A STUDY OF THE INTERACTION OF ZEISE'S DIMER WITH CYCLOPROANES

by

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1980
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Major Professor
To

My Parents and Annie Cheng
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I would like to thank my parents and wife for their encouragement.
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PUBLICATION


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HISTORICAL

Platinacyclobutanes are one of the most studied group of metalla-cyclobutanes. In 1955, Tipper\textsuperscript{1} prepared the first platinacyclobutane.

\[
\begin{align*}
  c-C_3H_6 + PtCl_4 \cdot 2HCl \cdot 6H_2O & \xrightarrow{Ac_2O} (\triangle -PtCl_2)_n \\
  1 + & \xrightarrow{} PtCl_2(C_3H_6)Py_2
\end{align*}
\]

Originally, it was proposed that compound (1) was a platinum(II)-cyclopropane complex. But later in 1961, Adams\textsuperscript{2,3} deduced that the structure of 1 was a chloride-bridged polymer built from dichloro-(trimethylene)platinum(IV), (2).

\[
\begin{align*}
  & \text{Cl} \quad \text{Pt} \\
  & \text{Cl}
\end{align*}
\]

Adams' formulation was based on the low solubility of 1 suggesting a polymeric platinum(IV) complex, and on IR and NMR studies of 1 and its bis(pyridine) adduct, PtCl₂(C₃H₆)(C₃H₂N)₂ (2). For example, the \(^1\text{H} - ^{195}\text{Pt}\) NMR coupling constant \(J(\text{Pt-CH}_2)\) for 2 was found to be comparable with similar values for methylplatinum compounds and suggested the ring-opened formation.\textsuperscript{3} Numerous X-ray examination of 2 have established the platinacyclobutane as the true structure.\textsuperscript{4-9} Further support came from the mass spectrum of 1 which indicated that it was a tetrameric structure PtCl₂(C₃H₆)₄ analogous to that of \((\text{Me}_3\text{PtI})_4\).

McQuillin and Powell\textsuperscript{10,11} extended Scheme 1 to monosubstituted cyclopropanes. A series of monosubstituted cyclopropanes had been shown to displace ethylene from Zeise's dimer, \([\text{Pt}(C_2H_4)Cl_2]_2\), with
formation of substituted (propane-1,3-diyl)PtCl₂ derivatives. This kind of displacement was impeded or inhibited by electron-withdrawing substituents. From the ¹H-NMR spectra of the bis(pyridine) derivatives, (RC₂H₆₅)PtCl₂(Py)₂, it was postulated that the insertion occurred preferentially into the less-substituted cyclopropane bond when R was n-hexyl, benzyl, nitrophenyl, and phenyl. However, when R was p-tolyl, the principle product arose from insertion into the more-substituted bond of the cyclopropane. The reactivity sequence implied that this insertion reaction depended upon the electron donor capacity of the cyclopropane ring, and that the PtCl₂ residue acted as an electrophile. In 1976, Puddephatt¹² reported that reaction of Zeise's dimer with phenylocyclopropane gave [(PtCl₂(C₂H₅Ph))₄ which with pyridine gave[(PtCl₂(Py)₂(C₂H₅Ph)]. When freshly prepared, the latter complex had structure ⁴ (α-isomer). But readily to give an equilibrium mixture of ⁴ and ⁵ (β-isomer) in relative proportions 1:2.3±0.3. The isomerization was completed in 45 min at 50°C in CDCl₃ solution.

A number of mechanisms have been proposed for the rearrangement of ⁴ to ⁵. A carbene-olefin mechanism (Scheme 1) had been suggested, but was discounted by Puddephatt¹² since styrene was not found among the reaction products. The formation of ⁶ requiring the loss of pyridine, has been demonstrated.¹²-¹⁴
An alternative mechanism proposed by Puddephatt involved a concerted rearrangement (Scheme 2). This mechanism involves an intramolecular rearrangement with concerted cleavage and formation of a set of C-C and Pt-C bonds.
Johnson\textsuperscript{15} considered two possible modes by which phenylcyclopropane might participate in the rearrangement of 4 to 5 (Scheme 3 and 4). He established that neither 4 or 5 could be prepared from

**Scheme 3**

\[
4 \rightleftharpoons \text{Ph} + \text{PtCl}_2(\text{Py})_2 \rightleftharpoons \text{Ph} - \text{PtCl}_2(\text{Py})_2
\]

**Scheme 4**

\[
4 \rightleftharpoons \text{Py} + 6 \rightleftharpoons \text{Ph} \text{PtCl}_2(\text{Py}) \rightleftharpoons \text{Ph} \text{PtCl}_2(\text{Py})
\]

\[
8 \rightleftharpoons \text{PtCl}_2(\text{Py}) \rightleftharpoons \text{Ph} \]

\[
9 \rightleftharpoons \text{Py} \rightarrow \text{Ph} \text{PtCl}_2(\text{Py})_2
\]
cis- or trans-dichlorobis(pyridine)platinum(II) and phenylcyclopropane. Thus, the mechanism given in Scheme 4 was ruled out. He also observed only very modest phenylcyclopropane exchange (3%) by reacting 4 with phenylcyclopropane-d₁ (89% enriched), 1:1, in chloroform under the rearrangement conditions. Clearly, a phenylcyclopropane exchange does occur, but the amount of exchange was too modest to account for the observed amount of rearrangement. Johnson pointed out that the data was consistent with the mechanism in Scheme 2. His results ruled against a mechanism requiring phenylcyclopropane exchange as a step in the rearrangement.

Theoretically, chloride ion could also be dissociating during the rearrangement. To test for possible chloride ion dissociation, a sample of 4 was treated with radioactive ³⁸Cl⁻ under the rearrangement conditions. Recovery and subsequent analysis of the platinumcyclobutane revealed no incorporation of ³⁸Cl⁻. Therefore, Johnson pointed out that under rearrangement conditions, chloride ion does not appear to dissociate.¹⁵

Recent work by Puddephatt indicated that the rearrangement also occurs with other mono- and di-substituted platinitraclobutanes.¹³

It was reported that Zeise's dimer did not react with electron-deficient cyclopropanes.¹¹ But Yarrow and Ibers¹⁶ found that (PPh₃)₄Pt readily reacted with 1,1,2,2-tetracyanocyclopropane to give a platinitraclobutane.

McQuillin and Powell¹¹ pointed out that in terms of the bent-bond model for cyclopropane, insertion of PtCl₂ may be rationalized as a process of rehybridization as the electrons of the C-C bond overlaps with a hybrid vacant orbital of platinum.
Thermal decomposition of dichlorobis(pyridine)(propane-1,3-diyl)-platinum(IV) produced cyclopropane and propene. If the decomposition was carried out in the solid state, the ratio of propene/cyclopropane was greater than 1.\textsuperscript{17} However, the reverse was true in solution.\textsuperscript{18} The photolysis of dichlorobis(pyridine)(propane-1,3-diyl)platinum(IV) at 25°C also gave cyclopropane and propene.\textsuperscript{19,20} Varying the ligands about a platinacyclobutane will vary the proportion of cyclopropane to propene.

Dominelli and Oehlschlager\textsuperscript{21} used compound \textbf{10} and \textbf{11} to investigate the stereochemistry of addition of cyclopropanes to Zeise's dimer. There are three stereochemical courses which could be observed during the addition of Zeise's dimer to the C\textsubscript{2}-C\textsubscript{3} bond of the cyclopropane. These are shown in Scheme 5: (a) retention of configuration \((R,R)\) at both carbon centers \((C_2\) and \(C_3\)), (b) inversion of configuration \((I,I)\) at both carbon centers \((C_2\) and \(C_3\)), and (c) retention of configuration at one carbon center, and inversion at the other center \((R,I)\). It was anticipated that the distinction between these three possibilities would be evident from examination of chemical shifts\textsuperscript{11} and vicinal coupling constants\textsuperscript{22,23} of \(H_2\) and \(H_3\) in \textbf{10} and \textbf{11} and their Pt(II) adducts.

It was shown by NMR analysis of the deuterated cyclopropanes
and the bis(pyridine) derivatives of the adducts that the structures of the adducts from 10 and 11 were 10a and 11a, respectively. It pointed out that the Pt(II)-cyclopropane reaction was stereospecific and involved retention of configuration at both reacting carbons.

Recently, Brown\textsuperscript{24} isolated a platinum-olefin complex from a platinacyclobutane which in turn liberated the free olefin upon
warming. This observation established the intermediacy of a platinacyclobutane in the rearrangement of a cyclopropane to an olefin by platinum. (Scheme 6) Brown suggested that this reaction might involve either a direct 1,2-methyl migration, or a prior rearrangement to an isomeric platinacyclobutane which then isomerized to the olefin via a hydride shift.

\[
\text{Scheme 6}
\]

\[
\begin{align*}
\text{12} & \quad + \quad \left[ \text{Pt(C}_2\text{H}_4\text{)}\text{C}_2\text{H}_6\text{Cl}_2 \right]_2 \\ & \quad \text{Py} \quad \frac{40^\circ \text{C}}{} \\ & \quad \text{Py}_2 \\ \rightarrow & \quad \text{PtCl}_2\text{C}_2\text{H}_6\text{Py}_2
\end{align*}
\]

\[
\begin{align*}
\text{13} & \quad \rightarrow \quad \text{PtCl}_2\text{C}_2\text{H}_6\text{Py}_2 \\ & \quad \text{PtCl}_2\text{C}_2\text{H}_6\text{Py}_2 \\ & \quad \text{PtCl}_2\text{C}_2\text{H}_6\text{Py}_2 \\ & \quad \text{C}_2\text{H}_6\text{Py}_2
\end{align*}
\]

Dichlorobis(tetrahydrofuran)(propane-1,3-diyl)platinum(IV) when allowed to react with arylcyclopropanes \((4-\text{XC}_6\text{H}_4\text{C}_2\text{H}_5, \text{X=Me, OEt, H)}\) gave aryl-substituted platinacyclobutanes.\(^{25}\) The kinetic data showed that these reactions were first order in both arylcyclopropane and platinum complex. The mechanism shown below was suggested to account for these observations. (Scheme 7)

McQuillin\(^{11}\) indicated that the chemistry of platinacyclobutanes formed from alkyl cyclopropanes was dominated by olefin formation. Recently, Johnson\(^{26}\) reported upon the mechanism of olefin formation
was also the dominant pathway in the decomposition of platinacyclo-
pentanes.\textsuperscript{27-29}

Scheme 7

\[
\text{PtCl}_2S_2 + \text{Ar} \text{S} \xrightarrow{-S} \text{Cl} \quad \text{Cl}
\]

\[S = \text{THF}\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]
RESULTS AND DISCUSSION

The chemistry of platinacyclobutanes formed from alkylcyclopropanes is dominated by olefin formation.\textsuperscript{11} This is also the dominant pathway in the decomposition of platinacyclopentanes.\textsuperscript{27-29} Both aryl- and alkyl-substituted platinacyclobutanes will give cyclopropanes upon treatment with phosphines or aqueous KCN\textsuperscript{1,11} and there has been a rearrangement observed for one alkyl-substituted platinacyclobutane.\textsuperscript{24} In this thesis, a study of olefin formation from reactions of Zeise’s dimer with compounds 1,1-Dimethyl-2-methyl-d\textsubscript{3}-cyclopropane-2,3,3-d\textsubscript{3}(17a), 1,1-Dimethyl-d\textsubscript{3}-2-methylcyclopropane(17b), 1,1,2-Trimethylcyclopropane-3,3-d\textsubscript{2}(17c), Bicyclo[4.1.0] heptane(18), 1-Methylbicyclo 4.1.0 heptane(19) and exo,exo-Tetracyclo[3.3.1.0\textsuperscript{2,4}.0\textsuperscript{6,8}]nonane(20).

![Chemical structures](image)

Complex 14 was decomposed in CHCl\textsubscript{3} at 25\textdegree C ± 2\textdegree C to give 2,3-dimethyl-1-butene as the major product. The olefin could arise by three independent routes from the platinacyclobutane shown in Scheme 8.
These three decomposition pathways could be differentiated using specifically labeled cyclopropanes. The three deuterium-labeled compounds used in this study were prepared as shown in Scheme 9.

**Scheme 9**

\[
\begin{align*}
\text{H(a)} & \quad \text{H(a)} \\
\text{CH}_3 & \quad \text{PtCl}_2(\text{Py})_2 \\
\text{H(b)} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{c} & \quad \text{c} \\
\text{14} & \quad \text{21}
\end{align*}
\]

- **1)** α-hydrogen abstraction(a)  
- **2)** reductive elimination

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3(c) \\
(b) & \quad \text{H(a)} \\
& \quad \text{CH}_3(c) \\
& \quad \text{c} \\
\text{21}
\end{align*}
\]

- **1)** β-hydrogen abstraction(b)  
- **2)** reductive elimination

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3(c) \\
(a) & \quad \text{H(b)} \\
& \quad \text{CH}_3(c) \\
& \quad \text{c} \\
\text{21}
\end{align*}
\]

- **1)** β-hydrogen abstraction(c)  
- **2)** reductive elimination

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3(c) \\
(c) & \quad \text{H(c)} \\
& \quad \text{H(c)} \\
& \quad \text{CH}_3 \\
\text{21}
\end{align*}
\]
The three deuterium-labeled cyclopropanes, 17a-c, were individually reacted with Zeise's dimer and with pyridine to give platinum-cyclobutanes 22a-c. Decomposition of these complexes in CHCl₃ at 25°C gave the olefins shown in Scheme 10.
Scheme 10

The ratio of \(23:24\), \(25:26\), and \(27:28\) were 1.1, 0.2, and 2.2, respectively. The ratio analysis and structure determination were determined by \(^1\)H-NMR and \(^{13}\)C-NMR. Table I summarizes the NMR data for 2,3-dimethylbut-1-ene(16).
Table I. Chemical Shifts for Carbons and Protons for 2,3-Dimethylbut-1-ene (16)\(^a\).

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<th>Shift, ppm</th>
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<th>Shift, ppm</th>
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<tr>
<td>a</td>
<td>4.71(^c)</td>
<td>a</td>
<td>151.07</td>
</tr>
<tr>
<td>b</td>
<td>2.35(^d)</td>
<td>β</td>
<td>107.47</td>
</tr>
<tr>
<td>c</td>
<td>1.78(^c)</td>
<td>γ</td>
<td>20.02</td>
</tr>
<tr>
<td>d</td>
<td>1.00(^e)</td>
<td>δ</td>
<td>35.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ε</td>
<td>21.35</td>
</tr>
</tbody>
</table>

\(^{a}\) Downfield from Me\(_4\)Si in CDCl\(_3\). \(^{b}\) The proton and carbon designation shown in Figure 1. \(^{c}\) Singlet. \(^{d}\) Septuplet. \(^{e}\) Doublet. \(J = 6.5\) Hz.

![Figure 1](image_url)

Figure 1. Designation of protons (Roman) and carbons (Greek) for 2,3-dimethylbut-1-ene (16).

In the pair of olefins 23 and 24, the \(^{13}\)C-NMR showed a triplet centered at 34.41 ppm in place of the peak at 35.13 ppm consistent with complete deuterium substitution at C\(_8\). (see Figure 1) The C\(_\alpha\) was now represented by a singlet at 107.5 ppm and a septuplet centered at 106.94 ppm consistent with a mixture of 23 and 24. Both of the peaks at 21.35 and 20.02 ppm have clusters of smaller peaks at their base line which overlap with one another and make the exact assignment of multiplicity difficult. One would expect two different septuplets and one pentuplet in addition to the two singlets.
for 23 and 24.

The $^1$H-NMR of this mixture (23 and 24) confirms the complete deuteriation at carbon δ as the signal at 1.78 ppm was no longer present. The height of the integrated area for the vinylic proton (H_a) was 28 mm$^2$ while the height of the integrated area for the methyl protons (H_d) was 110 mm. In this particular pair of olefins, there is no common proton to both 23 and 24 as is the case for the olefin pairs 25 and 26 and 27 and 28. Therefore, this ratio determined for 23 and 24 will have a larger error than the ones determined for the other two sets of olefins. The ratio of 23 to 24 can be determined from the above integrals by the following procedure. The vinyl protons (H_a) are due only to 24 and correspond to 14 mm per proton. The methyl protons (H_d) are due to both 23 and 24. The olefin 24, however, has one proton and five deuteriums substituted on the C_δ. Therefore, 14 mm (the value for one proton—see above) was subtracted from 110 mm to give a value of 96 mm for the protons due to 23. Compound 23 has six H_d protons and this corresponds to a height for the integrated area of 16 mm per proton. Taking these values per proton we arrived at the ratio of 23;24 as 1.1.

In the olefin pair 25 and 26, the $^{13}$C-NMR gave a single peak at 35.10 ppm indicating the substitution of a proton at C_δ of each isomer. The $^1$H-NMR showed a peak centered at 2.35 ppm in agreement with the $^{13}$C-NMR results. The methyl peaks were as complex as described for 23 and 24 above. The C_δ was also as described for 23 and 24. In 25 and 26 the allylic proton (H_c) is common to both 25 and 26 (i.e. both 25 and 26 have a proton only substituted at C_δ). The height of the integrated areas for H_a, H_b, H_c, and H_d were 58, 89, 35, and 30 mm, respectively. Using the height of
the integrated area for \( H_c \) as representing 100%, we found that \( H_a \) and \( H_b \) were 83-84% of the theoretical area if only \( 26 \) was present, and \( H_d \) was only 17% of the theoretical area. This corresponds to the ratio of \( 26 : 26 \) as 0.2.

The \( ^1\text{H}-\text{NMR} \) of the olefin pair \( 27 \) and \( 28 \) looks similar to the other two pairs for the vinylic \( C_\alpha \). However, clean singlets for \( C_\gamma \) and \( C_\delta \) and a singlet and a pentuplet for \( C_\epsilon \) were observed consistent with the structural assignments of \( 27 \) and \( 28 \). The \( ^1\text{H}-\text{NMR} \) exhibited peaks for all of the protons \( H_a - H_d \). Protons \( H_c \) was again common to both \( 27 \) and \( 28 \) (as was \( H_d \)) and its integrated area is taken as 100%. The heights of the integrated areas for \( H_a \), \( H_b \), \( H_c \), and \( H_d \) were 10.5, 52.17, and 92 mm, respectively. Using \( H_c \) as the standard, we found that \( H_a \) was 31% of the theoretical area. The height of the integrated area per proton for \( 28 \) is ca. 5.3 mm. This value multiplied by four (for the four \( H_d \) protons in \( 28 \)) was then subtracted from the integrated area of 92 mm for the total \( H_d \) protons gave a value of 71 mm for the six \( H_d \) protons due to \( 27 \). This value was 69% of the theoretical area. These analyses are consistent with ratio of \( 27 : 28 \) being 2.2.

Olefins \( 23, 26 \), and \( 27 \) are the major olefins in each set and can be formally derived from process (b) in Scheme 9. The minor olefins \( 24, 25 \), and \( 28 \) can be formally derived from process (c) in Scheme 9. The olefins formed from \( 22a \) and \( 22b \) would not distinguish between an \( \alpha \)-hydrogen abstraction and a \( \beta \)-hydrogen abstraction process. However, platinacycle \( 22c \) does distinguish between these two possibilities. An olefin formed via an \( \alpha \)-hydrogen abstraction route from \( 22c \) would have the structure \( 29 \). The olefin
29 is distinguishable from 27 and 28 in the following ways. First, 29 would give a triplet for the Cα and Cδ in the 13C-NMR whereas Cα was observed as a singlet and pentuplet and Cδ was observed as a singlet. Second, the methyl Cα-H's should appear as a broad singlet in the 1H-NMR spectrum whereas a doublet was observed indicating the presence of a proton instead of a deuterium at Cδ. It is apparent that a mixture of 27-29 would be observable from both the 1H-NMR and 13C-NMR spectra.

Furthermore, the olefins obtained from 22b clearly indicate that the rearrangement of 13 to 14 does not occur by a 1,2-methyl migration. Had such a migration occurred, the product olefins would have been 31 and 32 instead of the observed olefins 25 and 26 (see Scheme 11).

Scheme 11

![Diagram showing chemical structures and reactions](attachment:image.png)
The olefins 25 and 26 could be distinguished from the olefins 31 and 32 in the following manner. The $^{13}$C-NMR, as previously described, confirmed the presence of a mixture of olefins. However, we would not be able to distinguish between a mixture of 25 and 26 vs. one containing 31 and 32 by the $^{13}$C-NMR. The key difference between the two pairs of olefins rests upon the observation that in the olefin pair 25 and 26 the $C_a$ and $C_y$ always contain the same type of hydrogen isotope, i.e. both positions are substituted with deuteriums or both are substituted with protons. In the olefins pair 31 and 32 the opposite case exists, i.e. one of the carbons is substituted with protons while the other is substituted with deuteriums. Thus, if the olefins obtained were 25 and 26, then the integrated area for $H_a$ to $H_b$ must be 2:3. However, if the olefins obtained were 31 and 32, the height of the integrated area for $H_a$ to $H_b$ would be the same as the ratio of 31 to 32. The heights of the integrated areas of $H_a$ and $H_b$ were 58 and 89 mm, respectively. This corresponds to a 2:3 ratio in agreement with the structural assignment of 25 and 26 instead of 31 and 32. In the case where the ratio of 31 to 32 happened to be 2:3 and, therefore, would give a correct integration for $H_a$ vs. $H_b$, we can calculate that the height of the integrated area for $H_d$ must then be 174 mm. In fact, the value is only 30 mm, which is, again, consistent with the structural assignment of 25 and 26 and not with 31 and 32.

McQuillin and Powell\textsuperscript{11} reported that bicyclo[4.1.0]heptane reacted with Zeise's dimer to give an orange complex which then was decomposed by aqueous potassium cyanide to yield methylene-
cyclohexane (33), 1-methylcyclohexene (34), and cycloheptene (35). They proposed a π-allyl mechanism (Scheme 12).

We reexamined this reaction and obtained the same three products reported by McQuillin and Powell. However, we obtained a 33:34:35 ratio of 6.4:1.4:1, respectively, compared to the reported values of 2:2:1.11 All three olefins can be derived from β-hydrogen abstraction followed by reductive elimination.
In order to obtain a deeper insight into the bicyclo[4.1.0]heptane system, we synthesized 1-methylbicyclo[4.1.0]heptane and ran the same experiment. If 1-methylbicyclo[4.1.0]heptane underwent the $\beta$-hydrogen abstraction-reductive elimination process, seven possible compounds could be produced (Scheme 13). However, due to steric constraints during the hydride abstraction process, 37 would be greatly favored over 38. Also, 40-42 would be favored over 39 for the same reason. The insertion product from which 36 is derived is itself highly disfavored and, therefore, 36 was not expected to be a significant product.

Scheme 13

\[
\begin{align*}
\text{Scheme 13} & \\
\text{1-methylbicyclo[4.1.0]heptane} & \rightarrow \text{PtCl}_{2}(\text{Py})_{2} \rightarrow \text{36} \\
\text{1-methylbicyclo[4.1.0]heptane} & \rightarrow \text{PtCl}_{2}(\text{Py})_{2} \rightarrow \text{37} + \text{38} \\
\text{1-methylbicyclo[4.1.0]heptane} & \rightarrow \text{PtCl}_{2}(\text{Py})_{2} \rightarrow \text{39} + \text{40} \\
& \quad \quad + \text{41} + \text{42}
\end{align*}
\]
Analysis of the reaction products by g.l.c., showed that \( 38 \) and \( 39 \) were the major products and \( 37 \) was a minor product. Compounds \( 40-42 \) were shown to undergo rearrangement under the reaction and/or analysis conditions to give compound \( 39 \). At this stage, it appeared that the \( \beta \)-hydrogen abstraction-reductive elimination mechanism was not a good explanation for the bicyclo[4.1.0]heptane system.

On the other hand, a \( \pi \)-allyl mechanism would be expected to favor \( 38 \) over \( 37 \) and \( 39 \) over \( 40 \) (Scheme 14). From the data we obtained, it appeared that the \( \pi \)-allyl mechanism of McQuillen and Powell was a more viable mechanism than the \( \beta \)-hydrogen abstraction-reductive elimination process. Accordingly, the reaction was not investigated further.

**Scheme 14**

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\text{ex}_{o}, \text{ex}_{o}-\text{Tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane (20) was reported to react with Zeise's dimer to give the PtCl}_{2} \text{ derivative (43).}^{11} \text{ The structure of (43) was assigned by analogy and elemental analysis. In}
\]
order to obtain spectral confirmation of this structure, the yellow solid reaction product was dissolved in DMSO-46 which was the only solvent it was soluble in. However, the 13C-NMR spectrum of this solution revealed that "platinum" had reacted with exo,exo-tetra-cyclo[3.3.1.02,4.06,8]nonane to give 44. The structure of 44 was assigned by comparison to the 13C-NMR spectrum of an authentic sample.34,35

This analysis does not mean that the yellow sample reported by the original workers, and that obtained in the present work was 43.36 If the structure is 43, then it is very labile in DMSO and undergoes an olefin-forming reaction similar to the other cyclopropanes reported in this study. Interestingly, only one of the two cyclopropanes undergoes rearrangement to the olefin. This suggests that the platinum may only interact with one of the cyclopropanes.

In summary, formation of 2,3-dimethylbut-1-ene from 14 occurs by what is formally a β-hydrogen abstraction process followed by a reductive elimination reaction. Protons may be abstracted either from the ring or from substituents of the metallacycle as long as they are attached to carbons which are β to the platinum. There is a preference to abstract a hydrogen from the ring over that of a methyl substituent in 14.37 The rearrangement of 13 to 14 does
not occur via a 1,2-methyl migration. However, Zeise's dimer a-
parently can also react with cyclopropanes by standard \( \pi \)-allyl
platinum reactions as well. In some instances, e.g. with bicyclo-
\([4.1.0]\) heptane, it appears that the \( \pi \)-allyl mechanism is favored
over the \( \beta \)-hydrogen abstraction-reductive elimination process. The
features of a cyclopropane which may favor one mode of reaction
over the other are unknown at this time. It is significant, however,
that cyclopropanes which undergo formation of platinacyclobutanes
produce olefins by one mode, whereas cyclopropanes which do not
form platinacyclobutanes favor the \( \pi \)-allyl platinum mode of olefin
formation.
EXPERIMENTAL SECTION

The $^{13}$C-NMR spectra were recorded on a Varian XL-100 spectrometer and the $^1$H-NMR spectra were recorded on either a Varian T-60 or Varian XL-100 spectrometer. All of the NMR spectra are reported relative to Me$_4$Si using CDCl$_3$ as a solvent. Melting points and boiling points are uncorrected. All of the compounds synthesized in this study are known in their unlabeled form. The preparation of all labeled compounds was first performed on non-labeled materials and identified by spectroscopic comparison to authentic samples. The position of the deuteriums was determined by comparison with the unlabeled compound.

Methyl 2,2-Dimethyl-3-oxobutanoate-$4,4,4$-$d_3$. To 1000-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and addition funnel were added 500 mL of anhydrous THF and 50.5 g (0.5 mol) of diisopropylamine. The flask was cooled to $-78^\circ$C and 210 mL (0.5 mol) of 2.4 M n-butyllithium was added. After the mixture was stirred at $-78^\circ$C for 2 h, 51 g (0.5 mol) of methyl isobutyrate was added over a period of 2 h. After the addition was completed, the reaction mixture was stirred for 0.5 h and then 36 mL (0.5 mol) of acetyl-$d_3$ chloride (Aldrich) was added over a period of 1.5 h. Then the mixture was allowed to warm to room temperature and was stirred for 3 h, after which time 125 mL of 6N HCl and 200 mL of H$_2$O were added to the reaction mixture. The organic layer was separated, washed four times with 100-mL portions of saturated sodium bicarbonate, dried over an-
hydrous sodium sulfate, filtered, and evaporated in vacuo. The residue was distilled, giving 29.2 g (41%) of the title compound: bp 90-93°C (30 mmHg), $^1$H-NMR (CDCl$_3$) $\delta$ 3.6 (s, 3H) and 1.3 (s, 6H).

2,2-Dimethyl-1,3-butanediol-1,1,3,4,4,4-d$_6$. To a 1000-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and addition funnel were added 500 mL of anhydrous ether and 9.0 g (0.2 mol) of lithium aluminum deuteride (Stohler Isotopes). To this stirred mixture was added a solution of 33.5 g (0.23 mol) of methyl 2,2-dimethyl-3-oxobutanoate-$^{4,4,4}$-d$_3$ in 250 mL of anhydrous ether. The solution was added at a rate which maintained reflux. After the addition was completed, the reaction mixture was refluxed for 3 h. The reaction mixture was then cooled and worked up by adding dropwise amounts of the following reagents: 9 mL of H$_2$O, then 9 mL of 1% aqueous NaOH, and then 12 mL of H$_2$O. This gave a precipitate which was removed by filtration. The filtrate was washed once with 200 mL of H$_2$O, the layers were separated, and the organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The residue was distilled, giving 17.9 g (62%) of the product: bp 78-79°C (0.3 mmHg); $^1$H-NMR (CDCl$_3$) $\delta$ 4.11 (br, 2H), and 0.82 (s, 6H).

2,2-Dimethyl-1,3-butanediol-1,1,3,4,4,4-d$_6$ Dimesylate. To a 1000-mL Erlenmeyer flask, cooled to 0°C, were added 300 mL of dry pyridine, 32.7 g (0.28 mol) of methanesulfonyl chloride, and 16.8 g (0.14 mol) of the above diol. The Erlenmeyer flask was stoppered and refrigerated for 3 days. The resultant solid was removed by filtration
and the filtrate was poured into 1500 mL of ice water. The aqueous solution was extracted with two 450-mL portions of chloroform. The chloroform extract was then washed with eight 150-mL portions of 5% aqueous potassium bisulfate and once with 150 mL of water. The chloroform solution was dried over anhydrous sodium sulfate and then concentrated in vacuo. The resultant oil was taken up in 12 mL of warm methanol and then cooled, whereupon crystallization took place. Filtration of crystals gave 36.1 g (95%) of the product which was used without further purification: mp 68-69°C.

1,1-Dimethyl-2-methyl-d_2-cyclopropane-2,3,3,-d_3 (17a). To a mechanically stirred suspension of 111 g of zinc dust, 21 g of sodium carbonate, 1nd 277 g of acetamide in a 500-mL, three-necked, round-bottomed flask maintained at 170-175°C was added, portionwise, 32.1 g (0.12 mol) of the above dimesylate from a 100-mL Erlenmeyer which was connected by means of Gooch tubing to the round-bottomed flask. The product was allowed to distill out of the reaction into a trap which had been precooled to -78°C. After addition of the dimesylate was completed, the suspension in the flask was thoroughly purged with nitrogen for 15 min to expel any residual amounts of the product. The material in the trap was then microdistilled, giving 1.6 g (16%) of 17a: bp 55-57°C; \textsuperscript{1}H-NMR (CDCl\textsubscript{3}) 81.00 (s, 6H).

Ethyl 2,2-Dimethyl-d_2-3-oxobutanoate. This compound was prepared in 49% yield by the method of Marshall and Cannon\textsuperscript{38} from ethyl acetoacetate and methyl-d_2 iodide (Aldrich).
2,2-Dimethyl-d₃-1,3-butanediol. This compound was prepared in 85% yield from ethyl 2,2-dimethyl-d₃-3-oxobutanoate and LiAlH₄ in the same manner as described for the reaction of methyl 2,2-dimethyl-3-oxobutanoate-4,4,4-d₃ with LiAlD₄ except that a 100% excess (0.4 mol) of LiAlH₄ was employed.

2,2-Dimethyl-d₃-1,3-butanediol Dimesylate. This compound was prepared in 94% yield from the above diol and methanesulfonyl chloride in the same manner as described for the previous dimesylate.

1,1-Dimethyl-d₃-2-methylcyclopropane (17b). This compound was prepared in 21% yield from the above dimesylate by the same procedure used to prepare 17a: ¹H-NMR (CDCl₃) δ 1.10 (s, 3H), 0.30-1.00 (br, 2H), and -0.05 (br, 1H).

1,1-Dichloro-2,2,3-trimethylcyclopropane. To a solution containing 21.2 g (0.3 mol) of 2-methyl-2-butenes, 0.6 g of benzyltriethylammonium bromide, and 60 mL of chloroform was added, under N₂, 120 mL of 50% aqueous NaOH over a period of 4 h. After the addition was completed, the reaction mixture was stirred at 50°C for 1 h. The reaction mixture was then cooled, diluted with 150 mL of H₂O, acidified with 3N HCl, and extracted with three 150-mL portions of ether. The ethereal solution was dried over anhydrous magnesium sulfate, filtered, and then concentrated in vacuo. The residue was distilled, giving 31.4 g (68%) of the product: bp 45-46°C (30 mmHg); nD²⁴ 1.4557 (lit. 39 64.3-64.7°C (47 mmHg); nD²⁰ 1.4577); ¹H-NMR δ 1.20 (s, 3H) and 1.08 (s, 7H).
1,1,2-Trimethylcyclopropane-3,3-d$_2$ (17c). To a mechanically stirred suspension of 80 mL of anhydrous diglyme and 17.2 g of finely divided sodium metal was added, dropwise, a solution composed of 28.5 g (0.18 mol) of 1,1-dichloro-2,2,3-trimethylcyclopropane, 37.6 g (0.37 mol) of cyclohexanol-0-d, and 3 mL of D$_2$O. The reaction was exothermic and the mixture needed to be cooled intermittently in order to maintain a reaction temperature below 120°C. Under these conditions, the product distilled out of the reaction into a trap which had been pre-cooled to -78°C. After the addition had been completed, the reaction mixture was thoroughly purged with N$_2$. The material in the trap was distilled, giving 3.6 g (22%) of 17c: bp 55-57°C; $^1$H-NMR (CDCl$_3$) δ 1.02 (s, 9H) and 0.32-0.70 (br, 1H).

**Dichlorobis(pyridine)(1,1-dimethyl-2-methyl-1,3-d$_3$-propane-2,3,3-d$_3$-1,3-diyl)platinum(IV) (22a).** This compound was prepared from 17a, Zeise's dimer and pyridine according to the procedure of Cushman and Brown.

**Dichlorobis(pyridine)(1,1-dimethyl-d$_3$-2-methylpropane-1,3-diyl)platinum(IV) (22b).** This compound was prepared from 17b, Ziesi's dimer and pyridine according to the procedure of Cushman and Brown.

**Dichlorobis(pyridine)(1,1,2-trimethylpropane-3,3-d$_2$-1,3-diyl)platinum(IV) (22c).** This compound was prepared from 17c, Zeise's dimer and pyridine according to the procedure of Cushman and Brown.

Deomposition of Platinacycles (22a-c). These compounds were de-
composed in CDCl$_3$ at 25±2°C according to the procedure of Cushman and Brown.$^{24}$

Bicyclo[4.1.0]heptane (18). This compound was prepared in 22% yield by the method of R. S. Monson$^{40}$ from cyclohexene, zinc-copper couple and methylene iodide. This compound was purified by use of 10' x 1/4", 10% DC 550 silicone column at 120°C. Carrier gas was helium.

1-Methylbicyclo[4.1.0]heptane (19). This compound was prepared in 8% yield by the method of N. Dominelli and A. C. Oehlschlager$^{21}$ from 1-methylcyclohexene. This compound was purified by use of a 10' x 1/4", 10% DC 550 silicone column at 120°C. Carrier gas was helium.

exo,exo-Tetracyclo[3.3.1.0$^2$,4.0$^6$,8]nonane (20). This compound was prepared in 60% yield by the method of J. Kottwitz and H. Vorbruggen$^{41}$ from norboradiene, diazomethane and palladium acetate.

Reaction of bicyclo[4.1.0]heptane with Zeise's dimer. This reaction was run according to the procedure of McQuillin and Powell.$^{11}$

Reaction of 1-methylbicyclo[4.1.0]heptane with Zeise's dimer. This reaction was run according to the procedure of McQuillin and Powell.$^{11}$

Reaction of exo,exo-tetracyclo[3.3.1.0$^2$,4.0$^6$,8]nonane with Zeise's dimer. This reaction was run according to the procedure of McQuillin and Powell.$^{11}$
REFERENCES AND NOTES


30. By $^1$H-NMR, the deuterium incorporation was in excess of 95% and is sufficient for the studies reported here.

31. The reported integrals are the average of seven separate integrations.

32. The potential error is within the range 5% to 10%.

33. For example, the area of $H$ in 26 is due to two protons, so one has 58 divided by 2 and obtains 29 mm per proton. However, the theoretical amount is 35 mm and 29 mm is ca. 83% of this value. Similar calculations were done for the other protons.


36. Structure was based on the elementary analysis by the original worker. The dec. point of compound 43 was 142°C.

37. The numerical value of this preference is approximately 12:1.


A STUDY OF THE INTERACTION OF AEISE'S
DIMER WITH CYCLOPROANES

by

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AN ABSTRACT OF A MASTER'S THESIS

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Abstract: Three deuterium-labeled cyclopropanes were synthesized and reacted with Zeise's dimer to give three different platinacyclobutanes. Decomposition of these platinacyclobutanes gave deuterium-labeled 2,3-dimethylbut-1-enes. The results indicated that the formation of olefins occurs by what is formally a β-hydrogen abstraction process followed by a reductive elimination. Two types of β-hydrogen abstraction process were possible and both occurred, although β-hydrogen abstraction from the ring of the platinacyclobutane was favored over β-hydrogen abstraction from a methyl substituent. The results also indicated that an α-hydrogen abstraction process was not operative and the rearrangement of dichlorobis(pyridine)(1,2,2-trimethylpropane-1,3-diyl)platinum(IV) to dichlorobis(pyridine)(1,1,2-trimethylpropane-1,3-diyl)platinum(IV) did not occur via a 1,2-methyl migration, which had been previously suggested as a possible rearrangement route.

However, Zeise's dimer can also react with cyclopropanes by standard π-allyl platinum reactions as well. It is significant that cyclopropanes which undergo formation of platinacyclobutanes produce olefins by one mode, whereas cyclopropanes which do not form platinacyclobutanes favor the π-allyl platinum mode of olefin formation.