

Radical Reactions in the Coordination Sphere. 4.¹ Addition of Carbon Tetrachloride to *cis*-Cyclooctene Catalyzed by Dichlorotris(triphenylphosphine)ruthenium(II)

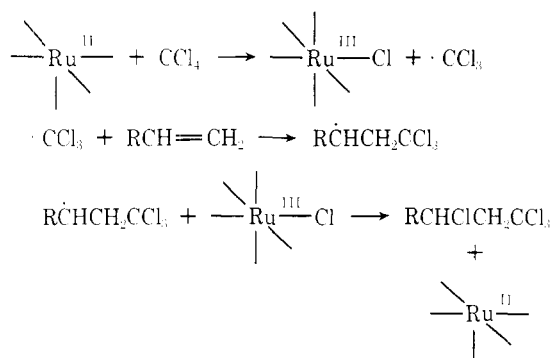
Hideyuki Matsumoto,* Taichi Nakano, Keizo Takasu, and Yoichiro Nagai

Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan

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Addition of carbon tetrachloride to *cis*-cyclooctene catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) gave a mixture of 1,2 and 1,4 adducts, in which 1-chloro-4-(trichloromethyl)cyclooctane predominated, in exceedingly high yields. Relative amounts of the two products were found to be linearly correlated with the catalyst concentrations at a stipulated temperature. With a fixed concentration of the catalyst, the product ratios were determined at different temperatures and activation parameters for the 1,2 and 1,4 additions were estimated.

Carbon tetrachloride and other organic polyhalides are known to add olefins in the presence of various catalysts such as peroxides,² metal salts,³ or metal carbonyls.³ Recently, we have found that these addition reactions can be best effected by a homogeneous ruthenium complex, dichlorotris(triphenylphosphine)ruthenium(II).^{1,4} This newly found catalytic reaction has been shown to contain several distinctive features (high yields of 1:1 adducts, unique selectivities, highly efficient catalytic cycles, etc.) and a homolytic mechanism being operative in the coordination sphere was suggested.

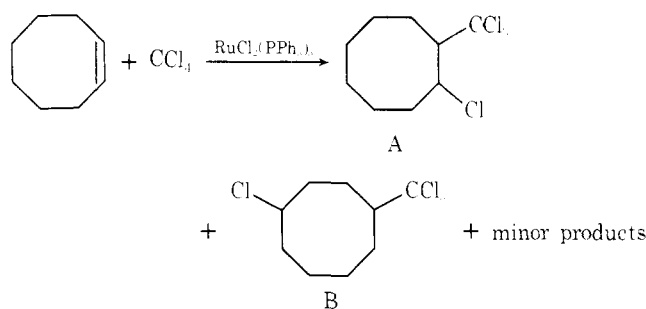


In the present investigation, the ruthenium(II) complex catalyzed addition of carbon tetrachloride to *cis*-cyclooctene was examined in some detail in order to shed further light into the mechanistic aspects of the catalytic processes. This choice was made because there are available extensive investigations of Traynham and Couvillon⁵ on the free-radical additions of carbon tetrachloride and other polyhalides to *cis*-cyclooctene under various conditions. They showed that photochemically or thermally initiated additions of carbon tetrachloride give mainly stereoisomeric 1-chloro-4-(trichloromethyl)cyclooctanes, products of transannular addition, with minor amounts of the stereoisomeric 1,2-addition products.^{5a,b} The ruthenium(II) complex catalyzed reactions are also expected to give similar product mixtures and the present work aims to determine relative amounts of the two sets of the addition products from which activation parameters would be derived for the transannular hydrogen and intermolecular chlorine abstractions by the intermediate 2-(trichloromethyl)cyclooctyl radical. A comparison of these parameters between the reported free radical and the present additions is made, for it seemed to us that such a comparison would provide better understanding about the factors controlling unique selectivities exhibited in the ruthenium(II) catalysis.

Results and Discussion

Product study experiments were conducted in a sealed Pyrex tube at 90 °C. When *cis*-cyclooctene was allowed to react with 4 equiv of carbon tetrachloride in the presence of

0.7 mol % (based on the olefin charged) of dichlorotris(triphenylphosphine)ruthenium(II), a mixture of isomeric C₉H₁₄Cl₄ compounds was obtained in 93% yield. Formation of by-products was of little importance and only (trichloromethyl)cyclooctane was detected by GLC in 2% yield. Other very minor products were also found by GLC but their structures were not further examined. The mixture of C₉H₁₄Cl₄ compounds was shown by GLC analysis to consist of 25% 1-chloro-2-(trichloromethyl)cyclooctane (A) and 75% 1-chloro-4-(trichloromethyl)cyclooctane (B). These values



were doubly checked by NMR integration of signals for CHCl protons which are diagnostic to differentiate the 1,2 and 1,4 isomers^{5a,b} and the sample was found to be a 26:74 mixture of A and B. Structures of these products were confirmed by comparing their IR and NMR spectra with the reported values.^{5b}

Interestingly, the relative amounts of the 1:1 adducts were found to depend upon the concentration of the ruthenium(II) complex. As the catalyst concentration increases, the ratio of amount of A to that of B increases. For example, the ratio was 0.09 at a catalyst concentration of 0.12 mol % and 0.74 at 1.5 mol % (see Table I). In a single experiment, however, the ratio was virtually constant throughout the reaction (see Figure 1). Furthermore, in control experiments,⁶ isomerization between A and B in the presence of the ruthenium(II) complex was found not to occur to any detectable extent. From these observations, it must be concluded that the dependency of the product ratio on the catalyst concentration is real.

In a simplified interpretation of these phenomena, the intermediacy of Ru^{III}Cl complex from which the (trichloromethyl)cyclooctyl radicals abstract a chlorine atom, as suggested before, can be invoked.^{4,5b} If we accept this view, the product determining in addition processes may be envisioned as shown below.⁷

According to the proposed scheme, rate expressions for the formation of the products, A and B, are

$$d[A]/dt = k_1[R^1\cdot][\text{Ru}^{\text{III}}\text{Cl}] \quad (1)$$

$$d[B]/dt = k_3[R^2\cdot][\text{Ru}^{\text{III}}\text{Cl}] \quad (2)$$

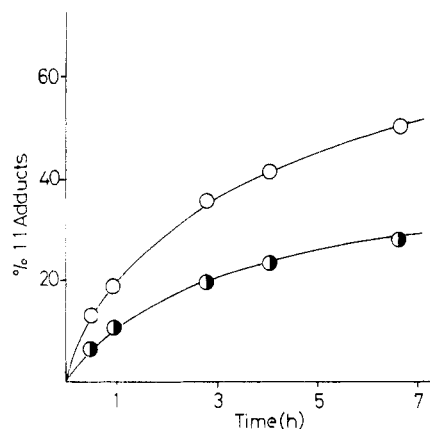
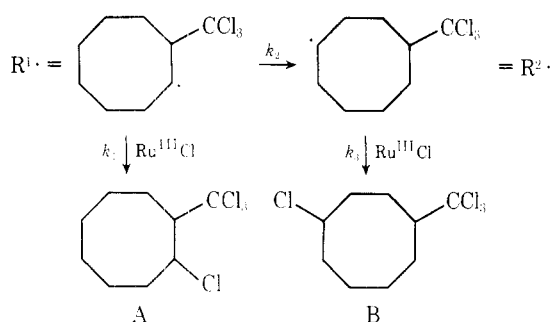


Figure 1. Typical concentration–time profiles for 1,2 adduct, A, and 1,4 adduct, B, in the reaction of *cis*-cyclooctene (10 mmol) with carbon tetrachloride (42 mmol) catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3$ (0.12 mmol) at 90 °C: (○) A, (●) B.

Table I. Effect of the Catalyst Concentration on the 1,2 Adduct/1,4 Adduct Ratios^a

$[\text{RuCl}_2(\text{PPh}_3)_3]$, mmol	[1,2 adduct]/[1,4 adduct]	$[\text{RuCl}_2(\text{PPh}_3)_3]$, mmol	[1,2 adduct]/[1,4 adduct]
0.012	0.09	0.088	0.49
0.023	0.13	0.116	0.58
0.059	0.28	0.153	0.74

^a Reaction conditions; *cis*- C_8H_{14} (10 mmol), CCl_4 (42.2 mmol), C_6H_6 (5 mL) at 90 °C for 0.5–3 h. ^b Determined by GLC. ^c Average in triplicate runs.



Since the steady-state treatment can be applied to the intermediate R^2 ,

$$d[\text{R}^2]/dt = k_2[\text{R}^1] - k_3[\text{R}^2][\text{Ru}^{\text{III}}\text{Cl}] = 0$$

and there results

$$k_3[\text{R}^2][\text{Ru}^{\text{III}}\text{Cl}] = k_2[\text{R}^1]$$

This substituted into eq 2 yields

$$d[\text{B}]/dt = k_2[\text{R}^1] \quad (3)$$

The simultaneous eq 1 and 3 are readily solved, giving

$$d[\text{A}]/d[\text{B}] = (k_1/k_2)[\text{Ru}^{\text{III}}\text{Cl}] \quad (4)$$

The concentration of the reactive intermediate complex, $\text{Ru}^{\text{III}}\text{Cl}$, is considered to be proportional to initial concentration of the added complex, $\text{RuCl}_2(\text{PPh}_3)_3$, so that we find after integration

$$[\text{A}]/[\text{B}] = (k_1/k_2)C[\text{RuCl}_2(\text{PPh}_3)_3] \quad (5)$$

where C is the proportionality constant.⁸

The final result, eq 5, implies that the ratio of the product concentrations, $[\text{A}]/[\text{B}]$, must be linearly correlated with the initial catalyst concentration. This was found to be the case

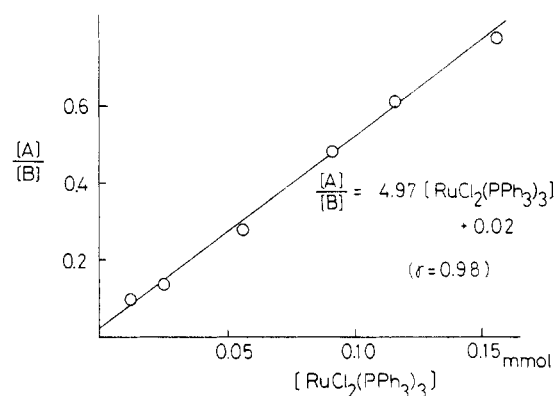


Figure 2. Dependence of relative amounts of the 1,2 and 1,4 adducts on the catalyst concentration.

Table II. Temperature Dependences of [1,2 Adduct (A)]/[1,4 Adduct (B)]

System	A/B
$\text{RuCl}_2(\text{PPh}_3)_3$ catalysis ^a	1/4.6 (90 °C) ^b ; 1/7.8 (155 °C) ^b
Photochemically and thermally induced reactions ^c	1/17 (44 °C); 1/99 (150 °C)

^a Reactions were carried out using 10.0 mmol of *cis*- C_8H_{14} , 42.2 mmol of CCl_4 , 0.43 mmol of $\text{RuCl}_2(\text{PPh}_3)_3$, and 5 mL of C_6H_6 for 0.3–2 h. ^b Determined by GLC. ^c From ref 5.

Table III. Activation Parameters for Intermolecular Chlorine Abstraction and for Transannular Hydrogen Abstraction^a

Initiation	$\Delta\Delta H^\ddagger$, kcal/mol ^b	$\Delta\Delta S^\ddagger$, eu ^c
$\text{RuCl}_2(\text{PPh}_3)_3$	-3	-4
Photochemical and thermal	-4	-21

^a Obtained from the data in Table II. ^b $\Delta\Delta H^\ddagger = \Delta H^\ddagger(\text{A}) - \Delta H^\ddagger(\text{B})$. ^c $\Delta\Delta S^\ddagger = \Delta S^\ddagger(\text{A}) - \Delta S^\ddagger(\text{B})$.

as is shown in Figure 2, where $[\text{A}]/[\text{B}]$ is plotted against $[\text{RuCl}_2(\text{PPh}_3)_3]$ under a certain set of conditions (see Table I).

The relative extents of vicinal and transannular additions were next determined at different temperatures. Results are listed in Table II together with reported $[\text{A}]:[\text{B}]$ ratios for photochemically and thermally induced additions.^{5b} These data lead to calculated differences in enthalpy change [$\Delta\Delta H^\ddagger = \Delta H^\ddagger(\text{A}) - \Delta H^\ddagger(\text{B})$] as well as those in entropy change [$\Delta\Delta S^\ddagger = \Delta S^\ddagger(\text{A}) - \Delta S^\ddagger(\text{B})$] for the two sets of addition reactions (see Table III). In both cases it appears that the enthalpy of activation favors the bimolecular chlorine abstraction from $\text{Ru}^{\text{III}}\text{Cl}$ complex or from carbon tetrachloride by the 2-(trichloromethyl)cyclooctyl radical over the unimolecular transannular hydrogen abstraction by 3 or 4 kcal/mol, while the entropy of activation favors the latter reaction over the former by 4 or 21 eu, respectively. However, it was felt that, because of possible uncertainties involved in the calculated figures, an exact interpretation of the difference in energy of activation is difficult. Nevertheless, it seemed at least qualitatively true that loss in the entropy of activation for the 1,2 addition compared to the 1,4 addition is very much larger in the typical free-radical reaction than in the ruthenium(II) complex catalyzed reaction. The large difference in entropy change between the two additions (4 vs. 21 eu) might be explained by considering the degree of freedom associated with the intermediate 2-(trichloromethyl)cyclooctyl radical. Under

free-radical conditions, little interaction is expected between the intermediate radicals and other chemical species present. On the other hand, the 2-(trichloromethyl)cyclooctyl radical produced in the ruthenium(II) catalysis is likely to be coordinated to the metal center. This is to say that in the ruthenium(II) complex catalyzed reaction the degree of freedom associated with the intermediate radical abstracting chlorine atom would not be as large as in the typical free-radical reactions. Thus, the smaller loss in entropy of activation for the 1,2 addition found in the present case perhaps will reflect coordination of radicals to the metal center and can be taken as support for the homolytic mechanism which is operative in the coordination sphere.

Experimental Section

Boiling points are uncorrected. NMR spectra were recorded on Varian A-60D and HA-100 spectrometers in 15–20% carbon tetrachloride solution. IR spectra were recorded on a Hitachi EPI-3G spectrophotometer with neat samples. GLC analyses were performed with a Ohkura Model 802T instrument equipped with a thermal conductivity detector. Teflon columns (150–200 × 0.4 cm) packed with 10% DCQF-1, 10% polydiethylene glycol adipate 10% SF-96 on 60–80 mesh Chromosorb W, were utilized for analytical studies. Corrections were made for thermal conductivity of the various components.

Carbon tetrachloride, *cis*-cyclooctene, and benzene were commercially available chemicals of over 99% purity and purified by distillation under nitrogen prior to use. Dichlorotris(triphenylphosphine)ruthenium(II) was prepared according to the literature.⁹

Reaction of *cis*-Cyclooctene with Carbon Tetrachloride in the Presence of Dichlorotris(triphenylphosphine)ruthenium(II). Examples of Product Study. A mixture of *cis*-cyclooctene (8.08 g, 73.3 mmol), carbon tetrachloride (45.1 g, 293 mmol), the ruthenium(II) complex (0.51 g, 0.53 mmol), and benzene (15 mL) in a heavy-walled Pyrex tube was cooled in liquid nitrogen, degassed (one time) at 0.3 mm, sealed, and heated at 90 °C for 21 h with stirring. GLC analysis of the resulting mixture disclosed that the olefin had been completely consumed and that the two principal products and some by-products had been formed. The mixture was then diluted with 60 mL of *n*-pentane to precipitate the catalyst which was removed by filtration. Excess carbon tetrachloride and the solvent were evaporated from the filtrate under reduced pressure and vacuum distillation of the residual oil gave two fractions: (a) 0.65 g, a colorless oil, bp 85–105 °C (1.3 mm); (b) 17.1 g, a colorless viscous oil, bp 105–134 °C (1.3 mm).

Among the by-products, only (trichloromethyl)cyclooctane was isolated in approximately 95% purity from fraction (a) by GLC. The IR and NMR spectra of this compound corresponded to the reported spectra:^{5b} IR (neat) 2960, 2850, 1470, 1450, 1360, 1245, 985, 890, 760 (s, C-CCl₃), 705 cm⁻¹; NMR (CCl₄) δ 2.35 (m, 1 H), 2.18 (m, 4 H), 1.63 (m, 10 H). There existed two peaks (27:73) on the GLC chromatogram of fraction (b) and each component was isolated in pure form by GLC separation. The IR and NMR spectra of the first eluted compound agreed with the reported spectra^{5b} of a mixture of *cis*- and *trans*-1-chloro-2-(trichloromethyl)cyclooctane: IR (neat) 2950, 2860, 1470, 1445, 1240, 975, 830, 760 (s, CCl₃), 690 cm⁻¹ (w, CCl); NMR (CCl₄) δ 4.89 (m, 0.2 H, CHCl (*cis* isomer)), 4.53 (m, 0.8 H, CHCl (*trans* isomer)), 2.86 (m, 1 H), 2.25 (m, 4 H), 1.68 (m, 8 H). The IR and NMR

spectra of the second peak corresponded to the reported spectra^{5b} of 1-chloro-4-(trichloromethyl)cyclooctane: IR (neat) 2950, 2860, 1470, 1445, 1240, 980, 950, 840, 760 (s, CCl₃), 675 (w, CCl), 670 cm⁻¹ (w, CCl); NMR (CCl₄) δ 4.17 (m, 1 H), 2.71 (m, 1 H), 2.23 (m, 8 H), 1.65 (m, 4 H).

In order to obtain precise data of the product composition, an addition reaction was carried out at 90 °C for 21 h using 2.21 g (20.1 mmol) of *cis*-cyclooctene, 13.02 g (84.6 mmol) of carbon tetrachloride, 0.138 g (0.14 mmol) of the ruthenium(II) complex, and 6 mL of benzene. GLC analysis of the resulting mixture showed production of a 25:75 (26:74 by NMR analysis) mixture of the 1,2 and 1,4 isomers in 93% yield, along with 2% yield of (trichloromethyl)cyclooctane.

Dependence of the Ratios of the 1,2 and 1,4 Adducts on the Catalyst Concentration. Solutions of *cis*-cyclooctene (1.10 g, 10.0 mmol), carbon tetrachloride (6.49 g, 42.2 mmol), the ruthenium(II) complex (0.0113–0.147 g, 0.012–0.153 mmol), and benzene (5 mL) were heated in sealed Pyrex tubes at 90 °C for 0.5–3.0 h during which time reactions proceeded to 15–40% completion. The relative concentrations of the 1,2 and 1,4 adducts were determined by GLC. All runs and determinations were performed in triplicate and the results are presented in Table I.

Temperature Dependence of the Ratios of the 1,2 and 1,4 Adducts. A solution of *cis*-cyclooctene (1.10 g, 10.0 mmol), carbon tetrachloride (6.49 g, 42.3 mmol), the ruthenium(II) complex (0.041 g, 0.043 mmol), and benzene (5 mL) was heated in a sealed Pyrex tube at 90 °C for 1–2 h and 155 °C for 0.3–0.6 h. The resulting mixture was submitted to GLC analysis. The results are presented in Table II. Values listed were obtained from triplicate runs.

Registry No.—*cis*-Cyclooctene, 931-87-3; CCl₄, 56-23-5; RuCl₂(PPh₃)₃, 15529-49-4; (trichloromethyl)cyclooctane, 7540-99-0; *cis*-A, 65311-43-5; *trans*-A, 65311-44-6; B, 16844-39-6.

References and Notes

- (1) For part III in this series, see H. Matsumoto, T. Nikaïdo, and Y. Nagai, *J. Org. Chem.*, **41**, 396 (1976).
- (2) For reviews, see (a) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957, p 247; (b) C. Walling and E. S. Huyser in "Organic Reactions", Vol. 13, C. Cope Ed., Wiley, New York, N.Y., 1963, p 91; (c) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry", MacMillan, New York, N.Y., 1964, p 19.
- (3) For reviews, see (a) Y. Mori and J. Tsuji, *Kagaku No Ryoiki*, **27**, 197 (1973); (b) R. Kh. Freidlina and E. C. Chukovskaya, *Synthesis*, 477 (1974); (c) F. Minisci, *Acc. Chem. Res.*, **8**, 165 (1975).
- (4) (a) H. Matsumoto, T. Nakano, and Y. Nagai, *Tetrahedron Lett.*, 5147 (1973); (b) H. Matsumoto, T. Nakano, and Y. Nagai, *ibid.*, 899 (1975).
- (5) (a) J. G. Traynham and T. M. Couvillon, *J. Am. Chem. Soc.*, **87**, 5806 (1965); (b) *ibid.*, **89**, 3205 (1967); (c) J. G. Traynham, T. M. Couvillon, and N. S. Bhacca, *J. Org. Chem.*, **32**, 529 (1967).
- (6) A sample of 1.20 g (4.9 mmol) of a 34:66 mixture of 1-chloro-2-(trichloromethyl)cyclooctane and 1-chloro-4-(trichloromethyl)cyclooctane, 0.052 g (0.054 mmol) of the ruthenium(II) complex, 5 mL of carbon tetrachloride, and 3 mL of benzene remained intact when heated in a sealed Pyrex tube at 90 °C for 25 h or 155 °C for 6 h.
- (7) Supporting evidence for the homolytic nature of the present reaction comes from the result that the reaction was strongly retarded by adding a small amount of galvinoxyl to the reaction mixture.
- (8) To the first approximation, the value of the proportionality constant, *C*, is likely to be unity, since the RuCl₂(PPh₃)₃ catalyst appears to be fully converted to the intermediate complex, Ru^{III}Cl, during the reaction. This hypothesis is derived from the facts that the ruthenium(II) catalyst was completely dissolved and also that [CCl₄] >> [RuCl₂(PPh₃)₃].
- (9) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).