^{-4}$ M. If one assumes that all rhodium-containing species are at steady-state concentrations, then rate law 10 is obtained, where f is the ratio of dimeric species to

$$-\frac{d[\mathrm{Q}]}{dt} = \frac{k_5[\mathrm{Q}][\mathrm{Cat}]_0}{1 + \dfrac{1}{K_3[\mathrm{NBD}]} + \dfrac{1}{2}k_5[\mathrm{Q}]\left(\dfrac{1}{k_6} + \dfrac{f}{k_7}\right)} \qquad (10)$$

all species produced by the decay of intermediates **7** and **8** (equal to 0.25 at 25 °C). For this rate law, one may easily deduce that at high concentrations of NBD ($\geq$0.3 M) and Q ($\geq$20 mM) the quantity $1 + 1/K_3[\mathrm{NBD}]$ is negligible, so that eq 10 readily reduces to a rate law which is zero order in Q (eq 10′). We may equate the quantity $2k_6k_7/(fk_6 + k_7)$ with

$$-\frac{d[\mathrm{Q}]}{dt} = \frac{2k_6k_7}{fk_6 + k_7}[\mathrm{Cat}]_0 \qquad (10')$$

the observed rate constant 0.64 ($\pm$10%) s^{-1}. The curvature observed on the [Q] vs. time plots when [Q] drops below 20 mM is apparent; we may assume that the term ${}^1/_2k_5[\mathrm{Q}](1/k_6 + f/k_7)$ has decreased to a value, say, only a factor of 5 larger than $1 + 1/K_3[\mathrm{NBD}]$. A crude estimate of k_5 which will account for this behavior is $k_5 \simeq 300$ M^{-1} s^{-1}. On the other hand, when $[\mathrm{NBD}]_0$ is small, e.g. $<\sim$0.3 M, the quantity $1 + 1/K_3[\mathrm{NBD}]$, eq 10, becomes significant but decreases as more NBD is produced in the reaction; the integrated form of the resulting equation predicts that autocatalytic behavior will be observed. One may also consider the situation which will occur when $[\mathrm{Cat}]_0$ is sufficiently small that the monomeric Rh species, as determined by K_8 and K_9, become the predominant species. Under these circumstances, the steady-state concentrations of intermediates **5**–**8** become negligible and the limiting rate law becomes $-d[\mathrm{Q}]/dt = k_5[\mathrm{Q}] \times f\{K_3,K_7,K_8,[\mathrm{NBD}],[\mathrm{Cat}]_0\}$, i.e., limiting first order in Q, which is observed.

In the introductory section it was mentioned that an acyl–rhodium complex had been trapped in the *stoichiometric* reaction[8] of Q with $\mathrm{Rh_2(CO)_4Cl_2}$, and, by analogy, a rhodocyclobutane complex was postulated[8] in the *catalytic* isomerization of Q with $\mathrm{Rh_2(NBD)_2Cl_2}$. Mango[1b] has raised the question of whether such an analogy is safe. Our spectroscopic evidence for the low-temperature stoichiometric production of rhodocyclohexanes (arising from the trapping of rhodocyclobutane precursors) is therefore significant in that the same species at higher temperatures participate in a catalytic reaction. A similar trapping of a nickelocyclobutane by activated olefins has recently been suggested[9] as the mechanism for the cycloaddition of Q to olefins catalyzed by bis(acrylonitrile)nickel; however, no intermediate was detected in that study.

Most of the spectroscopically observed intermediates in the present study have only transient existence and extensive discussion of their probable structures would not be warranted; but it does seem appropriate to discuss the structure of the species $\mathrm{Rh_2(NBD)_3(AcO)_2}$, which reacts with Q. An X-ray structural study of $[\mathrm{Rh(NBD)(AcO)}]_2$ has shown[13] that the Rh atoms are each in essentially square-planar coordination with respect to two oxygen atoms and the midpoints of two olefinic bonds. The dihedral angle between the least-squares planes is 50.1° and the Rh–Rh separation is 3.150 Å. Space-filling models reveal that the distortion from the idealized geometry of parallel square planes arises from crowding of the bulky norbornadiene ligands. The positions trans to the Rh–Rh vector are vacant. By means of space-filling models the possibilities for coordination of an additional molecule of norbornadiene without dissociation into monomeric species have been examined. The results show clearly that cleavage of a Rh–O bond reduces the steric interference of NBD hydrogens and allows the addition of a monodentate[24] norbornadiene. Such a partially cleaved structure would be ideally suited to proceed via reaction 5 to the two fragments postulated.

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Registry No. **1**, 18067-61-3; **2**, 17926-98-6; **5**, 69897-26-3; **6**, 69897-26-3; $[\mathrm{Rh(NBD)(AcO)}]_2$, 36570-53-3; Q, 278-06-8; NBD, 121-46-0.

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Nitrito–Nitro Linkage Isomerization in the Solid State. 2. A Comparative Study of the Structures of Nitrito- and Nitropentaamminecobalt(III) Dichloride

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The mechanism of the isomerization in the solid state of nitritopentaamminecobalt(III) dichloride to the thermodynamically more stable nitro compound and of the reverse photochemical nitro → nitrito reaction have been investigated. Freshly synthesized crystals of $[Co(NH_3)_5ONO]Cl_2$ and crystals of the same compound aged for 1 half-life have been used for structure determinations. The intensity data were collected by a computer-controlled diffractometer. The two structures are orthorhombic, space group $P2_1nb$, with $Z = 4$. Monomeric cobalt complexes and chloride ions are linked by electrostatic forces and by a network of hydrogen bonds. The coordination around cobalt is close to octahedral. A comparison of the X-ray structures of the nitrito and nitro compounds and the changes in the powder diffractograms with time indicate that the thermal nitrito → nitro isomerization consists of two consecutive steps. The first step involves an intramolecular change of the coordination mode, most likely via a seven-coordinated transition state. The second step consists of a slow rearrangement which can be interpreted as a cooperative ~90° rotation of half of the number of the coordination polyhedra, or as a pseudo-C_3-rotation or an intramolecular twist. The nitro → nitrito photoisomerization gives a nitrito compound with a structure different from the one originally synthesized. The photoreaction is probably also intramolecular, proceeding via a seven-coordinated transition state.

Introduction

It is well-known that the ambidentate NO_2^- ligand can be coordinated either to oxygen or to nitrogen in cobalt(III) complexes. The latter mode is thermodynamically favored, at least for $[Co(NH_3)_5NO_2]Cl_2$ at room temperature, although heating the nitro compound in the solid seems to result in a slight formation of the nitrito form.[2] Nitrito complexes may be prepared,[3] but they isomerize both in solution and in the solid state to the more stable nitro form. Since Cr(III) prefers oxygen donors over nitrogen donors,[4] only the nitrito complexes of Cr(III) have been prepared so far.

A previous discussion[5] of the mechanism of the nitrito → nitro isomerization (eq 1) in the solid state was based on

$$\textit{trans}\text{-}[Co(en)_2(NCS)ONO]X \rightarrow \textit{trans}\text{-}[Co(en)_2(NCS)NO_2]X \quad (1)$$

structure determinations of the two isomers (en = ethylenediamine; $X^- = ClO_4^-$ or I^-). We will here extend the investigation by using structure determinations of the compounds $[Co(NH_3)_5ONO]Cl_2$, $[Co(NH_3)_5(ONO)_{1/2}(NO_2)_{1/2}]Cl_2$, and $[Co(NH_3)_5NO_2]Cl_2$. Crystals of the latter compound were prepared from an aqueous solution and the structure (space group $C2/c$) was investigated by Börtin.[6] The mechanism of the photochemical nitro → nitrito isomerization will also be briefly discussed.

In the following text we denote the compounds in the thermal reaction (2) as A, B, and C and the compounds in

$$\underset{A}{[Co(NH_3)_5ONO]Cl_2(s)} \rightarrow \underset{B}{[Co(NH_3)_5NO_2]Cl_2(s)} \rightarrow \underset{C}{[Co(NH_3)_5NO_2]Cl_2(s)} \quad (2)$$

the photoreaction (3) as D and E.

$$\underset{D}{[Co(NH_3)_5NO_2]Cl_2(s)} \xrightarrow{h\nu} \underset{E}{[Co(NH_3)_5ONO]Cl_2(s)} \quad (3)$$

F is the compound $[Co(NH_3)_5(ONO)_{1/2}(NO_2)_{1/2}]Cl_2$ formed by A during the first half-life of the thermal reaction A → B; cf. Table I.

Experimental Section

Preparation. Microcrystalline $[Co(NH_3)_5ONO]Cl_2$ (A) and $[Co(NH_3)_5NO_2]Cl_2$ (D) were prepared from aqueous solutions as described by Adell.[3a,c] The products were purified by dissolving them in water followed by a precipitation with solid ammonium chloride until satisfactory elemental analyses were obtained.

Single crystals of the nitrito compound, formed as slightly distorted octahedra, were obtained at 278 K from an aqueous solution by slow evaporation.

Isomerization in the solid state gives an intermediary nitro compound (B) with a structure different from C (cf. powder diffractograms (c) and (g) in Figure 1 and the section: Mechanism of the Reaction A → B → C). For the investigation of the structure of B, single crystals of A were aged at 283 K for 1 half-life ($t_{1/2} \approx$ 15 days at 283 K; cf. Adell[3c]) corresponding to the reaction A → B in eq 2. Fragmentation of the single crystal was reduced by the slow isomerization rate at 283 K. If the crystals were aged for longer periods of time, the amount of fragmentation increased resulting in poorer quality of the intensity data. The amount of the compound C formed after only 1 half-life is negligible; cf.: Mechanism of the Reaction A → B → C.

$[Co(NH_3)_5ONO]Cl_2$ was also prepared photochemically by illumination of samples of D with light from a 100-W tungsten filament bulb. About 10 mg of D in powder form was placed in a thin layer between two parallel glass plates, cooled by a stream of cold air. After 6 h the isomerization was complete. An aqueous solution of the sample gave an absorption spectrum in the visible region identical with that of freshly prepared A. A powder diffractogram of the illuminated sample showed a different structure from that of the nitrito compound A (cf. diffractogram (a) in Figures 1 and 2). The new compound is denoted E.

X-ray Study: Data Collection and Structure Determination and Refinement of $[Co(NH_3)_5ONO]Cl_2$ (A) and $[Co(NH_3)_5(ONO)_{1/2}(NO_2)_{1/2}]Cl_2$ (F). Tables I and II contain crystal data and information on the collection and reduction of the sets of intensity data and the least-squares refinements; for further experimental details, see ref 7. The intensitites of three standard reflections were measured at regular time intervals during the data collections in order to obtain information about possible systematic changes in intensity due to deterioration of the crystal and to errors in the equipment used. The intensitites of these reflections showed no systematic variations, thus there was

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