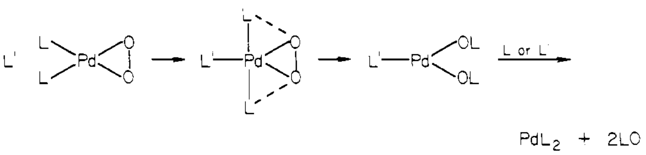
at 355 and 330 nm, respectively.

Step 4 in the proposed mechanism is probably a composite of several reactions which are not completely determinable by our photochemical results. The presence of L′ ligands on the *trans*-dichloropalladium(II) photoproduct in solutions containing excess L′ could be explained by a mechanism similar to that proposed by Halpern for thermal reactions of platinum.[17]



Acknowledgment. The support of the National Science Foundation and a Camille and Henry Dreyfus Teacher-Scholar Award (to J.I.Z.) are gratefully acknowledged. We thank Professor C. S. Foote for assistance in the tests for singlet oxygen.

Registry No. $Pd(PPh_3)_2O_2$, 29933-60-6; $Pd(PPh_2Me)_2O_2$, 78591-75-0; $Pd(PPh_3)_4$, 14221-02-4; $Pd(PPh_2Me)_4$, 24981-80-4; $Pd(PPh_3)_2Cl_2$, 28966-81-6; $Pd(PPh_2Me)_2Cl_2$, 26973-01-3; O_2, 7782-44-7.

Contribution from the Department of Chemistry,
Montana State University, Bozeman, Montana 59717

Solvent Effects on the Valence Isomerization Catalyst (Norbornadiene)rhodium Chloride Dimer

Richard B. Taylor and Paul W. Jennings*

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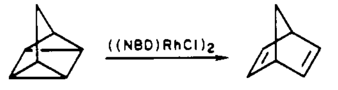
The valence isomerization of quadricyclane (eq 1) has been shown to be catalyzed by a myriad of metal complexes, including $((NBD)RhCl)_2$.[1]



1 2 (1)

Hogeveen and Volger[1b] were the first investigators to report on the reaction using $((NBD)RhCl)_2$. Subsequently, Halpern[1e] reported rate constants for the same isomerization of 1.9 and 2.1 $M^{-1}\ s^{-1}$ (40 °C) in CCl_4 and $CDCl_3$, respectively. He also reported that the reaction was not inhibited by the product norbornadiene (NBD). This was particularly interesting in light of the fact that Volger[2] had shown earlier that the rhodium dimer, **3**, was cleaved by NBD in $CDCl_3$–CD_2Cl_2 to a monomeric rhodium complex, **4** (eq 2). Extrapolation of Volger's equilibrium data to 40 °C, the temperature of Halpern's kinetic experiment, revealed that a mixture of dimeric and monomeric rhodium complexes would be changing during the course of the reaction ($K^{40\,°C} = 0.1\ M^{-1}$).

$$\underset{\mathbf{3}}{((NBD)RhCl)_2} + 2NBD \rightleftarrows \underset{\mathbf{4}}{2(NBD)_2RhCl} \qquad (2)$$

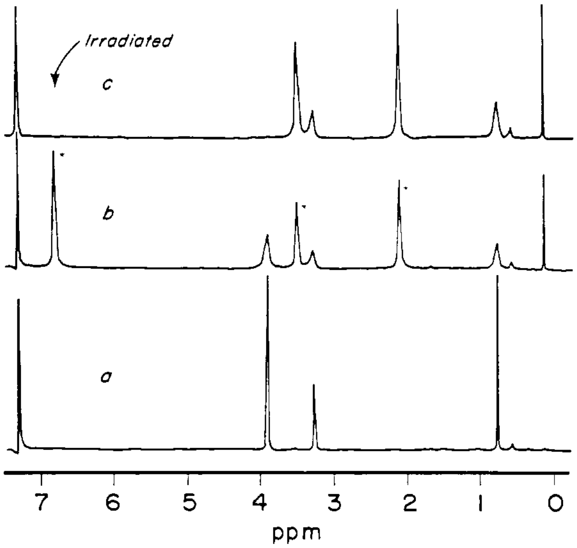


Figure 1. NMR spectra at 250 MHz of $((NBD)RhCl)_2$ in benzene at 25 °C: (a) rhodium complex alone; (b) rhodium complex and norbornadiene (1:4 molar ratio); (c) same as part b but decoupled at the olefinic resonance of uncomplexed NBD; (*) resonances attributed to uncomplexed NBD.

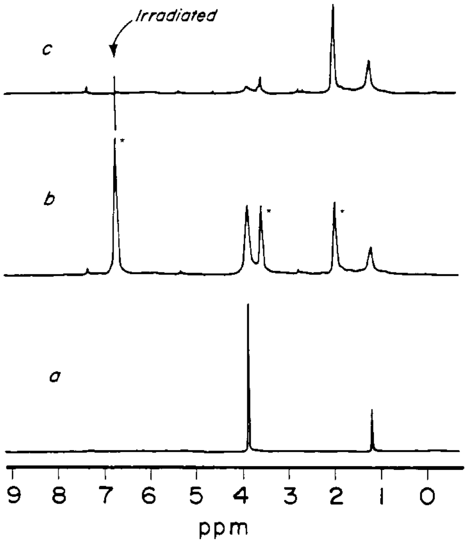


Figure 2. NMR spectra at 250 MHz of $((NBD)RhCl)_2$ in CCl_4 at 25 °C: (a) rhodium complex alone; (b) rhodium complex and norbornadiene (1:4 molar ratio); (c) same as part b but decoupled at the olefinic resonance of uncomplexed NBD; (*) resonances attributed to uncomplexed NBD.

The results herein reported show that a new equilibrium constant is warranted on the basis of the revised NMR assignments for monomer **4**. The new equilibrium constants are used to explain both the lack of an NBD effect on the rate constant at 40 °C and an enhanced rate constant at 1 °C from NBD.

Results

Characterization of Solvents Effects on $((NBD)RhCl)_2$. In this investigation, the characteristics of the rhodium complex were determined in $CDCl_3$, CCl_4, and benzene. Vapor-phase osmometry (VPO) and NMR spectroscopy studies showed that the integrity of the dimeric rhodium complex is preserved in each solvent at 25 °C in the absence of NBD (Figures 1a, 2a,

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(1) (a) Cristol, S. J.; Snell, R. L. *J. Am. Chem. Soc.* **1958**, *80*, 1950. (b) Hogeveen, H.; Volger, H. C. *Ibid.* **1957**, *89*, 2486. (c) Gassman, P. G.; Aue, D. H.; Patton, D. S. *Ibid.* **1968**, *90*, 7271. Gassman, P. G.; Patton, D. S. *Ibid.* **1968**, *90*, 7276. (d) Menon, B. C.; Pincock, R. E. *Can. J. Chem.* **1969**, *47*, 3327. (e) Cassar, L.; Halpern, J. *J. Chem. Soc. D* **1970**, 1082. (f) Manassen, J. *J. Catal.* **1970**, *18*, 38. (g) Koser, G. F.; Pappas, P. R.; Yu, S. *Tetrahedron Lett.* **1973**, 4943. (h) Noyori, R.; Umeda, I.; Kawauchi, H.; Takaya, H. *J. Am. Chem. Soc.* **1975**, *97*, 812. (i) Wilson, H. D.; Rinker, R. G. *J. Catal.* **1976**, *42*, 268. (j) Schwendiman, D. P.; Kutal, C. R. *Inorg. Chem.* **1979**, *18*, 1864. (k) Chen, M. J.; Feder, H. M. *Ibid.* **1979**, *18*, 1864.

(2) Volger, H. C.; Hogeveen, H. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1066.

(3) For reasons not known to us, saturation of the olefinic resonances of uncomplexed NBD saturate both the olefinic proton resonance of bound NBD and the bridgehead resonance of free NBD.

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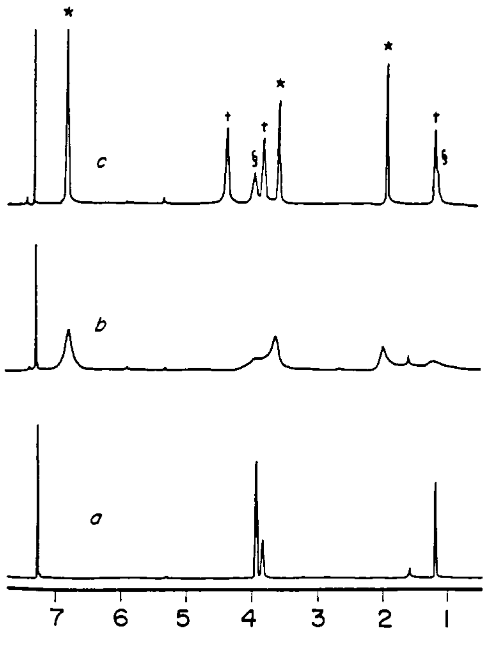


Figure 3. NMR spectra at 250 MHz of $((NBD)RhCl)_2$ in $CDCl_3$ at 25 °C: (a) rhodium complex alone; (b) rhodium complex and norbornadiene (1:4 molar ratio); (c) same as part b but at −55 °C; (*) resonances attributed to uncomplexed NBD; (†) resonances of the monomeric complex NBD_2RhCl. (§) resonances of the dimeric complex $(NBDRhCl)_2$.

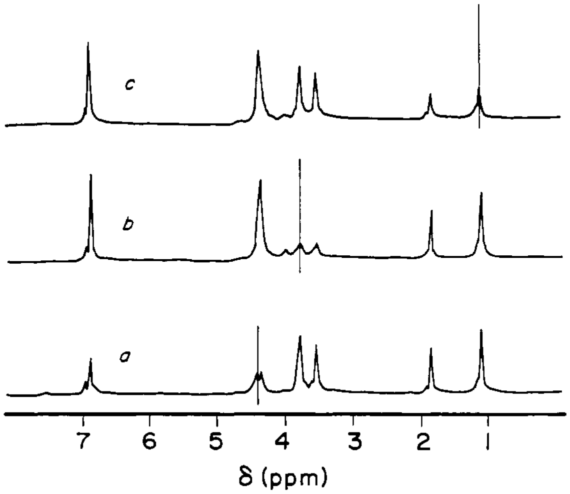


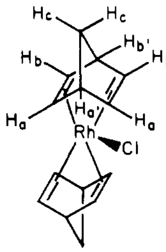
Figure 4. Saturation-transfer NMR spectra at 300 MHz of the 4:1 mixture of NBD and $((NBD)RhCl)_2$ in $CDCl_3$ at −55 °C: (a) irradiated at δ 4.38; (b) irradiated at δ 3.82; (c) irradiated at δ 1.17.

Table I. Equilibrium Data for the 4:1 Mixture of NBD and $((NBD)RhCl)_2$ in $CDCl_3$ at Several Temperatures[a]

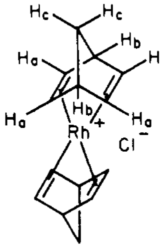
T, K	203	208	213	218	223	228	233
K_{eq}, M^{-1}	1.39	0.73	0.44	0.11	0.07	0.03	0.01

[a] Temperatures were determined using methanol. $\Delta H = -15.8$ kcal.

and 3a). However, upon the addition of NBD two features were observed. First, in all three solvents there was line broadening, suggesting an exchange equilibrium between $((NBD)RhCl)_2$ and NBD (Figures 1b, 2b, and 3b). For the solvents CCl_4 and benzene, the exchange equilibria were verified by NMR saturation-transfer experiments (Figures 1c and 2c). In $CDCl_3$, the resulting spectrum was not adequately resolved at 25 °C to interpret.



A



B

On reduction in temperature, the resolved resonance peaks for free NBD and **4** in $CDCl_3$ were easily observed (Figure 3c). The monomeric rhodium complex **4**, proposed by the earlier work[2] is structure A. In justifying this structure, protons H_a and $H_{a'}$ were thought to resonate at one frequency and protons H_b and $H_{b'}$ at another frequency. This yields an integration ratio of signals for the monomeric rhodium complex of 3:3:2. Integration of our spectrum, Figure 3c, showed that both the NBD resonances (*) and the monomeric rhodium complex resonances (†) were in a ratio of 2:1:1. This contrasting result suggested that the peaks at 4.35, 3.82, and 1.17 ppm were due to the olefinic, bridgehead, and bridge protons, respectively, of NBD bound in $(NBD)_2RhCl$. NMR saturation-transfer experiments on this mixture confirmed these assignments (Figure 4). Freezing point depression studies in $CDCl_3$ showed that $(NBD)_2RhCl$ was, by far, the major component in the mixture at −55 °C. Any proposed structure for $(NBD)_2RhCl$ will thus have to accommodate the new fact that the bridgehead protons are equivalent. On initial inspection, the bridgehead proton equivalence would automatically rule out structure A in favor of structure B. However, this conclusion must be tempered, as there are at least two means available to explain the observed equivalence of protons $H_{a'}$ and $H_{b'}$ of structure A. First, the exchange rate between free NBD and rhodium-bound NBD is fast enough on the NMR time scale to accomplish the task, as evidenced by the saturation-transfer results. Second, the bound NBD moieties could be exhibiting fluxional behavior. Thus, it is apparent that the complex $(NBD)_2RhCl$ has either a σ-bound chlorine or a very tight ion pair. The lack of a ^{35}Cl NMR spectrum corroborates these two possibilities but does not help refine the structure any further.

Equilibrium Data for Reaction 2. The equilibrium data previously reported by Volger for the reactions shown as eq 2 were made suspect by the above NMR spectral results since they had used the erroneous spectral data for structure **4**. Therefore, new equilibrium constants were determined in $CDCl_3$ by using NMR spectroscopy (Table I). Extrapolation of these data to 40 °C via the expression log K vs. $1/T$ (correlation coefficient = 0.99) gave an equilibrium constant of 3.5×10^{-6} M^{-1}. Thus, at the kinetic temperature used by Halpern, an insignificant amount of monomeric rhodium complex was present.

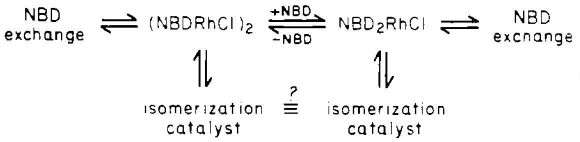
If this interpretation of the equilibrium (eq 2) is correct, it should also manifest itself in the rate constants at low temperatures in the presence of norbornadiene. Thus, the reaction rate was measured at 1 °C with and without NBD added. In the reaction without NBD, the pseudo-first-order plots were linear and gave an observed rate constant of $0.58 \times 10^{-3}\ s^{-1}$. In the reaction with NBD added, the resultant k_{obsd} was $0.98 \times 10^{-3}\ s^{-1}$. Thus, the k_{obsd} is increased by a factor of 1.7 at 1 °C with added norbornadiene. The equilibrium concentrations of complexes 3 and 4 are 9.57×10^{-4} and 4.31×10^{-5} M, respectively.

Discussion

Although Volger was correct in reporting that $((NBD)RhCl)_2$ is converted to $(NBD)_2RhCl$ by NBD in $CDCl_3$, his ^1H NMR assignments for the monomeric rhodium complexes are wrong. This led to erroneous equilibrium constants at various temperatures. The redetermined constants are smaller and are shown in Table I. Thus, at 40 °C, the equilibrium data show that reaction 2 lies very far to the left. Endogeneous NBD from the isomerization reaction would not decrease the concentration of $((NBD)RhCl)_2$ significantly, and one would not observe an effect of NBD on the rate constant. However, one would predict significantly less $((NBD)RhCl)_2$ at lower temperatures in the presence of NBD. In fact, the k_{obsd} is 1.7 times larger at 1 °C in the presence of NBD than in its absence. Assuming the k_{obsd} of $0.58 \times 10^{-3}\ s^{-1}$ is primarily due to $((NBD)RhCl)_2$, then the rate constant for 0.001 M $((NBD)RhCl)_2$ would be $0.58\ M^{-1}\ s^{-1}$ and the calculated rate constant for $(NBD)_2RhCl$ would be $9.8\ M^{-1}\ s^{-1}$, or approximately 17 times larger. The initial assumption is reasonable, for the amount of NBD generated in the unfortified case was insignificant. This is corroborated, as the rate data adhered to the pseudo-first-order plot. Thus, not only is this equilibrium intimately related to the catalytic process but also the monomeric rhodium complex $(NBD)_2RhCl$, or a derivative thereof, is shown to be more efficient than the $((NBD)RhCl)_2$-derived catalyst.

The NMR data for $((NBD)RhCl)_2$ dissolved in CCl_4 and benzene do not show the same results as those observed for $((NBD)RhCl)_2$ dissolved in $CDCl_3$. In these two nonpolar solvents the spectra for complex **3** is virtually the same with or without the addition of NBD (Figures 1 and 2). The only perturbation occurring on the addition of NBD is line broadening, which was shown to be exchange between free and rhodium-bound NBD. Thus, it would appear that the catalyst for quadricyclane isomerization in CCl_4 and benzene is derived from $((NBD)RhCl)_2$.

From the saturation-transfer results, it appears that complexes **3** and **4** exchange the rhodium-bound NBD with free NBD in all three solvent systems. The fact that this exchange does not apparently affect the reaction rate of quadricyclane isomerization says that the exchange and isomerization sites are not the same. Finally, it must be clear that the inorganic portion for the mechanism of catalyzed quadricyclane isomerization is complicated. The scheme shown in (3) is proposed.



(3)

Conclusions

The NMR spectral assignments for complex **4** are now firmly established, and new equilibrium constants for the reactions $((NBD)RhCl)_2 + 2NBD \rightleftharpoons 2(NBD)_2RhCl$ are determined in $CDCl_3$ solvent. At 40 °C the equilibrium is far enough to the left that the $[(NBD)_2RhCl]$ is insignificant and an effect from NBD is not observed in the catalytic isomerization of quadricyclane. However, at 1 °C in the presence of NBD where the equilibrium concentration is significant, there is a 1.7-fold increase in k_{obsd} for the isomerization. Thus, the monomeric rhodium complex $(NBD)_2RhCl$ appears to deliver a more efficient isomerization catalyst than dimeric rhodium complex $((NBD)RhCl)_2$. Both complexes exchange bound NBD with free NBD, which is not inhibiting the isomerization reaction. Thus, the true catalytic site does not bind to NBD. There was no evidence found for $(NBD)_2RhCl$ in CCl_4, benzene, and toluene-d_8 solutions over the available temperature ranges.

Experimental Section

General Data. $((NBD)RhCl)_2$ was obtained from Strem Chemicals (lot no. 2064B and 2169B). Purity for each lot was determined by ^1H NMR and UV–vis spectroscopy. $CDCl_3$ was obtained from Stohler Isotope Chemicals and benzene from Wilmad. Other reagents were purchased as reagent grade and used as such. Quadricyclane was prepared by the method of Smith[4] and purified to better than 99.8% by distillation on a 50-cm spinning-band column. The vapor-phase osmometry (VPO) experiments were conducted with a Hewlett-Packard Mechrolab 301A instrument. NMR spectra were run by using a Bruker WM 250 spectrometer.

Equilibrium Measurements. A mixture containing 21.5 mg (0.05 mmol) of $((NBD)RhCl)_2$ and 18.75 μL (0.18 mmol) of NBD in 0.60 mL of $CDCl_3$ was placed in an NMR tube and analyzed in the WM 250 spectrometer at various temperatures. At each temperature, four transients were taken with a delay time of 40 s. The integrations for free NBD were proportionally accurate, thus ensuring that the delay was sufficient for relaxation to be complete. Sufficient resolution in the NMR spectra was achieved in the temperature range 213–238 K. The slope of log K vs. $1/T$ gave $\Delta H = -15.8 \pm 1$ kcal.

Saturation Transfer. The saturation-transfer solution consisted of 50.9 mg (0.11 mmol) of $((NBD)RhCl)_2$ and 42.5 μL (0.42 mmol) of NBD in 0.5 mL $CDCl_3$. The experiments were run at −55 °C on the Varian SC 300 spectrometer using 2 W of decoupler power.

Vapor-Phase Osmometry. The following data were collected at 37 °C for mixtures containing 45.8 mg $((NBD)RhCl)_2$ in 2.0 mL of solvent.

		ΔR, Ω	
	concn, M	benzene	$CHCl_3$
benzil	0.05	29.5	28.47
benzil	0.10	46.5	50.00
$((NBD)RhCl)_2$	0.05	26.4	27.33

Freezing Point Depression Experiments (FPD). The freezing point depression mixture consisted of 146.0 mg (0.32 mmol) of $((NBD)RhCl)_2$, 97.0 μL (0.95 mmol) of norbornadiene, and 7.443 g of $CDCl_3$. The FPD was 0.63 ± 0.06 °C below that of Stohler $CDCl_3$. The calculated FPD value for $(NBD)_2RhCl$ was 0.627 °C. The calculated FPD values for other possible complexes such as $(NBD)RhCl$ and $((NBD)RhCl)_2$ were 1.05 and 0.837, respectively.

Kinetic Measurements at 1 °C. A 6-μL amount of quadricyclane and 484 μL of $CDCl_3$ were added to an NMR tube and allowed to come to thermal equilibrium in the probe of the Bruker WM 250 NMR spectrometer at 1.0 ± 0.5 °C. A 10-μL portion of a 0.050 M $((NBD)RhCl)_2$ in $CDCl_3$ solution was then injected and the reaction followed by integration of the vinyl resonance of the product, NBD, at 30-s intervals. In the second experiment, a mixture of 6 μL of quadricyclane, 6 μL of NBD, and 478 μL of $CDCl_3$ was prepared and analyzed by following the same procedure. The observed rate constants $\times 10^3$ are 0.58 ± 0.03 and 0.98 ± 0.07 s^{-1}. Slopes were calculated by the method of least squares, and all correlation coefficients were better than 0.99.

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Registry No. **1**, 278-06-8; **2**, 121-46-0; **3**, 12257-42-0; **4**, 58602-82-7.

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(4) Smith, C. D. *Org. Synth.* **1971**, *51*, 133.