# Selective Hydrogenation of 1,5,9-Cyclododecatriene to Cyclododecene Catalyzed by Ruthenium Complexes

DARRYL R. FAHEY

*Phillips Petroleum Company, Research and Development Department, Bartlesville, Oklahoma 74004*

*Received June 27, 1972*

Ruthenium complexes have been found to catalyze the selective homogeneous hydrogenation of 1,5,9-cyclododecatriene (CDT) to cyclododecene (CDE). The most useful complex, $(Ph_3P)_2(CO)_2RuCl_2$, when employed in the presence of a suitable Lewis base between 125 and 160° at 100–200 psig of hydrogen, affords yields of CDE as high as 98.5% along with 1.0% cyclododecadiene (CDD) and 0.5% cyclododecane (CDA). Upon repeated recyclization of the catalyst, after solvent and products were removed from reaction mixtures by distillation under diminished pressure, an equivalent of 32,100 mol of CDT was selectively hydrogenated per gram-atom of ruthenium metal without any apparent diminuation in catalyst activity. The ruthenium catalyst could be conveniently formed directly from $RuCl_3$, $PPh_3$, and CO under the CDT hydrogenation conditions, thereby obviating its prior synthesis. Rate measurements indicate that the hydrogenation is first order in olefin and catalyst. In the presence of $PPh_3$, the rate of CDE hydrogenation is considerably slowed, whereas the rates of CDT and CDD hydrogenations are not so greatly affected. The rates of *cis*-CDE to *trans*-CDE double bond isomerization and its reverse are $10^{2.8}$ and $10^{2.5}$ times faster, respectively, than the rate of CDE hydrogenation in the presence of $PPh_3$. These results are interpreted in terms of an increased steric crowding in a cyclododecylruthenium intermediate, in the presence of $PPh_3$, favoring metal–hydride elimination over hydrogenolysis.

Catalysts capable of effecting the selective hydrogenation of 1,5,9-cyclododecatriene (CDT) to cyclododecene (CDE) are of considerable practical importance. The CDE finds use as an intermediate to the polyamide monomers 1,12-dodecanedioic acid, 1,12-diaminododecane, and 12-aminododecanoic acid lactam. A high selectivity of CDT hydrogenation is especially desirable since CDE, CDT, cyclododecadiene (CDD), and cyclododecane (CDA) cannot be effectively separated by distillation owing to the close proximity of their boiling points. Any CDT and CDD present as impurities in the product mixture must be removed at later processing stages to prevent contamination in the end product.

In view of the high selectivities which may be achieved in homogeneous catalytic hydrogenations,[1] soluble coordination complexes are obvious choices as catalysts for the desired reaction. A soluble tertiary phosphine cobalt carbonyl catalyst has been found to accomplish the highly selective hydrogenation of CDT affording 98.7% CDE along with 1.3% CDA.[2] However, increasing the ratio of CDT to catalyst over that reported results in decreased selectivity and catalyst decomposition.[3] Subsequent to the completion of the work described herein, additional catalysts based on nickel[4a] and iridium[4b] were disclosed which also are effective for the selective hydrogenation of CDT.

In this paper, the use of ruthenium coordination complexes as catalysts for the selective hydrogenation of CDT is presented, and the catalytic behavior of the complex $(Ph_3P)_2(CO)_2RuCl_2$ under varying reaction conditions is described in detail. In the following discussion, selectivity is defined as [CDE]/([CDE] + [CDA]) and is determined at the point where CDE reaches its maximum concentration during a hydrogenation reaction. At higher conversions, the selectivity will be less since the CDE concentration is lower while the CDA concentration is higher. Lower conversions may show higher selectivities, but these are of little practical value.

## Results

**Ruthenium Complexes as Catalysts.**—Ruthenium complexes possessing triphenylphosphine, diethyl sulfide, carbon monoxide, methanol, pyridine (Py), 1,2-bis(diphenylphosphino)ethane (diphos), chloride, and hydride ligands were prepared by published methods. Their catalytic activities were examined by gradually increasing the temperature of their solutions with CDT under ~200 psig of hydrogen until gas absorption began. The temperature was further increased 10° and then held constant until gas absorption ceased. For several complexes, the hydrogenation activity was vastly improved when $NaBH_4$ was employed as a cocatalyst. All complexes surveyed were active hydrogenation catalysts under appropriate conditions, and those affording the most selective catalysts are arranged at the top under each solvent in Table I. Two distinct types of behavior were observed regarding the selectivities of the catalysts. The catalysts derived from the formally zero-valent complexes $(Ph_3P)_2(CO)_3Ru$ and $[(CO)_4Ru]_3$ were more active and generally more selective in benzene solutions (expt 1 and 2), while the higher-valent ruthenium complexes gave more selective catalysts in *N*,*N*-dimethylformamide (DMF) solutions (expt 4–7 and 9–14). The results obtained with a representative example from each class of complexes, *i.e.*, $(Ph_3P)_2(CO)_3Ru$ and $(Ph_3P)_3RuCl_2$, are given in both solvent categories for comparison. Most of the complexes gave catalysts which decomposed under the reaction conditions. Of those that did not decompose, $(Ph_3P)_2(CO)_2RuCl_2$ was selected for more detailed study, and the latter portion of the report is devoted to a description of its characteristics. The catalyst derived from $(Ph_3P)_3RuCl_2$ is presumably the $(Ph_3P)_3RuHCl$ hydrogenation catalyst previously described by Hallman, *et al.*[5] When

---

(1) J. E. Lyons, L. E. Rennick, and J. L. Burmeister, *Ind. Eng. Chem. Prod. Res. Develop.*, **9**, 2 (1970).

(2) I. Ogata and A. Misono, *Discuss. Faraday Soc.*, **No. 46**, 72 (1968); A. Misono and I. Ogata, *Bull. Chem. Soc. Jap.*, **40**, 2718 (1967).

(3) (a) M. Morita, Y. Iwai, J. Itakura, and H. Ito, U. S. Patent 3,567,790 (1971); (b) D. R. Fahey, unpublished studies (1968).

(4) (a) L. W. Gosser, U. S. Patent 3,499,050 (1970); M. T. Musser, U. S. Patent 3,631,210 (1971); (b) L. W. Gosser, U. S. Patent 3,513,210 (1970).

(5) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. A*, 3143 (1968).

TABLE I

HYDROGENATION OF CDT CATALYZED BY RUTHENIUM COMPLEXES[a]

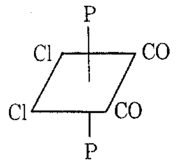
| Expt | Ru complex | Temp, °C | Reaction time, hr | Dec[b] | Yield, % |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | CDA | CDE | CDD | CDT |
|  |  |  | In Benzene Solution |  |  |  |  |  |
| 1 | $(Ph_3P)_2(CO)_3Ru$ | 158 | 1.2 | p | 2.7 | 94.6 | 2.3 | 0.4 |
| 2 | $[(CO)_4Ru]_3$ | 158 | 1.2 | p | 11.2 | 85.0 | 2.9 | 0.9 |
| 3 | $(Ph_3P)_3RuCl_2$ | 85 | 4.0 |  | 42.3 | 29.6 | 15.6 | 12.4 |
|  |  |  | In *N,N*-Dimethylformamide Solution |  |  |  |  |  |
| 4 | $(Et_2S)_3RuCl_3$ | 135 | 3.5 | p | 2.8 | 92.6 | 3.2 | 1.4 |
| 5 | $(Ph_3P)_2(CO)_2RuCl_2$ | 140 | 4.0 |  | 13.3 | 84.7 | 1.8 | 0.3 |
| 6 | $(Ph_3P)_2(CH_3OH)RuCl_3$ | 140 | 4.5 | p | 14.3 | 80.4 | 4.2 | 1.1 |
| 7 | $(Ph_3P)_3(CO)RuH_2$ | 140 | 5.0 | c | 5.3 | 74.8 | 13.2 | 6.7 |
| 8 | $(Ph_3P)_2(CO)_3Ru$ | 140 | 4.0 | c | 1.3 | 51.0 | 27.4 | 20.3 |
| 9 | $[(CO)_2RuCl_2]_n$ | 145 | 3.3 | c | 0.2 | 22.8 | 38.4 | 38.6 |
| 10 | $(Py)_4RuCl_2$ | 145 | 3.0 | c | 2.3 | 36.0 | 30.2 | 31.5 |
| 11 | $(Py)_4RuCl_2$–$NaBH_4$[c] | 110 | 1.8 | p | 36.0 | 59.8 | 2.4 | 1.7 |
| 12 | $(Py)_2(CO)_2RuCl_2$–$NaBH_4$[d] | 125 | 2.2 | p | 21.8 | 47.2 | 15.5 | 15.5 |
| 13 | $(Diphos)_2RuCl_2$–$NaBH_4$[d] | 105 | 2.1 | c | 8.6 | 29.0 | 22.5 | 39.9 |
| 14 | $(Ph_3P)_3RuCl_2$ | 125 | 5.0 |  | 31.4 | 51.1 | 8.4 | 9.1 |

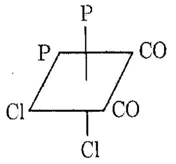
[a] Solutions were composed of 0.10 g of complex, 2.0 g (1.2 mmol) of CDT, and 20 ml of solvent. [b] p denotes partial catalyst decomposition during reaction and c denotes complete catalyst decomposition. [c] 0.10 g of $NaBH_4$. [d] 0.050 g of $NaBH_4$.

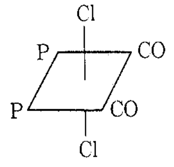
complexes decomposed, they formed black particles and a ruthenium mirror on the wall of the vessel. The ruthenium metal in this form was inactive as a hydrogenation catalyst.

**Preparation and Structure of $(Ph_3P)_2(CO)_2RuCl_2$.**—The $(Ph_3P)_2(CO)_2RuCl_2$, mp 309–312° dec, was synthesized by treating a solution of $[(CO)_2RuCl_2]_n$, prepared by bubbling CO through a refluxing ethanolic solution of $RuCl_3$, with $PPh_3$ according to the method of Stephenson and Wilkinson.[6] Alternately, the catalyst was more conveniently formed directly from $RuCl_3$ in a CDT hydrogenation reaction. For example, when $RuCl_3$, $PPh_3$, CDT, 4 psig of CO, and ethanol were stirred at 140° under hydrogen, the hydrogenation reaction proceeded in the usual manner, and a 98.0% yield of CDE was obtained along with 2.0% CDA. When the solution was cooled to 25°, colorless crystals precipitated which possessed an ir spectrum and C, H, Cl analyses identical with those of $(Ph_3P)_2(CO)_2RuCl_2$. The crystals were obtained in an essentially quantitative yield based on $RuCl_3$. The amount of CO employed is important. If too little is used, the conversion into the dicarbonyl complex is not complete, and with too much, the hydrogenation may cease before complete conversion of the polyenes. This presents no problem when the reaction vessel is pressured with greater than 4 psig of CO, and, after heating the mixture to the reaction temperature, the excess CO is vented. Repressuring the system with hydrogen allows the reaction to proceed normally. This technique has afforded CDT product yields of 1.0% CDA, 98.8% CDE, and 0.2% CDD. The $(Ph_3P)_2(CO)_2RuCl_2$ recovered from these reactions is recyclable.

Most syntheses[6-12] of $(Ph_3P)_2(CO)_2RuCl_2$ produce a white solid having two C≡O stretching vibrations, one between 2065 and 2050 $cm^{-1}$ and the other between 2001 and 1990 $cm^{-1}$. Configurations **1a**[6-11] and either **1b** or **1c**[13] have been assigned to the complex.


**1a**


**1b**


**1c**

A comparison of the ir spectrum of our $(Ph_3P)_2(CO)_2RuCl_2$ complex with that of *cis*-$Cl_2$-*trans*-$(MePh_2P)_2$-*cis*-$(CO)_2Ru$ (see Experimental Section) very strongly suggests that both have the same configuration, namely **1a**.[13a]

**Effect of Solvent.**—The selectivity of the hydrogenation of CDT catalyzed by $(Ph_3P)_2(CO)_2RuCl_2$ is dependent on the nature of the solvent as shown in Table II. In most solvents, the rates of reaction were about the same with the exceptions being dimethyl sulfoxide and sulfolane. The stability of the catalyst seemed to correlate with its selectivity in the solvents listed. In expt 15–19 where the catalyst selectivity was highest, each homogeneous pale yellow solution retained its physical appearance throughout the course of the reaction. However, in expt 20–23 where the catalyst was less selective, each solution acquired an orange coloration which became more pronounced as the reaction progressed. The ruthenium catalyst apparently undergoes a change in these latter solvents.

(6) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).

(7) J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, **87**, 4008 (1965).

(8) M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. A*, 1238 (1967).

(9) J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *ibid.*, 2162 (1968).

(10) W. Hieber and P. John, *Chem. Ber.*, **103**, 2161 (1970); P. John, *ibid.*, **103**, 2196 (1970).

(11) S. Cenini, A. Fusi, and G. Capparella, *J. Inorg. Nucl. Chem.*, **33**, 3579 (1971).

(12) N. Ahmad, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc. Dalton Trans.*, 843 (1972).

(13) B. R. James and L. D. Markham, *Inorg. Nucl. Chem. Lett.*, **7**, 373 (1971).

(13a) NOTE ADDED IN PROOF.—Configuration **1a** has now been confirmed for $(Ph_3P)_2(CO)_2RuCl_2$ by examination of its proton-decoupled $^{13}C$ nmr spectrum. The substituted, ortho, and meta carbon resonances of the phenyl groups are apparent 1:2:1 triplets with ($J_{CL} + J_{CP'}$) of 47.6, 9.8, and 9.2 Hz, respectively, indicative that the $PPh_3$ groups are mutually trans [see B. E. Mann, B. L. Shaw, and R. E. Stainbank, *J. Chem. Soc., Chem. Commun.*, 151 (1972)]. I thank Dr. J. C. Randall for recording this spectrum.

TABLE II

EFFECT OF SOLVENT ON THE HYDROGENATION OF CDT CATALYZED BY $(Ph_3P)_2(CO)_2RuCl_2$[a]

| Expt | Solvent | Reaction time, hr | Yield, % CDA | CDE | CDD | CDT |
|---|---|---|---|---|---|---|
| 15 | Dimethyl sulfoxide[b] | 29 | 1.0 | 97.8 | 0.9 | 0.5 |
| 16 | *N*-Methylpyrrolidone | 2.5 | 1.0 | 94.6 | 3.2 | 1.2 |
| 17 | Sulfolane | 7 | 0.1 | 27.1 | 28.2 | 44.7 |
| 18 | *N*,*N*-Dimethylformamide | 3 | 9.0 | 85.6 | 3.7 | 1.7 |
| 19 | *N*,*N*-Dimethylacetamide | 3 | 16.2 | 75.7 | 5.4 | 2.7 |
| 20 | Tetrahydrofuran | 2.5 | 11.3 | 55.1 | 16.5 | 17.0 |
| 21 | Ethyl acetate | 2 | 34.2 | 48.4 | 9.3 | 8.1 |
| 22 | 1-Butanol | 2 | 39.0 | 47.1 | 8.6 | 5.3 |
| 23 | Benzene | 2 | 24.1 | 45.2 | 12.3 | 18.4 |
| 24 | Acetonitrile | 3 | 0 | 0.1 | 3.9 | 96.0 |

[a] Solutions were composed of 0.10 g (0.13 mmol) $(Ph_3P)_2(CO)_2RuCl_2$, 2.0 g (1.2 mmol) of CDT, and 30 ml of solvent. The reaction temperatures were 140–160°. [b] *Caution.* In two of four reactions, a vigorous decomposition of the reaction solution occurred causing the reaction vessel to burst.

Acetonitrile as solvent severely inhibited the activity of the catalyst.

**Effect of Added Lewis Bases.**—The selectivity of the hydrogenation is also influenced by the presence of certain Lewis bases which may coordinate to ruthenium as a ligand. This dependence for several common ligands is given in Table III. The greatest selectivity was obtained with $PPh_3$. The yield of CDE increased with increasing $PPh_3$ concentration to a maximum of about 98%. Other experiments have shown the selectivity to be dependent on the *relative* concentrations of CDT and $PPh_3$. The introduction of small amounts of gaseous CO in precise quantities proved to be difficult, and, in expt 30, the actual concentration of CO is unknown. Although this quantity of CO did enhance the selectivity of the hydrogenation, perceptible hydrogen absorption ceased before completion of the hydrogenation. Treatment of $(Ph_3P)_2(CO)_3Ru$ with HCl evolves 1 equiv of CO along with $(Ph_3P)_2(CO)_2RuCl_2$.[7] Utilizing this reaction in expt 29, an improved selectivity over expt 23 was obtained, but it is not high as that obtained in reactions with added $PPh_3$. Added $AsPh_3$, $PBu_3$, and $HNEt_2$ were less effective than $PPh_3$, and the phosphine oxides had no effect on the selectivity. Other $PR_3$ compounds with at least one R more electronegative than carbon and chelating ligands destroyed the activity of the catalyst. No hydrogenation was observed with $P(OPh)_3$, $P(OEt)_3$, $P(OMe)Ph_2$, $P(morpholino)_3$, 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylarsino)ethane, or pyridine.

TABLE III

EFFECT OF ADDED LEWIS BASES ON THE HYDROGENATION OF CDT CATALYZED BY $(Ph_3P)_2(CO)_2RuCl_2$[a]

| Expt | Lewis base | Concentration, *M* | Yield, % CDA | CDE | CDD | CDT |
|---|---|---|---|---|---|---|
| 23 | None | | 24.1 | 45.2 | 12.3 | 18.4 |
| 25 | $PPh_3$ | 0.017 | 10.5 | 88.9 | 0 | 0.6 |
| 26 | $PPh_3$ | 0.034 | 4.4 | 95.6 | 0 | 0 |
| 27 | $PPh_3$ | 0.068 | 1.9 | 98.1 | 0 | 0 |
| 28 | $PPh_3$ | 0.13 | 0.6 | 97.8 | 1.5 | 0.5 |
| 29[b] | CO | 0.007 | 30.0 | 66.9 | 3.1 | 0 |
| 30 | CO | <6 psig | 0.1 | 45.7 | 30.2 | 24.0 |
| 31 | $HNEt_2$ | 0.050 | 36.1 | 63.0 | 0.7 | 0.2 |
| 32 | $AsPh_3$ | 0.015 | 26.6 | 53.7 | 9.7 | 10.0 |
| 33 | $PBu_3$ | 0.01 | 29.8 | 51.6 | 9.5 | 7.9 |
| 34 | $OPPh_3$ | 0.016 | 97.4 | 2.5 | 0 | 0.1 |
| 35 | $OP(octyl)_3$ | 0.01 | 96.7 | 3.3 | 0 | 0 |

[a] Solutions (except expt 29) were 0.006 *M* (0.10 g, 0.13 mmol) $(Ph_3P)_2(CO)_2RuCl_2$ and 0.55 *M* (1.8 g, 1.1 mmol) CDT in 20 ml of benzene. [b] 0.007 *M* in $(Ph_3P)_2(CO)_2RuCl_2$ prepared by the treatment of a 0.007 *M* $(Ph_3P)_2(CO)_3Ru$ solution with HCl.

**Effect of Reducing Agents.**—Since a ruthenium hydride or a reduced ruthenium complex is likely the actual catalytic species, the use of reducing agents as cocatalysts were investigated. The effect of several reducing agents upon the hydrogenation of CDT catalyzed by $(Ph_3P)_2(CO)_3RuCl_2$ is shown in Table IV. The only reducing agents which did not impair catalyst activity were $SnCl_2$ and $N_2H_4$. None allowed the reaction to occur at a lower temperature. The slightly shorter reaction times of expt 36 and 37 compared to expt 18 most likely result from an increased reaction temperature. Any beneficial effect these reagents may have had on the reaction is not obvious.

**Effect of Hydrogen Pressure.**—The hydrogenation was studied at pressures up to 600 psig, although high pressures are not necessary. If the hydrogen absorbed is not replenished during reactions, the pressure will drop to 0 psig, indicating that the reaction occurs even at very low pressures. The selectivity of the reaction is also dependent on the hydrogen pressure. In comparable reactions in benzene solution containing 0.036 *M* $PPh_3$, carried out at 100 and 200 psig hydrogen pressures, the maximum yields of CDE were 98.5 and 91.0%, respectively.

**Effect of Temperature.**—The temperature range 135–160° has been found to be most suitable for the reaction. Below 135°, the reaction occurs only very slowly or not at all. In fact, lowering the temperature of an initiated reaction to below 125° results in a cessation of hydrogen absorption. The hydrogenation may be resumed by increasing the temperature above 125–135°. As the temperature is increased above 135°, the rate of hydrogenation becomes very rapid and the selectivity is also enhanced. At 170°, a hydrogenation equivalent to expt 5 afforded a maximum yield of CDE of 91.6%. Above 160°, a side reaction occurs which affords undesirable by-products. At 170°, a 5.6 glpc area % yield of these by-products was obtained. The influence of temperature on this side reaction has been previously described elsewhere.[14] The hydrogenation reaction is exothermic, and the reaction tempera-

---

(14) C. G. McAlister, U. S. Patent 3,400,164 (1968); R. Levine, U. S. Patent 3,400,165 (1968); C. G. McAlister, U. S. Patent 3,400,166 (1968).

TABLE IV

EFFECT OF REDUCING AGENTS ON THE HYDROGENATION OF CDT CATALYZED BY $(Ph_3P)_2(CO)_2RuCl_2$[a]

| Expt | Reducing agent | Concn, $M$ | Solvent | Reaction temp, °C | Reaction time, hr | Added $PPh_3$ | Yields, %<br>CDA | <br>CDE | <br>CDD | <br>CDT |
|---|---|---|---|---|---|---|---|---|---|---|
| 36 | $SnCl_2$ | 0.02 | DMF | 148 | 2 | No | 3.2 | 95.1 | 1.4 | 0.3 |
| 37 | $N_2H_4$ | 0.02 | EtOH | 145 | 2 | Yes | 0 | 98.1 | 1.6 | 0.3 |
| 38 | Electrochemical reduction[b] | | $CH_3OCH_2CH_2OCH_3$ | 140 | ~3 | No | 0 | 0.4 | 10.9 | 88.7 |
| 39 | $AlEt_3$[c] | 0.03 | Benzene | 140 | 1.5 | Yes | 0 | 18.2 | 35.5 | 46.3 |
| 40 | $NaBH_4$[c] | 0.33 | EtOH | 150 | 3 | Yes | 0 | 0.4 | 2.8 | 96.8 |
| 41 | $NaBH_4$[c] | 0.07 | DMF + benzene (1:1) | 130 | 2 | No | 2.3 | 30.7 | 30.7 | 36.3 |

[a] Solutions (except expt 38) were composed of 0.006 $M$ (0.10 g, 0.13 mmol) $(Ph_3P)_2(CO)_2RuCl_2$, 2.0 g (1.2 mmol) of CDT, and 20 ml of solvent. [b] 25 ml of a 0.010 $M$ $(Ph_3P)_2(CO)_2RuCl_2$ solution containing $[Bu_4N][ClO_4]$, as a supporting electrolyte, was subjected to controlled potential electrolysis at −2.5 V until the current dropped to 0 mA. The resulting solution was combined with 1.0 g of CDT, and the hydrogenation was carried out in the typical fashion. [c] The catalyst became inactive.

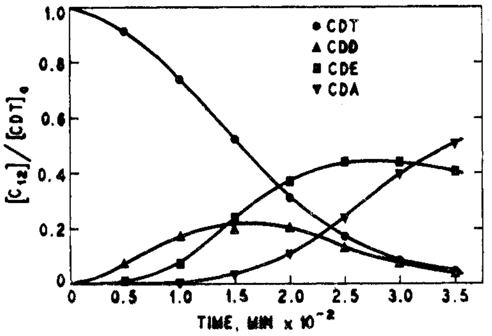


Figure 1.—Plot of relative concentrations of $C_{12}$ compounds *vs* time for the hydrogenation of CDT by 2.48 × $10^{-3}$ $M$ $(Ph_3P)_2(CO)_2RuCl_2$ without added $PPh_3$.

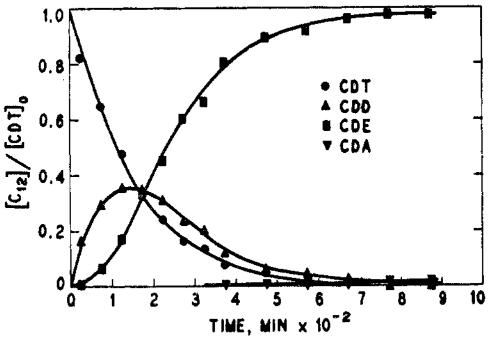


Figure 2.—Plot of relative concentrations of $C_{12}$ compounds *vs.* time for the hydrogenation of CDT by 2.48 × $10^{-3}$ $M$ $(Ph_3P)_2(CO)_2RuCl_2$ with 0.0356 $M$ $PPh_3$.

tures sometimes rapidly increased during large batch reactions. For this reason, it was necessary to monitor the temperature very closely on large-scale reactions.

**Productivity of Catalyst–Catalyst Recycle.**—A productivity determination was conducted by hydrogenating seven 50-g samples of CDT with 0.050 g of $(Ph_3P)_2(CO)_2RuCl_2$ in benzene solution with $PPh_3$ present under 500 psig of hydrogen. After each hydrogenation reaction was completed, the reaction mixture was distilled to dryness at reduced pressure, and the residue (Ru catalyst and $PPh_3$) was dissolved in benzene and recycled. No diminution in activity of the catalyst was observed. The first hydrogenation required over 6 hr and the remaining six lasted between 1 and 1.5 hr. The yield of CDE was 83–94% for each sample, but additional $PPh_3$ was occasionally added to maintain the selectivity. Subsequent experiments have shown that the $PPh_3$ is oxidized to $Ph_3PO$ when no precautions are taken to exclude atmospheric oxygen from reaction solutions. This study demonstrated that a *minimum* of 32,100 mol of CDT can be selectively hydrogenated per mole of $(Ph_3P)_2(CO)_2RuCl_2$. The maximum productivity of the catalyst certainly significantly exceeds this figure.

**Rate Studies.**—A brief kinetic study was undertaken to enable a greater insight into the origin of catalyst selectivity. A detailed kinetic treatment of this reaction would, of course, be vital to a mechanistic study, but would not significantly amplify the arguments presented here.

Reaction rates were determined at 140° in solutions containing 0.62–2.48 × $10^{-3}$ $M$ $(Ph_3P)_2(CO)_2RuCl_2$ and 0.254 $M$ CDT, while a constant 200 psig hydrogen pressure was maintained above the reaction solution. The reaction solutions containing all reagents except CDT were equilibrated for 60 min under 60 psig of hydrogen at 140°. The reaction was initiated by the addition of CDT from a reservoir, and samples were withdrawn through a dip tube at regular intervals.

Plots of relative concentrations of the $C_{12}$ intermediates *vs.* time for the hydrogenation in benzene solution without and with added $PPh_3$ are illustrated in Figures 1 and 2, respectively. The CDT and CDD concentration *vs.* time profiles are similar in both figures, but the CDE concentration attains a much higher maximum value and the CDA concentration increases more slowly in Figure 2. The collection of curves in each figure is typical of a consecutive first-order reaction. A linear relationship between the ln $[CDT]_0/[CDT]$ and time exists for these reactions (Figures 3 and 4) as well as the hydrogenation in DMF solution (not shown), neglecting any induction periods which are believed to involve formation of an active ruthenium hydride catalyst. Thus, a simple first-order dependence of the rate on olefin concentration is experimentally observed. Data from experiments with varying $(Ph_3P)_2(CO)_2RuCl_2$ concentrations are most consistent with the rate of CDT hydrogenation being first order in catalyst (Figure 5). Thus, the data can be accommodated by rate eq 1. Assuming the hydrogenation of CDD is also first order in both Ru and alkene, the rate of formation of CDD is that shown in eq 2. By invoking the steady-state approximation at the point where CDD reaches its maximum concentration during the reaction, *i.e.*, when $d[CDD]/dt = 0$, eq 2 reduces to eq 3 and the rate constant for the hydrogenation of CDD can be calculated. Equation 4 can be derived in a similar manner, and the rate con-

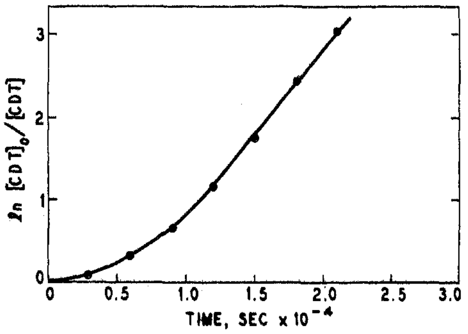


Figure 3.—First-order plot of ln $[CDT]_0/[CDT]$ *vs.* time for the hydrogenation of CDT by $2.48 \times 10^{-3}$ *M* $(Ph_3P)_2(CO)_2RuCl_2$ without added $PPh_3$.

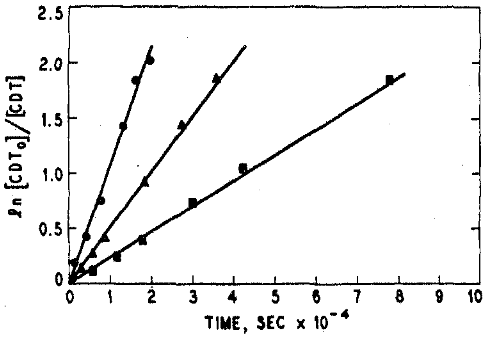


Figure 4.—First-order plot of ln $[CDT]_0/[CDT]$ *vs.* time for the hydrogenation of CDT by (●) $2.48 \times 10^{-3}$ *M*, (▲) $1.55 \times 10^{-3}$ *M*, and (■) $0.62 \times 10^{-3}$ *M* $(Ph_3P)_2(CO)_2RuCl_2$ with 0.0356 *M* $PPh_3$.

$$-d[CDT]/dt = K'[Ru][CDT] \qquad (1)$$

$$d[CDD]/dt = K'[Ru][CDT] - K''[Ru][CDD] \qquad (2)$$

$$K'' = K'[CDT]/[CDD] \text{ at } [CDD]_{max} \qquad (3)$$

$$K''' = K''[CDD]/[CDE] \text{ at } [CDE]_{max} \qquad (4)$$

stant for CDE hydrogenation, $K'''$, is determined from this equation at the point where CDE attains its maximum concentration. The three rate constants $K'$, $K''$, and $K'''$ undoubtedly contain terms for hydrogenation concentration (which was maintained constant) and for $PPh_3$ and DMF concentrations (which may account for some of the variation in each rate constant between the three systems in Table V).

Table V

Second-Order Rate Constants for the Hydrogenation of CDT Catalyzed by $(Ph_3P)_2(CO)_2RuCl_2$[a]

| Solvent system | K' [b] | K'' [b] | K''' [b] |
|---|---|---|---|
| Benzene | 83 | 189 | 43 |
| *N,N*-Dimethylformamide | 58 | 78 | 2.5 |
| Benzene + 0.0356 *M* $PPh_3$ | 43 | 66 | 0.58 |

[a] Rate constants presumably include terms for hydrogen, DMF, and $PPh_3$ concentrations. [b] Units of $mol^{-1}$ l. $sec^{-1} \times 10^3$.

In Table V, the rate constants determined in the two reactions illustrated in Figures 1 and 2 along with a reaction in *N,N*-dimethylformamide (DMF) solution are tabulated, and their relative values can be directly compared. As the table is descended, the values of $K'$ and $K''$ decrease slightly while $K'''$ greatly diminishes. Thus, the presence of DMF or $PPh_3$ in the system only slightly affects the rates of hydrogenation of CDT and CDD, but greatly slows the rate of CDE hydrogenation.

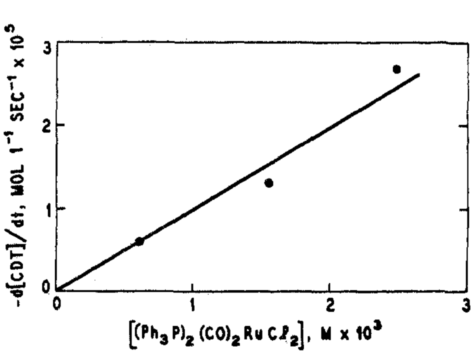


Figure 5.—Rate dependence of CDT hydrogenation on $(Ph_3P)_2(CO)_2RuCl_2$ concentration.

**Hydrogenation–Isomerization of *trans*-CDE.**—If a ruthenium hydride intermediate is the actual catalytic species, as it is for related soluble ruthenium hydrogenation catalysts,[5,15,16] the rate of metal hydride addition–elimination to and from the olefin would be reflected in the rate of olefin isomerization. The rate of isomerization of *trans*-CDE to the equilibrium trans/cis mixture and the rate of CDE hydrogenation were determined using the same solvent system and conditions as the third entry in Table V except that the *trans*-CDE concentration was 0.125 *M* and the $(Ph_3P)_2(CO)_2RuCl_2$ concentration was $6.36 \times 10^{-4}$ *M*. In the earlier study, the CDT concentration was 0.254 *M* and the $(Ph_3P)_2(CO)_2RuCl_2$ was $6.20 \times 10^{-4}$ *M*.

The rate of isomerization of the olefin in this reaction was very fast. Within 25 min, the isomerization had progressed 50% toward the equilibrium trans/cis mixture. Yet, after 1200 min, only 3.9% of the CDE was hydrogenated to CDA. The isomerization reaction under consideration is shown in eq 5 with the rate constants $k'$ and $k''$ to be determined. These constants were evaluated from eq 6 which is the expression for a reversible first-order reaction adapted to our pseudo-first-order reaction; where [*trans*-CDE] at time 0 is $A_0$, at time *t* is *A*, and at equilibrium is $A_e$. The equilibrium trans/cis ratio of CDE is 2.05. A plot of ln $(A_0 - A_e)/(A - A_e)$ *vs.* time was linear, and a value of 0.80 $mol^{-1}$ l. $sec^{-1}$ was obtained for the sum of the rate constants $k' + k''$. Since at equilibrium, $k'' = 2.05k'$, the values of $k'$ and $k''$ are 0.26 and 0.54 $mol^{-1}$ l. $sec^{-1}$, respectively.

$$RuH + trans\text{-}CDE \underset{k''}{\overset{k'}{\rightleftharpoons}} cis\text{-}CDE + RuH \qquad (5)$$

$$\ln (A_0 - A_e)/(A - A_e) = (k' + k'')[Ru]t \qquad (6)$$

Employing a pseudo-second-order rate equation equivalent to eq 1 for the hydrogenation of CDE, the rate constant $K''' = 0.80 \times 10^{-3}$ $mol^{-1}$ l. $sec^{-1}$ was calculated. This value should be compared with $K''' = 0.58 \times 10^{-3}$ $mol^{-1}$ l. $sec^{-1}$ reported in Table V. The agreement is fair, and a greater level of confidence should be placed with the $0.80 \times 10^{-3}$ figure since the glpc integration error was greater in the determination of the very small concentration of CDD

---

(15) D. Rose, J. O. Gilbert, R. P. Richardson, and G. Wilkinson, *J. Chem. Soc. A*, 2610 (1969).

(16) B. R. James, *Inorg. Chim. Acta Rev.*, **4**, 73 (1970).

for use in calculating the $0.58 \times 10^{-3}$ figure. The above figures clearly indicate that, for CDE, the rate of isomerization, and thus metal hydride addition–elimination, is much faster than hydrogenation.

**Hydrogenation–Isomerization of 1,5-COD.**—It is of interest to know if the double bonds become conjugated in the $C_{12}$ polyunsaturated intermediates prior to their hydrogenation. This has been claimed as the mechanism by which CDT is hydrogenated in the presence of the cobalt carbonyl catalyst.[2] The glpc chromatograms of the CDT hydrogenation mixtures at intermediate stages of the reaction are the same when either the ruthenium catalyst or the cobalt carbonyl catalyst is employed indicating that the same $C_{12}$ intermediates are formed in both reactions.

In the hydrogenation of 1,5-cyclooctadiene (1,5-COD) to cyclooctene catalyzed by the ruthenium complex, the 1,5-COD was isomerized to 1,4-COD and then to 1,3-COD faster than cyclooctene was formed. These observations, along with the knowledge that double bond isomerization is faster than hydrogenation (at least for CDE), are consistent with, but do not require, conjugated diolefins as intermediates in the ruthenium-catalyzed hydrogenation of CDT.

## Discussion

The mechanism of the reaction undoubtedly parallels that of other ruthenium hydride complex hydrogenations[5,15,16] and follows the course shown in eq 7, 8, and 9 where the hydrogenation steps are rate determining.

$$\mathrm{RuH} + \mathrm{CDT} \overset{K_1}{\rightleftharpoons} \mathrm{Ru(dienyl)} \xrightarrow[\mathrm{H_2}]{k_1} \mathrm{RuH} + \mathrm{CDD} \tag{7}$$

$$\mathrm{RuH} + \mathrm{CDD} \overset{K_2}{\rightleftharpoons} \mathrm{Ru(alkenyl)} \xrightarrow[\mathrm{H_2}]{k_2} \mathrm{RuH} + \mathrm{CDE} \tag{8}$$

$$\mathrm{RuH} + \mathrm{CDE} \overset{K_3}{\rightleftharpoons} \mathrm{Ru(alkyl)} \xrightarrow[\mathrm{H_2}]{k_3} \mathrm{RuH} + \mathrm{CDA} \tag{9}$$

Unfortunately, the true identity of the active ruthenium catalyst remains unknown. The absence of an induction period in rate studies with added $PPh_3$ suggests that $PPh_3$ acts as a base to accept HCl generated from the reaction of $(Ph_3P)_2(CO)_2RuCl_2$ with hydrogen in forming a RuH species as catalyst. The conversion of $(Ph_3P)_3RuCl_2$ into the active catalyst $(Ph_3P)_3RuHCl$ is similarly accelerated in the presence of certain bases such as $NEt_3$.[5] The induction period which occurs in the absence of added $PPh_3$ cannot be due to a slow dissociation of the neutral ligands. Since $(Ph_3P)_2(CO)_2RuCl_2$ was isolated from several hydrogenations after the reaction was completed, it is likely in equilibrium with the catalyst. Therefore, the composition of the catalyst must be only slightly different from $(Ph_3P)_2(CO)_2RuCl_2$ and is envisioned as $(Ph_3P)_2(CO)_2RuHCl$ or possibly $(Ph_3P)_2(CO)_2RuH_2$ with easily dissociated $PPh_3$ ligands. Complexes of these compositions are known.[9,13,17] To comply with the mechanism of related ruthenium-catalyzed hydrogenations,[5,15,16] both $PPh_3$ ligands must readily dissociate.

In the selective hydrogenation of olefin mixtures catalyzed by $RhCl(PPh_3)_3$, the degree of selectivity achieved is enhanced by the addition of polar solvents.[18] In Table VI, selectivities to CDE in several solvents are listed (taken from data in Table II) with the dielectric constant, $\epsilon$, of each solvent. There appears to be no correlation of selectivity with solvent $\epsilon$ in the hydrogenation of CDT catalyzed by $(Ph_3P)_2(CO)_2RuCl_2$.

TABLE VI

CDE SELECTIVITIES AND SOLVENT DIELECTRIC CONSTANTS FOR THE HYDROGENATION OF CDT CATALYZED BY $(Ph_3P)_2(CO)_2RuCl_2$

| Solvent | $\epsilon$ | Selectivity[a] |
|---|---|---|
| Dimethyl sulfoxide | 48.9 | 0.99 |
| *N,N*-Dimethylacetamide | 37.8 | 0.82 |
| *N,N*-Dimethylformamide | 36.7 | 0.91 |
| 1-Butanol | 17.8 | 0.55 |
| Ethyl acetate | 6.0 | 0.59 |
| Benzene | 2.3 | 0.65 |

[a] Selectivity = [CDE]/([CDE] + [CDA]) at the point of maximum yield of CDE during the hydrogenation.

The selectivity dependence on solvent and added Lewis bases could also arise from a competition between the solvent or added Lewis bases and the intermediate olefins for complexation to ruthenium, where CDE does not compete so well as does CDD and CDT. Related to this, previous workers have found that the relative hydrogenation rates of olefins catalyzed by $(Ph_3P)_3RuHCl$ are determined by the respective "coordinating power of the alkene."[19] Alternatively, RuH addition to the coordinated olefin may be more sterically hindered for CDE than for CDD or CDT when Lewis bases or solvents occupy coordination sites about ruthenium. This explanation has been put forth to explain rate differences in the hydrogenation of internal *vs.* terminal olefins catalyzed by $(Ph_3P)_3RuH(OAc)$.[15] The results of the present study eliminate both of the above in the selective hydrogenation of CDT. Since the isomerization of *trans*-CDE is very much faster than its hydrogenation, the RuH addition to the coordinated CDE is very facile in the presence of $PPh_3$. The increased selectivity of the hydrogenation when $PPh_3$ is added must result from either a slowed hydrogenation step or an increased RuH elimination rate for the Ru(alkyl) intermediate. The present data do not allow elimination of either possibility. We speculate that the cycloalkylruthenium intermediate formed by the addition of RuH to CDE is so sterically crowded in the presence of coordinated $PPh_3$ that the intermediate undergoes rapid RuH elimination before reaction with hydrogen. In the intermediates tormed by the RuH addition to CDD or CDT, a double bond in the cycloalkenyl ligand displaces a coordinated $PPh_3$ to form a $\sigma,\pi$-bonded chelate structure or a $\pi$-allylic complex. The extra stability gained by chelation and by relief of steric crowding (from loss of coordinated $PPh_3$) allows the intermediate a sufficient lifetime to react with hydrogen. In solutions without added $PPh_3$, the $PPh_3$ ligands remain largely dissociated from the catalyst, and differences in the stabilities of the inter-

---

(17) F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, **7**, 1290 (1968).

(18) J. P. Candlin and A. R. Oldham, *Discuss. Faraday Soc.*, No. **46**, 60 (1968).

(19) I. Jardine and F. J. McQuillin, presented at the British Chemical Society Annual Meeting, Nottingham, April 1969, and highlighted in *Chem. Brit.*, **5**, 321 (1969); *Tetrahedron Lett.*, 5189 (1968).

mediates formed from CDT, CDD, and CDE due to steric crowding would not be so important. Thus, these hydrogenations are less selective.

In summary, CDT can be selectively hydrogenated in 98–99% yield to CDE by the catalyst derived from $(Ph_3P)_2(CO)_2RuCl_2$ in the presence of certain solvents or added Lewis bases, *e.g.*, *N*,*N*-dimethylformamide or $PPh_3$. The ruthenium catalyst exhibits a remarkable stability under the reaction conditions as well as a resistance to attack by oxygen, water, or poisons present as impurities in the reagents used. Two precautions are suggested to obtain the maximum utility from the catalyst system: (1) atmospheric oxygen should be excluded from solutions to avoid the oxidation of $PPh_3$ to $OPPh_3$, and (2) the reaction temperature should be held below 160° to prevent by-product formation.

## Experimental Section[20]

**Materials.**—CDT and 1,5-COD were purchased from the Columbian Carbon Co. The CDT was a mixture of the all trans and the trans,trans,cis isomers in a 3:2 ratio. Smaller amounts of compounds believed to be the trans,cis,cis and the all cis isomers were also present. The CDT was routinely filtered through alumina prior to its use, although no noticeable differences in reactivity were observed with untreated samples. The 1,5-COD was used as commercially supplied. Pure *trans*-CDE was obtained by preparative glpc on a tris-1,2,3-(2-cyanoethoxy)propane column from a mixture comprised of 54% *trans*-CDE along with *cis*-CDE and other compounds. Hydrogen, CO, ligands, and solvents were all obtained commercially and were generally used without further purification. For the kinetic studies, benzene and DMF were distilled from $CaH_2$ before use.

$RuCl_3$ was purchased from Englehard as a hydrate containing 39 wt % Ru. The complex $[(CO)_4Ru]_3$ was purchased from Strem Chemical Co. Literature procedures were used in the preparation of $(Ph_3P)_3(CO)RuH_2$,[5] $[(CO)_2RuCl_2]_n$,[6] $(Ph_3P)_3RuCl_2$,[6] $(Ph_3P)_2(CO)_2RuCl_2$,[6] $(Py)_2(CO)_2RuCl_2$,[6] $(Ph_3P)_2(CH_3OH)RuCl_3$,[6] $(Ph_3P)_2(CO)_3Ru$,[7] $(Py)_4RuCl_2$,[21] $(Et_2S)_3RuCl_3$,[22] and $(diphos)_2RuCl_2$.[23] The complex $(MePh_2P)_2(CO)_2RuCl_2$ was prepared in the same manner as $(Ph_3P)_2(CO)_2RuCl_2$. The configuration of $(MePh_2P)_2(CO)_2RuCl_2$, mp 223–228° [lit.[24] mp 220–224°], is assigned **1a** based on infrared absorptions for $\nu_{CO}$ at 2055 and 1989 $cm^{-1}$ ($CH_2Cl_2$) (therefore CO groups) and for $\nu_{RuCl}$ at 308 and 284 $cm^{-1}$ (CsI wafer) (therefore cis Cl groups) along with the appearance of a well-defined apparent 1:2:1 triplet at $\tau$ 7.70 $(J_{PH} + J_{P'H}) = 10.7$ Hz, for the methyl protons in its pmr spectrum ($CDCl_3$) (therefore trans P groups).

Purification of $(Ph_3P)_2(CO)_2RuCl_2$ was achieved by filtering its $CH_2Cl_2$ solution through alumina followed by recrystallization from $CH_2Cl_2$–MeOH mixtures. It melts to a red liquid at 309–312° (lit. mp 233–236,[12] 257,[6] and 310°[10]) and exhibits $\nu_{CO}$ at 2058 and 1993 $cm^{-1}$ ($CH_2Cl_2$) and $\nu_{RuCl}$ at 300 and 275 $cm^{-1}$ (CsI wafer) (lit.[11] $\nu_{RuCl}$ 300 and 275 $cm^{-1}$) in its infrared spectrum.[25] The relative intensity of the phenyl ir absorption at 1570 $cm^{-1}$ is greater than that at 1583 $cm^{-1}$. This relationship appears to be general for platinum(II) complexes bearing *trans*-$PPh_3$ groups while, for cis complexes, the reverse is true.[26] *Anal.* Calcd for $C_{38}H_{30}Cl_2O_2P_2Ru$: C, 60.65; H, 4.02; mol wt, 752. Found: C, 60.34; H, 3.99; mol wt, 720 ± 35.

**Hydrogenations.**—Reactions at pressures below 250 psig were carried out in thick-walled glass vessels fitted with a stainless-steel cap and sealed by a neoprene rubber O-ring. The bottles had a 3-oz capacity and are referred to as aerosol compatibility tubes by the Fisher-Porter Co. The cap was fitted with a pressure gauge, a hydrogen line, and in some cases, a dip tube through which aliquots of the solution could be withdrawn. Reaction temperatures were controlled by immersing most of the tube and a thermometer in an oil bath heated by a stirrer–hot-plate. Stirring was accomplished by a magnetic stirring bar. Reaction mixtures were usually composed of 0.10 g of ruthenium complex, 2.00 g of CDT, 20 ml of solvent, and any additional reagent. After sealing the reaction vessel charged with reagents, hydrogen was pressured into the tube, and the reaction was initiated by increasing the temperature of the oil bath. When hydrogen absorption began, the temperature was increased an additional 10° and then held constant. Hydrogen absorption was detected by a decrease of pressure in the system. Each time the pressure dropped to 150–180 psig, the system was repressured with hydrogen to 210–220 psig. When hydrogen absorption stopped, the mixture was cooled and the reaction solution was analyzed by glpc. In some experiments where the catalysts were not very selective, samples were withdrawn from the dip tube at selected intervals, and the composition of the sample with the highest percentage of CDE is reported. When reactions were conducted in ethanol, colorless crystalline precipitates usually formed when the reaction solutions were cooled. The ir spectra (Nujol) of these precipitates exhibited $\nu_{CO}$ at 1985 and 2058 $cm^{-1}$ [the same $\nu_{CO}$ as in $(Ph_3P)_2(CO)_2RuCl_2$] and occasionally additional absorptions between 1950 and 2058 $cm^{-1}$ which we were unable to assign.

***In Situ* Preparation of Catalyst.**—A 3-oz tube containing 0.10 g (0.38 mg-atom of Ru) of $RuCl_3 \cdot (H_2O)_n$, 0.40 g (1.5 mmol) of $PPh_3$, 2.0 g (12.3 mmol) of CDT, and 20 ml of ethanol was pressured to 4 psig with CO and then to 180 psig with hydrogen. The hydrogenation was conducted as usual at ~140° until the gas absorption ceased. Upon cooling the solution to 25°, white crystals of $(Ph_3P)_2(CO)_2RuCl_2$ (*ca.* 0.30 g, 103%) precipitated and were collected by suction filtration, washing with pentane. Analysis of the mother liquors by glpc revealed the presence of CDA (2.0%), CDE (98.0%), and CDD and CDT (0%).

**Catalyst Recycle.**—A 300-ml Magnedash autoclave was charged with 0.050 g (0.065 mmol) of $(Ph_3P)_2(CO)_2RuCl_2$, 1.00 g (3.82 mmol) of $PPh_3$, 50.3 g (310 mmol) of CDT, and 20 ml of benzene. The autoclave was flushed with nitrogen, pressured to 500 psig with hydrogen, and heated as its contents were rapidly stirred. Hydrogen absorption was noted by the pressure decrease in the system. Each time the pressure dropped to 400–500 psig, the system was repressured to 600 psig with hydrogen. This large-scale reaction was markedly exothermic making the reaction temperature difficult to maintain between 145 and 150°. At times, the temperature approached 165–170°. After completion of the hydrogen absorption, the contents of the autoclave were cooled and transferred to a distillation flask, and the mixture was distilled at 6 mm. The colorless liquid distilling at 56–58° was collected as the product (49.9 g, 96.9%), and it was composed of CDA (5.6%), CDE (91.0%), CDD (3.4%), and CDT (0%). The dark yellow residue in the distillation flask was dissolved in 20 ml of benzene and recycled with another 50 g of CDT, repeating the operations described above. In this manner, the catalyst was recycled six times, with the occasional addition of $PPh_3$ to compensate for its loss by oxidation to $Ph_3PO$. The first hydrogenation lasted 6.3 hr, and the last six required slightly over 1 hr to be completed. A total of 343.3 g of CDT was reduced to CDE in yields of 83–94%, usually 91–93% in each batch.

**Rate Studies.**—Solutions composed of $(Ph_3P)_2(CO)_2RuCl_2$, 40.0 ml of solvent, and $PPh_3$, when desired, were equilibrated in a 140° constant temperature oil bath under 60 psig of hydrogen for 60 min. The bath temperature fluctuated less than ±0.4° during each run. The reaction was initiated by the addition of 1.77 g (10.9 mmol) of CDT and 1.0 ml of benzene from a reservoir in the hydrogen line. The pressure in the system was increased to 200 psig and maintained constant by the regulator on the hydrogen tank. After the addition of CDT, aliquots were withdrawn from the dip tube at selected intervals. A 2-ml forerun was discarded before each aliquot was collected, and the composition of each sample was determined by glpc.

**Product Analysis.**—Samples were routinely analyzed by glpc on a 20 ft × 0.25 in. tris-1,2,3-(2-cyanoethoxy)propane (TCEP)

---

[20] Infrared and nmr spectra were obtained on Perkin-Elmer Model 621 and Varian T-60 instruments, respectively. The ir spectra are accurate to within ±2 $cm^{-1}$. Glpc measurements were made using a Hewlett-Packard Model 5750 chromatograph employing a flame ionization detector. Electrochemical reduction of $(Ph_3P)_2(CO)_2RuCl_2$ was accomplished by controlled-potential electrolysis by Dr. W. B. Hughes.

[21] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

[22] J. E. Fergusson, J. D. Karran, and S. Seevaratnam, *ibid.*, 2627 (1965).

[23] J. Chatt and R. G. Hayter, *ibid.*, 896 (1961).

[24] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. A*, 2645 (1969).

[25] Very weak far-ir absorptions were also noted at 283 and 258 $cm^{-1}$.

[26] W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc. A*, 2062 (1969).

column at 140°. Pure samples of each $C_{12}$ product analyzed were not available thus precluding a determination of their relative response factors. The results reported are based only on the relative peak area. The assignment of glpc peaks is as follows: CDA (10.8 min), *trans*-CDE (12.9 min), *cis*-CDE (14.3 min), CDD (15.1 min), CDD (16.4 min), *trans,trans,trans*-CDT (17.2 min), CDD (18.4 min), CDD (19.7 min), *cis,trans-trans*-CDT (21.2 min), CDD (22.5 min), *cis,cis,trans*-CDT (24.7 min), and *cis,cis,cis*-CDT (26.4 min). As a check on this procedure, samples were occasionally reanalyzed by glpc on a 150-capillary squalane column at 120°. The relative yields obtained with this column were always within 3% of those obtained with the TCEP column. For hydrogenations carried out at temperatures over 160°, by-products were formed which had retention times very close to *cis*- and *trans*-CDE on the TCEP column. This interference did not occur with the capillary column, and the yields were obtained with this procedure.

**Registry No.**—**1a,** 29079-66-1; *all-trans*-CDT, 676-22-2; *trans,trans,cis*-CDT, 706-31-0; *cis*-CDE, 1129-89-1; *trans*-CDE, 1486-75-5.

**Acknowledgments.**—Rewarding discussions with Dr. E. A. Zuech are gratefully acknowledged. Thanks are also extended to Dr. W. B. Hughes for helpful suggestions and to G. R. Birdsong and C. G. Long for experimental assistance.

---

# Silicon Heterocyclic Compounds. Ring Closure by Hydrosilation[1,2]

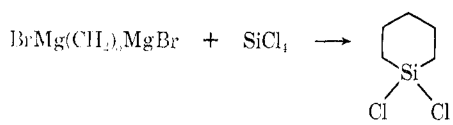
RALPH J. FESSENDEN* AND WILLIAM D. KRAY

*Department of Chemistry, University of Montana, Missoula, Montana 59801*

*Received July 24, 1972*

The hydrosilation reaction has been utilized for the synthesis of silicon heterocyclic compounds. With an appropriately substituted silane, the ring-closure reaction results in a silacyclopentane rather than the expected silacyclohexane. 5-(Dimethylsilyl)-1-hexene, upon treatment with chloroplatinic acid, yields equal amounts of *cis*- and *trans*-1,1,2,5-tetramethylsilacyclopentane.

The principal methods for the preparation of silicon heterocyclic compounds utilize some type of organometallic ring-closure reaction. For example, the standard method for the preparation of silacycloalkanes is the reaction of a di-Grignard reagent with a dichlorosilane.[3] The major disadvantage of this method is the limited number of functional groups that can be introduced into the ring system.



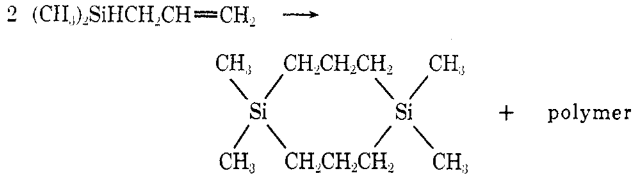
The present study was aimed at the exploration of the use of the hydrosilation reaction for a ring-closure method with particular emphasis on ring systems that contain an $\alpha$-alkyl substituent.

Silicon hydrides add cleanly across terminal double bonds to yield $n$-alkylsilanes in the presence of both free-radical catalysts[4] (dibenzoyl peroxide) and ionic catalysts[5] (chloroplatinic acid). If the olefin contains an internal double bond and with chloroplatinic acid as catalyst, the double bond migrates to a terminal position before the addition occurs. For example, 2-pentene yields only $n$-pentylsilane.[5]

$$Cl_3SiH + CH_2{=}CHCH_2CH_2CH_3 \xrightarrow{H_2PtCl_6} Cl_3SiCH_2CH_2CH_2CH_2CH_3$$

$$Cl_3SiH + CH_3CH{=}CHCH_2CH_3 \xrightarrow{H_2PtCl_6} Cl_3SiCH_2CH_2CH_2CH_2CH_3$$

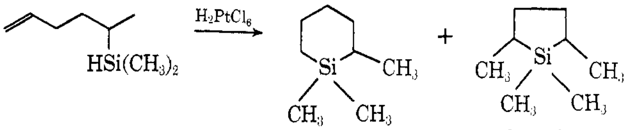
Ring closure reactions involving hydrosilation have been reported.[6]



$$2\ (CH_3)_2SiHCH_2CH{=}CH_2 \longrightarrow$$

## Results and Discussion

Syntheses of the appropriate starting materials are presented in the Experimental Section. Treatment of 5-(dimethylsilyl)-1-hexene with chloroplatinic acid in pentane yields a mixture principally composed of *cis*- and *trans*-1,1,2,5-tetramethylsilacyclopentane (**2**) (73% yield) and only a trace of the expected 1,1,2-trimethylsilacyclohexane (**1**). The five-membered ring was also observed as the major product when 5-(methylchlorosilyl)-1-hexene was used as the starting material.



**1**, trace **2**, major

This unexpected path of ring closure finds probable explanation in the mechanism for hydrosilation as proposed by Chalk and Harrod.[7] In their proposed mechanism, a seven-membered ring would be required as the key intermediate in the formation of **1**, whereas a six-membered ring intermediate would lead to **2**.

Using the hydrosilation ring-closure reaction, 1,1-dimethylsilacyclopentane was obtained in 60% yield from dimethyl(3-butenyl)silane. The hydrosilation

---

[1] This work was supported in part by Grant AM 12794 from the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

[2] Taken in part from the Ph.D. Thesis of William D. Kray, University of Montana.

[3] R. West, *J. Amer. Chem. Soc.*, **76**, 6012 (1954).

[4] C. Eaborn, "Organosilicon Compounds," Academic Press, New York, N. Y., 1960, p 45.

[5] J. L. Speier, J. A. Webster, and G. Barnes, *J. Amer. Chem. Soc.*, **79**, 974 (1957).

[6] J. W. Curry and G. W. Harrison, *J. Org. Chem.*, 1219 (1958).

[7] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, **87**, 16 (1965).