# Ring Expansion of Platinacyclobutanes: The Scope and Mechanism of the Reaction

J. Thomas Burton and Richard J. Puddephatt*

*Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7*

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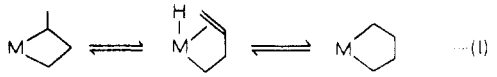
New platinacyclobutylcarbinyl esters of formula $Cl_2L_2\overline{PtCH_2CR^1(CHR^2OR^3)CH_2}$] ($R^1$ = H, Me, or Ph; $R^2$ = H or Me; $R^3$ = methanesulfonyl or 4-nitrobenzoyl; L = pyridine or $L_2$ = 2,2′-bipyridine) have been prepared and characterized. On solvolysis in aqueous acetone these complexes give the ring-expanded platinacyclopentanol products [$Cl_2L_2\overline{PtCHR^2CR^1(OH)CH_2CH_2}$], which have been isolated and characterized. The ring expansions occur with greater selectivity than in the corresponding solvolyses of cyclobutylcarbinyl esters, but the scope of the reactions is limited by the low thermal stability of the platinacyclobutane precursors. It was not possible to catalyze the ring expansion of platinacyclobutylcarbinols to the corresponding platinacyclopentanols. The solvolyses of [$Cl_2py_2\overline{PtCH_2CH(CH_2OMs)CH_2}$] (**3a**, OMs = mesylate), [$Cl_2(bpy)\overline{PtCH_2CH(CH_2OMs)CH_2}$] (**3b**), and [$Cl_2py_2\overline{PtCH_2CMe(CH_2OMs)CH_2}$] (**3c**) in acetone–water (60% v/v) at 36 °C follow good first-order kinetics and give the products [$Cl_2L_2\overline{PtC^1H_2C^2R(OH)C^3H_2C^4H_2}$]. The solvolysis of **3a** is retarded by the presence of free pyridine, and the limiting rate in the presence of excess pyridine is almost the same as for **3b**. The solvolysis of **3c** is affected only slightly by the presence of free pyridine. Solvolysis of analogous complexes labeled at the $CH_2O$ center with $^{13}C$ (**3a***** and **3b***) or $^2H$ (**3a****, **3b****, **3c****) gave the products with the label at $C^1$ or $C^3$. In the absence of pyridine, **3a**** and **3c**** gave the corresponding products labeled at $C^1$, 86% and 10%, respectively, and at $C^3$, 14% and 90%, respectively, while in the presence of pyridine they gave the label at $C^1$, 32% and 0%, and at $C^3$, 68% and 100%, respectively. Complex **3b**** gave the label at $C^1$, 27%, and $C^3$, 73%, as determined by integration of $^2H\{^1H\}$ NMR spectra. The data are rationalized in terms of a mechanism in which skeletal isomerization of the fragment $\overline{PtCH_2CR(CD_2OMs)CH_2}$ (**6**), to give [$\overline{PtCH_2CH_2CR(CD_2OMs)}$] (**7**), may occur in the absence of free pyridine for **3a**** and **3c**** but not in its presence and cannot occur for **3b****. Solvolysis of **6** gives exclusively (**3c****) or largely (**3a****, **3b****) the product labeled at $C^3$ whereas solvolysis of **7** gives exclusively the product labeled at $C^1$. Similarities with and differences between these reactions and the analogous organic ring expansions are discussed.

## Introduction

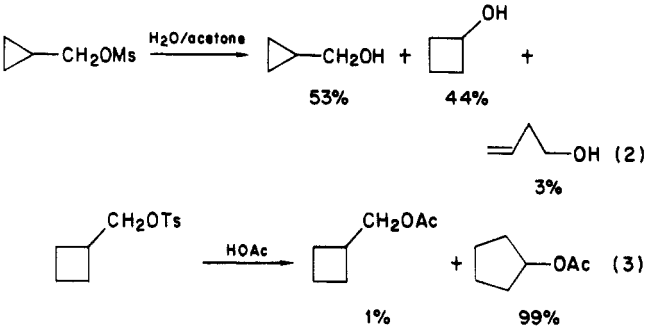
Rearrangements involving metallocycloalkanes continue to attract attention, because they can serve as models for catalytic reactions. However, ring expansion reactions, such as shown in eq 1, have proved to be elusive.



(1)

For example, 2-methyl-1-platinacyclobutanes do not rearrange to platinacyclopentanes,[1] though there is evidence for the reverse reaction during thermolysis of tantalacyclopentanes and rhenacyclopentanes.[2,3] Other approaches to ring expansion, such as insertion of a $CH_2$ unit from diazomethane into a platinacyclobutane to give a platinacyclopentane, have also met with limited success though useful organic products were obtained.[4] It has been possible to synthesize a platinacyclopentanone by insertion of CO into a platinacyclobutane.[5]

For development of further routes to ring expansion of platinacyclobutanes, the solvolysis of platinacyclobutanecarbinol derivatives was investigated. The approach was based on the known ring expansions which occur on solvolysis of strained cycloalkylcarbinol derivatives. For example, hydrolysis of cyclopropylcarbinyl mesylate (Ms = mesylate) or cyclopropylcarbinyl tosylate (Ts = tosylate) gave the products of eq 2 and 3.[6,7]




There has been great controversy about the mechanisms of these reactions, particularly with respect to the possible intermediacy of nonclassical carbonium ions.[6-10] The rates and product ratios depend on the solvent, the leaving

(1) Al-Essa, R. J.; Puddephatt, R. J.; Perkins, D. C. L.; Rendle, M. C.; Tipper, C. F. H. *J. Chem. Soc., Dalton Trans* **1981**, 1738.
(2) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451.
(3) Yang, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129.
(4) Jennings, P. W.; Ekeland, R. E.; Waddington, M. D.; Hanks, T. W. *J. Organomet. Chem.* **1985**, *285*, 429.
(5) Klinger, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2147.
(6) This topic has been reviewed. Richey, H. G., Jr.; Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J., III In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. 3, pp 1201, 1295.
(7) Wiberg, K. B.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 4433. Gajewski, J. J.; Lyle, R. L.; Gajewski, R. P. *Tetrahedron Lett.* **1970**, *14*, 1189.
(8) Majerski, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 665.
(9) Majerski, Z.; Borčič, S.; Sunko, D. E. *Tetrahedron* **1969**, *25*, 301.
(10) Brown, H. C. *The Non-classical Ion Problem*; Plenum: New York, 1977. Interpretation of this observation is not straightforward, since the minor amounts of unrearranged product in the cyclobutylmethyl solvolyses probably arise from $S_N2$-like displacement, whereas unrearranged product from cyclopropylmethyl solvolyses probably occur by the $S_N1$ mechanism followed by solvent attack on the much more stable cyclopropylcarbinyl cation. We thank a reviewer for this information.

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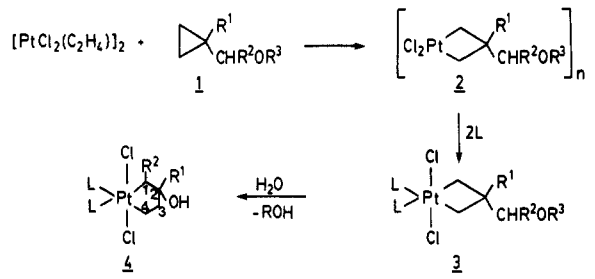
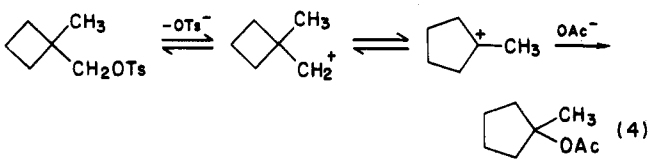
**Scheme I**

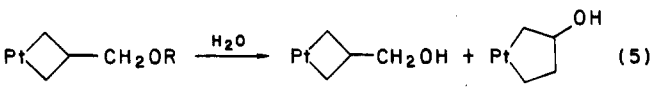


group, the temperature, and other experimental variables. However, other factors being equal, it is generally accepted that the rate of solvolysis is greater when there is greater strain in adjacent CC bonds of the reactant while the extent of ring expansion is greater when overall ring strain is reduced to the greatest extent as a result of the ring expansion.[10] Total strain energies for cyclopropane, cyclobutane, and cyclopentane are 27.6, 26.4, and 6.5 kcal $mol^{-1}$, respectively. It is expected and found that the rate of solvolysis is greater for cyclopropylmethyl than for cyclobutylmethyl derivatives but that the extent of ring expansion is greater for cyclobutylmethyl (eq 3) than for cyclopropylmethyl derivatives (eq 2). The relative stabilities of carbonium ions in the order 3° > 2° > 1° is also an important factor,[6-12] and ring expansion is therefore particularly favored for (1-methylcyclobutyl)methyl derivatives, which give a tertiary carbonium ion on ring expansion (eq 4).[13]



(4)

It was of interest to determine how the solvolysis of the platinacyclobutane derivatives would fit into this pattern, and the partial reactions expected are shown in eq 5, where OR is a leaving group such as mesylate.



(5)

The ring strain in platina(IV)cyclobutanes has been estimated[14] to be 9–13 kcal $mol^{-1}$; a similar value of 15 kcal $mol^{-1}$ has been estimated in thoracyclobutanes,[15] but the ring strain in platina(II)cyclobutanes[16] is thought to be much lower. There is probably negligible ring strain in the platinacyclopentane products.[14,16] The energy gain on ring expansion should therefore be ~10 kcal $mol^{-1}$ which is midway between the values for ring expansion of the cyclopropylmethyl (1.3 kcal $mol^{-1}$) and cyclobutylmethyl (19.9 kcal $mol^{-1}$) derivatives. Since the ring strain is lower in platinacyclobutanes than in cyclobutanes, a lower rate of solvolysis of the platinacyclobutanes might be expected.

This paper reports the synthesis and characterization of precursor platinacyclobutanes and a study of the solvolysis reactions. The characterization of new platinacyclopentanol derivatives is given, and the scope and limitations of the ring expansion are discussed. A detailed study of the mechanism of the solvolysis is then described. Preliminary accounts of parts of this work have been published.[17,18]

## Results and Discussion

The synthetic work is summarized in Scheme I and is discussed below.

**Synthesis and Characterization of Platinacyclobutanes** Platinacyclobutanes were prepared by reaction of the required cyclopropane with Zeise's dimer (Scheme I).[14,19] In this way, new derivatives with the good leaving groups mesylate (OMs) or 4-nitrobenzoate (OPNB) could be prepared, as well as the parent platinacyclobutylcarbinols which have been described previously.[20] The primary cyclopropylcarbinyl mesylates **1a–c** were prepared without difficulty, but mesylates of secondary or tertiary alcohols could not be prepared in pure form and this problem limited the range of platinum derivatives which could be prepared. For this reason, 4-nitrobenzoate derivatives **1d** and $CH_2CH_2CHCMe_2OPNB$ (**1e**) of these alcohols were prepared. In all cases, the cyclopropyl derivatives reacted with Zeise's dimer to give the oligomeric platinacyclobutanes **2**,[21] and then reaction with either pyridine or 2,2′-bipyridine gave the soluble, monomeric derivatives **3** (py = pyridine, bpy = 2,2′-bipyridine). As well as the compounds **3a–f** shown, the complex tertiary ester $[Cl_2py_2PtCH_2CH(CMe_2OPNB)CH_2]$ was prepared in this way.

The new platinacyclobutanes were characterized by their $^1H$ and $^{13}C$ NMR spectra. Only the isomers **3** with the substituents on the β-carbon of the platinacyclobutane ring could be detected. As observed for many related platinacyclobutanes,[14,22] the coupling constants $^1J(PtC)$ and $^2J(PtC)$ for the ring carbons of **3** were in the ranges 356–368 and 90–104 Hz, respectively. Details are given in the Experimental Section. The values of $^1J(PtC)$ are much lower than for other alkylplatinum(IV) complexes, almost certainly due to the low CPtC bond angles of 70–75° in the ring, while the $^2J(PtC)$ values are high due to "through-space" coupling.[14]

**Solvolysis of the Platinacyclobutanes.** The most successful reactions involved solvolysis of the mesylate derivatives **3a–c** in aqueous acetone at 36 °C to give **4a–c** respectively. The isolated yields of the ring-expanded products **4a–c** were over 80%, and monitoring by $^1H$ NMR indicated quantitative conversion. The solvolyses in 60% aqueous acetone were slow at 36 °C, being complete in 1–4 days, but use of higher temperatures gave some general decomposition. The pyridine complex **3a** was solvolyzed more rapidly than the 2,2′-bipyridine derivative **3b**. The β-phenyl derivatives **3d** and **3e** gave less satisfactory results with **3d** giving only $[PtCl_2py_2]$ and **3e** giving the ring-expanded product **4e** in less than 50% yield.

Solvolysis of the 4-nitrobenzoate derivatives **3f** and **3g** occurred more slowly, presumably because the OPNB

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(12) Roberts, D. D. *J. Org. Chem.* **1968**, *33*, 2712.
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(14) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.
(15) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824.
(16) Whitesides, G. M.; DiCosimo, R.; Ibers, J. A. *Organometallics* **1982**, *1*, 13. Aydin, A.; Gunther, H.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 1301.
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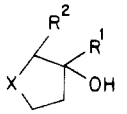
(18) Puddephatt, R. J. In *Inorganic Chemistry: Toward the 21st Century*; Chisholm, M. H., Ed.; ACS Symposium Series 211; American Chemical Society: Washington, DC, 1983; p 353.
(19) Littlecott, G. W.; McQuillin, F. J.; Powell, K. G. *Inorg. Synth.* **1976**, *16*, 113.
(20) Burton, J. T.; Puddephatt, R. J.; Jones, N. L.; Ibers, J. A. *Organometallics* **1983**, *2*, 1487.
(21) Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 1370.
(22) Ekeland, R. A.; Jennings, P. W. *J. Organomet Chem.* **1985**, *281*, 397.

**Table I. $^{13}C$ NMR Chemical Shift Data for Complexes of the Type**

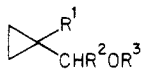


| compd | | | X = $CH_2$ | | X = $PtCl_2py_2$ | | |
|---|---|---|---|---|---|---|---|
| $R^1$ | $R^2$ | carbon positn | δ | ref | compd no. | δ | Δδ/ppm[a] |
| H | H | C-1 | 35.3 | 26 | **4a** | 28.8 | +6.5 |
| | | C-2 | 73.6 | | | 77.0 | −3.4 |
| | | C-3 | 35.3 | | | 41.1 | −5.8 |
| | | C-4 | 23.7 | | | 17.0 | +6.7 |
| $CH_3$ | H | C-1 | 41.2 | 27 | **4c** | 34.0 | +7.2 |
| | | C-2 | 79.7 | | | 81.0 | −1.3 |
| | | C-3 | 41.2 | | | 46.9 | −5.7 |
| | | C-4 | 24.3 | | | 18.5 | +5.8 |
| | | $CH_3$ | 28.3 | | | 25.8 | +2.5 |
| Ph | H | C-1 | 41.8 | 28 | | 38.8 | +3.0 |
| | | C-2 | 83.3 | | | 84.4 | −1.1 |
| | | C-3 | 41.8 | | | 46.6 | −4.8 |
| | | C-4 | 23.8 | | | 21.0 | +2.8 |

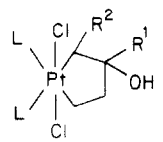
| compd | | | X = $CH_2$ | | | X = $PtCl_2py_2$ | | Δδ/ppm[a] | |
|---|---|---|---|---|---|---|---|---|---|
| $R^1$ | $R^2$ | | cis | trans | ref | compd no. | δ | if cis | if trans |
| H | $CH_3$ | C-1 | 40.1 | 42.2 | 29 | **4f** | 38.8 | +1.3 | +3.4 |
| | | C-2 | 75.5 | 80.1 | | | 80.8 | −5.3 | −0.7 |
| | | C-3 | 34.6 | 34.1 | | | 39.1 | −4.4 | −5.0 |
| | | C-4 | 22.3 | 21.7 | | | 10.7 | +11.6 | +11.0 |
| | | $CH_3$ | 14.0 | 18.6 | | | 19.3 | −5.3 | −0.70 |

[a] $\Delta\delta = \delta(X = CH_2) - \delta(X = PtCl_2py_2)$.

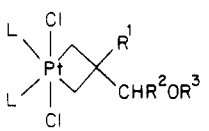
group is not as good a leaving group as OMs. Complex **3f** gave the ring-expanded product **4f** in over 50% yield, though **3g** gave no such solvolysis product and decomposed to give $[PtCl_2py_2]$ and $CH_2CH_2CHCMe_2OPNB$, the parent cyclopropane.



**1a**, $R^1 = R^2 = H$, $R^3 = Ms$
**b**, $R^1 = Me$, $R^2 = H$, $R^3 = Ms$
**c**, $R^1 = Ph$, $R^2 = H$, $R^3 = Ms$
**d**, $R^1 = H$, $R^2 = Me$, $R^3 = PNB$



**4a**, $R^1 = R^2 = H$, L = py
**b**, $R^1 = R^2 = H$, $L_2$ = bpy
**c**, $R^1 = Me$, $R^2 = H$, L = py
**d**, $R^1 = Ph$, $R^2 = H$, L = py
**e**, $R^1 = Ph$, $R^2 = H$, $L_2$ = bpy
**f**, $R^1 = H$, $R^2 = Me$, L = py



**3a**, $R^1 = R^2 = H$, $R^3 = Ms$, L = py
**b**, $R^1 = R^2 = H$, $R^3 = Ms$, $L_2$ = bpy
**c**, $R^1 = Me$, $R^2 = H$, $R^3 = Ms$, L = py
**d**, $R^1 = Ph$, $R^2 = H$, $R^3 = Ms$, L = py
**e**, $R^1 = Ph$, $R^2 = H$, $R^3 = Ms$, $L_2$ = bpy
**f**, $R^1 = H$, $R^2 = Me$, $R^3 = PNB$, L = py

In all of the solvolysis reactions which were successful, the ring-expanded platinacyclopentanol products **4** were formed without any of the alternative platinacyclobutylcarbinol products. Such product, which have been prepared and characterized independently,[20] would have been detected if present in 1–2% yield.

Only in an isolated case was more than one platinacyclopentanol product isolated. In this one case, solvolysis of **3a** gave **4a** and two isomers of **4a**, differing only in the relative orientations of the pyridine and chloride ligands about platinum. Similar isomers of platina(IV)cyclopentanes have been observed previously.[23]

Besides the reactions described above, a large number of unsuccessful ring expansion reactions were attempted. For example, reaction of **3a** with methanol or ethanol as solvents led only to slow general decomposition and gave none of the platinacyclopentyl ethers, expected by alcoholysis with ring expansion.

Many attempts were made to catalyze ring expansion of the parent platinacyclobutylcarbinols, but none was successful. For example, reactions of $[L_2Cl_2PtCH_2CH(CH_2OH)CH_2]$, where L = py or $L_2$ = bpy, in aqueous acetone with acid catalysis using HCl, $CH_3CO_2H$, or $HClO_4$ led to either general decomposition or recovery of starting materials. This is disappointing since such reactions of cyclopropylmethanol do occur and give a useful synthesis of cyclobutanol, and cyclobutylcarbinyl esters undergo acetolysis with ring expansion.[7,24] Clearly, the platinacyclobutane derivatives are not stable to forcing conditions, and only those ring expansions which can occur under very mild conditions and in the absence of strong acids are useful.

From a practical point of view, these reactions of **3** to give **4** are only useful for the mesylate derivatives, and only hydrolysis to the platinacyclopentanols **4** has been successful.

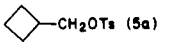
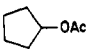
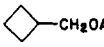
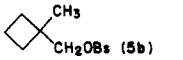
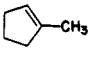
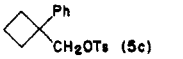
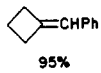
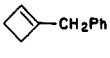
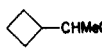
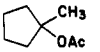
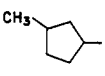
**Characterization of Platinacyclopentanols 4.** Complexes **4** were most readily characterized structurally by their $^{13}C$ NMR spectra, and confirmation was obtained by elemental analysis and $^1H$ NMR, and mass spectrometry.

Consider, as an example, the $^{13}C$ NMR spectra of **4c**. Two signals were observed in the $^{13}C\{^1H\}$ NMR spectrum with large $^1J(PtC)$ couplings at δ 18.4 [$^1J(PtC)$ = 494 Hz] and δ 34.0 [$^1J(PtC)$ = 541 Hz], assigned as due to $C^4$ and $C^1$, respectively. Each was shown to be a $CH_2$ group by the triplet appearance in the off-resonance-decoupled $^{13}C$ NMR spectrum. The magnitudes of the $^1J(PtC)$ couplings are much too high for a platinacyclobutane but in the range

(23) Brown, M. P.; Hollings, A.; Houston, K. J.; Puddephatt, R. J.; Rashidi, M. *J. Chem. Soc., Dalton Trans.* **1976**, 786.

(24) Caserio, M. C.; Graham, W. H.; Roberts, J. D. *Tetrahedron* **1960**, *11*, 171.

**Table II. Solvolysis Products from Cyclobutylcarbinyl Esters**

| reagent | products | | ref |
|---|---|---|---|
|  |  99% |  1% | 7 |
|  |  59% |  41% | 30 |
|  |  95% |  | 31 |
|  |  23% |  22% | 32 |
| |  20% cis, 33% trans |  2% | |

expected for a platinacyclopentane.[14,25] The signals due to the β-carbons were at δ 81.0 [$^2J$(PtC) = 15 Hz] due to the *C*MeOH group and at δ 46.9 [$^2J$(PtC) = 6 Hz] due to the β-$CH_2$ group, while the methyl signal was at δ 25.7 [$^3J$(PtC) = 34.5 Hz]. The assignments were confirmed by the multiplicities in the off-resonance-decoupled $^{13}C$ NMR spectra. Structures of the other platinacyclopentanols were deduced in a similar way, and there is an obvious correlation of carbon chemical shifts of the platinacyclopentanols with those of the corresponding cyclopentanols as shown in Table I.

The only difficult case was that of **4f**, where it is not possible to determine unambiguously the stereochemistry about the ring, in particular whether the methyl substituent, $R^2$, and hydroxyl substituent are mutually cis or trans with respect to the ring. Table I shows the correlation of $^{13}C$ chemical shifts, which is more consistent with the trans structure, but does not prove it.

The $^1H$ NMR spectra of complexes **4** were very complex but were assigned by using homonuclear decoupling and deuterium labeling studies. Details are given in the Experimental Section, and the spectra are fully consistent with the proposed structures.

The mass spectra of complexes **4a** and **4b** were recorded. They did not give a parent ion, but the highest mass observed was due to loss of $C_2H_4$, and then further loss of $CH_2CHOH$ occurred to give $PtCl_2L_2$ where L = py or $L_2$ = bpy.

**Summary of the Synthetic Work.** The scope of the ring expansion reactions is limited by the rather low thermal stability of the platinacyclobutane precursors. Only those derivatives which are solvolyzed at temperatures of 45 °C or less gave reasonable yields, since at higher temperatures the platinacyclobutanes decompose by reductive elimination of the corresponding cyclopropane derivative. However, when solvolysis of a complex **3** does occur, ring expansion to give **4** occurs in very high yield.

It is interesting to compare the products formed from **3** with those formed by solvolysis of the analogous cyclobutane derivatives (Table II). In making these comparisons it should be noted that the experimental conditions, particularly the temperature and solvent, are much more forcing for the organic compounds, since these are not solvolyzed easily in aqueous acetone, and hence qualitative differences only are discussed. The platinum complexes rearrange in a more selective manner, always by ring expansion. The solvolysis products of **3a** and **5a** are analogous, but there are differences in all other cases. Solvolysis of **5b** occurs with ring expansion, but some deprotonation of the intermediate carbonium ion occurs to give 1-methylcyclopentane. No such alkene product was formed from **3c**. Solvolysis of **5c** occurs with migration of the phenyl group to the exocyclic $CH_2$ group followed by deprotonation without ring expansion, but no phenyl migration occurred on solvolysis of **3e** and the ring-expanded product **4e** was formed. Solvolysis of **5d**, which gives a secondary carbonium ion on ionization of tosylate, occurs with only partial ring expansion and also gives all possible isomers of the ring-expanded product methylcyclopentyl acetate. The related solvolysis of **3f** gave complete ring expansion, and only one isomer **4f** was formed. These differences are significant and indicate that the metal has a profound effect on the course of the solvolysis reactions. A study of the mechanism was therefore made.

**Kinetic Studies of the Ring Expansion Reactions.** The solvolyses of the complexes $[Cl_2py_2PtCH_2CH(CH_2OMs)CH_2]$ (**3a**) $[Cl_2(bpy)PtCH_2CH(CH_2OMs)CH_2]$ (**3b**), and $[Cl_2py_2PtCH_2CMe(CH_2OMs)CH_2]$ (**3c**) were conducted in 60% acetone-$d_6$–$D_2O$ mixtures at 36 °C, and the rates were monitored by $^1H$ NMR. The ring expansion reactions to give **4a**, **4b**, and **4c**, respectively, were quantitative and followed good first-order kinetics. The rate constants were $2.40 \times 10^{-5}$ $s^{-1}$, $5.86 \times 10^{-6}$ $s^{-1}$, and $1.81 \times 10^{-5}$ $s^{-1}$ for **3a**, **3b**, and **3c**, respectively.

In organic systems a β-methyl substituent accelerates the reaction. For example, $CH_2CH_2C(Me)CH_2X$ is solvolyzed five times faster than $CH_2CH_2CHCH_2X$, when X = tosylate or 3,5-dinitrobenzoate,[33] whereas **3c** is solvolyzed slightly more slowly than **3a**. The rates of solvolysis of **3a–c** were slower than for cyclopropylmethyl mesylate under similar conditions but much faster than for the cyclobutylmethyl derivatives, with first-order rate constants estimated to be $\sim 2.5 \times 10^{-3}$ $s^{-1}$ and $3 \times 10^{-7}$ $s^{-1}$, respectively.[17] Ring strain arguments given in the introduction should lead to lower rates for platinacyclobutanes than for cyclobutanes. These observations indicate that the platinum atom plays an important role in the solvolysis reactions.

The observation that the 2,2′-bipyridine complex **3b** was solvolyzed four times slower than the pyridine complex **3a** led us to suspect that pyridine dissociation might be involved in the solvolysis of **3a**. Several reactions of platinacyclobutanes are known to occur after dissociation of a pyridine ligand.[14,34] Kinetic studies of the solvolysis of **3a** in the presence of free pyridine confirmed this. The observed first-order rate constants for different concentrations of pyridine were as follows: $k_1 = 2.40 \times 10^{-5}$ $s^{-1}$, [py] = 0; $9.73 \times 10^{-6}$ $s^{-1}$, $1.29 \times 10^{-2}$ M; $7.99 \times 10^{-6}$, $2.58 \times 10^{-2}$ M; $6.85 \times 10^{-6}$ $s^{-1}$, $6.45 \times 10^{-2}$ M; $6.10 \times 10^{-6}$ $s^{-1}$, $3.23 \times 10^{-1}$ M. The rate constants fall to a limiting value, $k_\infty$

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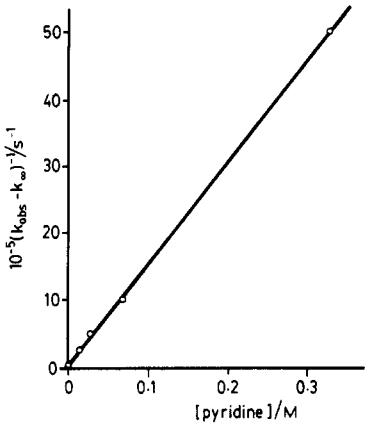



**Figure 1.** Plot of $(k_{obsd} - k_\infty)^{-1}$ vs. [pyridine] for solvolysis of **3a** at 36 °C, where $k_{obsd}$ is the observed first-order rate constant and $k_\infty = 5.90 \times 10^{-6}$ s$^{-1}$.

$\approx 5.90 \times 10^{-6}$ s$^{-1}$, at high pyridine concentration, and a plot of $(k - k_\infty)^{-1}$ vs. [py] was linear as shown in Figure 1. These data lead to a two-term rate law for the solvolysis with the observed first-order rate constants given by the expression $k/s^{-1} = 5.90 \times 10^{-6} + (1.81 \times 10^{-5})/(1 + 275[py])$. The value of $k_\infty$ ($5.90 \times 10^{-6}$ s$^{-1}$) is almost the same as the rate constant for solvolysis of **3b** ($5.86 \times 10^{-6}$ s$^{-1}$) and represents the rate constant for solvolysis without prior dissociation of a pyridine ligand.

The inhibition by free pyridine was not a general effect. Thus, solvolysis of **3c** was not significantly affected by free pyridine, the first-order rate constant being reduced from $1.8 \times 10^{-5}$ s$^{-1}$ in the absence of pyridine to $1.66 \times 10^{-5}$ s$^{-1}$ in the presence of 1.03 M pyridine. The solvolysis of **3c** is actually about three times faster than for **3a** in the process not involving pyridine dissociation. It is the extra reaction pathway for **3a** which leads to the unexpected result that there is an overall higher rate of solvolysis of **3a** than of **3c** in the absence of pyridine.

**Labeling Studies. (a) $^{13}$C Labeling.** The cyclopropane $C_3H_5C^*H_2OMs$ was prepared, enriched to 7.5% with $^{13}$C at the position indicated, and this was used to prepare the complexes $[Cl_2py_2PtCH_2CH(C^*H_2OMs)CH_2]$ (**3a***) and $[Cl_2(bpy)PtCH_2CH(C^*H_2OMs)CH_2]$ (**3b***). Characterization by $^{13}$C NMR showed no scrambling of the label at this stage.

Solvolysis of each of these compounds was carried out in the usual way. Figure 2 shows the $^{13}$C NMR spectra of the platinacyclopentanol products. Complex **3a*** gave the product with greatest $^{13}$C enrichment at C$^1$ but with some enrichment at C$^3$, whereas the product from **3b*** had greater enrichment at C$^3$ than at C$^1$ (see Scheme I for definitions). In neither case was significant enrichment of $^{13}$C at positions C$^2$ or C$^4$ observed.

In contrast, the analogous solvolysis reactions of cyclopropylmethyl esters occur with extensive scrambling of methylene groups due to rapid equilibration between the carbocation intermediates, but hydride shifts are not observed.[6-10] Similar studies of cyclobutylcarbinyl derivatives are less complete, but scrambling of methylene groups may occur to some extent during solvolysis. For example, solvolysis of c-$C_4H_7{}^{13}CH_2OTs$ (OTs = tosylate) gave cyclopentyl acetate with the $^{13}$C label distributed 20% at C$^1$, 64% at C$^2$ and C$^5$, and 16% at C$^3$ and C$^4$. Presumably hydride shifts do occur to some extent in this case.[11] Since it is difficult to use $^{13}$C NMR in a quantitative way, further labeling studies were carried by using $^2$H labels.

**(b) $^2$H Labeling.** The labeled platinacyclobutanes $[Cl_2py_2PtCH_2CH(CD_2OMs)CH_2]$ (**3a****), $[Cl_2(bpy)PtCH_2CH(CD_2OMs)CH_2]$ (**3b****), and $[Cl_2py_2PtCH_2CMe(CD_2OMs)CH_2]$ (**3c****) were prepared from the corresponding labeled cyclopropanes. These complexes were solvolyzed in the usual way, and the products were characterized by $^1$H, $^2$H, and $^{13}$C NMR.

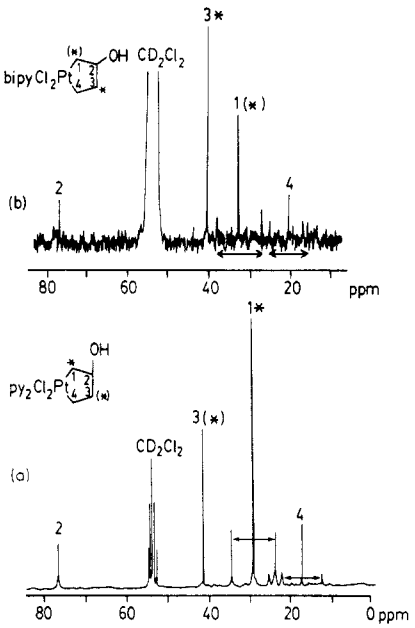



**Figure 2.** $^{13}$C{$^1$H} NMR spectra (50.4 MHz) of the products of solvolysis of (a) **3a*** and (b) **3b***. The major and minor sites of $^{13}$C incorporation are indicated by an asterisk and (an asterisk), respectively, and the $^1J$(PtC) couplings are indicated on the spectra.

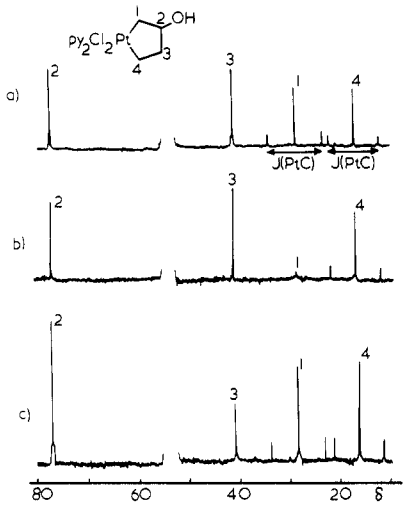



**Figure 3.** $^{13}$C{$^1$H} NMR spectra (50.4 MHz) of products formed by solvolysis of (a) **3a**, (b) **3a**** in the absence of free pyridine (most label at C$^1$), and (c) **3a**** in the presence of pyridine (0.32 M) (most label at C$^3$). The extent of label incorporation can be estimated very roughly by comparison of peak intensities of the C$^1$ and C$^3$ resonances with the intensity of the C$^2$ resonance, since there is no deuterium incorporation at C$^2$.

Figure 3 shows the $^{13}$C{$^1$H} NMR spectra of the platinacyclopentanol products from **3a**** solvolyzed either in the absence of free pyridine or in the presence of 0.32 M pyridine. This shows very clearly that the label is mostly at the C$^1$ position in the product formed in the absence of pyridine but mostly at C$^3$ in the presence of pyridine and confirms the result obtained by $^{13}$C labeling. It also shows that no significant amount of scrambling of the deuterium label by migration between methylene groups occurs, since no CHD groups could be detected by $^{13}$C NMR. A small isotope effect[35] on the $^{13}$C chemical shifts

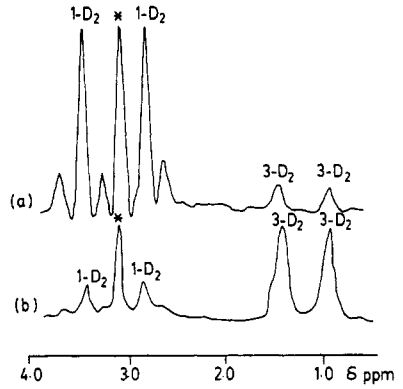



**Figure 4.** $^2H\{^1H\}$ NMR spectra (30.8 MHz) of products of solvolysis of (a) **3a**** in the absence of free pyridine (most label at $c^1$) and (b) **3a**** in the presence of pyridine (0.32 M) (most label at $C^3$). The peak marked asterisk is due to OD groups and decreases with $H_2O$ washing.

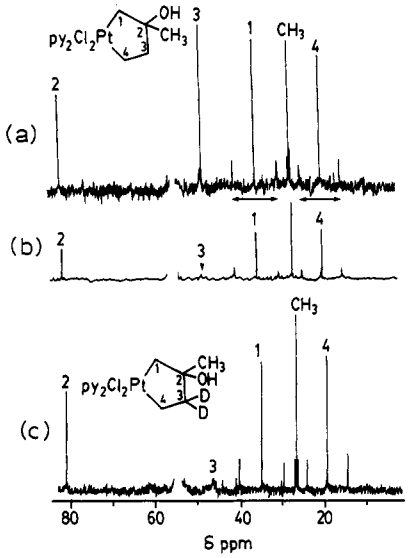



**Figure 5.** $^{13}C\{^1H\}$ spectra (50.4 MHz) of products of solvolysis of (a) **3c**, (b) **3c**** in the absence of free pyridine, and (c) **3c**** in the presence of pyridine (0.78 M). In both (b) and (c) the label is very largely at $C^3$.

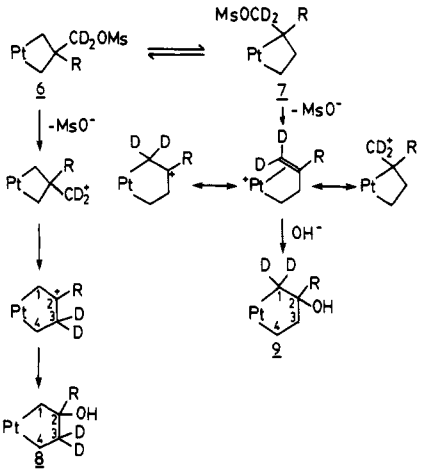
was observed in some cases, for example, on the $C^4$ resonance in Figure 3c.

The $^2H\{^1H\}$ NMR spectra (Figure 4) confirm these results and allow the relative amounts of the $C^1D_2$ and $C^3D_2$ species to be determined by integration. These results are given in Table I. The $C^1D_2$ resonances show distinct coupling to $^{195}Pt$, each with $^2J(PtD) = 13.2$ Hz as expected. Each $CD_2$ group gives two $^2H$ resonances (Figure 4) because there is no plane of symmetry containing the $PtC_4$ ring.

The products from solvolyses of **3b**** and **3c**** were characterized in a similar way. As shown in Figure 5 and Table I, the products from solvolysis of **3c**** were not much affected by the presence or absence of free pyridine. Overall there is a clear correlation of the rate constants $k_1$ for solvolyses and the isomer ratios of products as shown by the data in Table III.

**The Mechanism of Reaction.** Most of the kinetic and labeling results can be rationalized in terms of the mechanism shown in Scheme II. According to this scheme solvolysis of **6**, by direct analogy with the organic precedents but without methylene scrambling,[8] should give **8** with the label at the $C^3$ position. However, if **6** can equilibrate

**Scheme II**




with its less stable skeletal isomer **7** and if solvolysis of **7** is much faster than solvolysis of **6**, the product is expected to be **9** with the label at $C^1$. It has been shown previously that the skeletal isomerization of $[Cl_2py_2PtCH_2CH_2CDPh]$ to give $[Cl_2py_2PtCH_2CDPhCH_2]$ is retarded by added pyridine and that the analogous isomerization of the 2,2′-bipyridine derivative does not occur.[14,36] It was demonstrated that a pyridine ligand must dissociate before the isomerization could occur. Thus, the observation that **3a**** in the absence of free pyridine gives largely **9** but, in the presence of pyridine, gives largely **8** and that **3b**** gives largely **8** are rationalized.

Solvolysis of **3c**** gave very little of isomer **9**, presumably because the extra steric bulk of the methyl substituent R in Scheme II leads to a less favorable isomerization of **6** to give **7**.[14,37] In addition, the direct reaction of **6** to give **8** is faster for **3c**** than for **3a**** by a factor of $(1.66 \times 10^{-5})/(5.9 \times 10^{-6}) = 2.8$. This factor is similar to those found in analogous organic ring expansion reactions.[33] Both factors favor formation of isomer **8** as observed.

Why is isomer **7** solvolyzed so much faster than **6**? Remember that the equilibrium concentration of **7** is too low to be detected, yet three quarters of the product formed by solvolysis of **3a**** in the absence of added pyridine is formed from this isomer according to Scheme II. Since 2% of isomer **7** could be detected, it must be solvolyzed at least 150 times as fast as **6**, in the case of complex **3a****. Indeed the kinetics are most readily interpreted in terms of rate-determining isomerization followed by rapid solvolysis of **7**. Ionization of **7** can lead directly to the carbonium ion which is platinum-stabilized through the 3-butenyl resonance form as shown in Scheme II. However, this extra stabilization of the carbonium ion is not gained directly on ionization of **6** but only after the ring expansion step (Scheme II). Hence much faster ionization of **7** is expected. Since platinacyclobutanes are less strained than cyclobutanes,[14-16] the rate of solvolysis of isomer **6** might be expected to be lower than for cyclobutylmethyl mesylate, but it is in fact higher with $k = 5.9 \times 10^{-6}$ s$^{-1}$ as opposed to $\sim 3 \times 10^{-7}$ s$^{-1}$. The platinum center appears therefore to have an activating effect even for isomer **6**.[38]

The above mechanism accounts for all of the experimental observations on complex **3c**** and many of those

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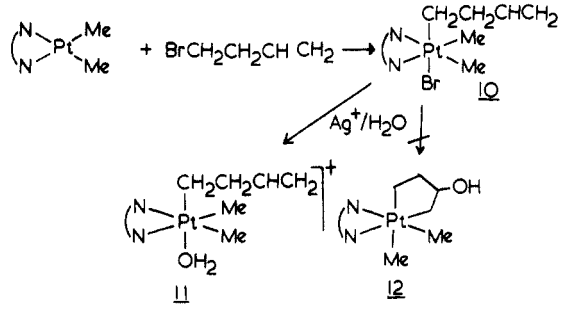
(38) This may be related to the activation of the C–I bond in $Pt^{IV}C-H_2CH_2CH_2I$ complexes compared to $CH_3CH_2CH_2I$. Monaghan, P. K.; Puddephatt, R. J. *Inorg. Chim. Acta* **1983**, *76*, L237.

**Table III. First-Order Rate Constants, $k_1$, for Solvolyses of 3a, 3b, and 3c and Product Distributions from Solvolyses of Corresponding Deuterium Labeled Platinacyclopentanes 3a**, 3b**, and 3c****

| complex | [py]/M | $k_1/s^{-1}$ | % product 1-$D_2$ | % product 3-$D_2$ |
|---|---|---|---|---|
| **3a** | 0 | $2.40 \times 10^{-5}$ | 86 | 14 |
| **3a** | 0.32 | $6.10 \times 10^{-6}$ | 32 | 68 |
| **3b** | 0 | $5.86 \times 10^{-6}$ | 27 | 73 |
| **3c** | 0 | $1.81 \times 10^{-5}$ | 10 | 90 |
| **3c** | 0.78 | $1.66 \times 10^{-5}$ | 0 | 100 |

**Scheme III**




on complexes **3a**** and **3b**** as discussed above. However, **3a**** in the presence of excess pyridine and **3b**** are predicted by this mechanism to give only isomer **8** whereas both give ~30% of isomer **9** (Table III). This observation cannot be explained by the general scrambling of methylene groups observed in the analogous organic ring expansions[6] because no label is incorporated at the $C^4$ position. There are two possible explanations. Either there is a second mechanism of isomerization of **6** to **7** which does not involve prior ligand dissociation (we note that this would rule out a carbene–alkene intermediate in the isomerization since it would be a 20e complex),[14,36,37] or there is a mechanism whereby ionization of isomer **6** can lead to **9** without a prior skeletal isomerization step to give intermediate **7**. It is not possible to distinguish between these possible pathways.

A key step in Scheme II is the attack of hydroxide on the cationic 3-butenylplatinum(IV) intermediate to give the platinacyclopentanol product, and we have attempted to demonstrate this step directly. Despite many attempts, the only 3-butenylplatinum(IV) complex we were able to prepare was **10** (Scheme III). Reaction of **10** with $AgBF_4$ gave only the aqua complex **11**. This is not surprising since attack of hydroxide on the alkenyl group would lead to mutually trans alkyl groups in **12** and so would be thermodynamically unfavorable.[39] This step is clearly established in the analogous organic ring expansions,[6] and there is no reason to doubt that it would occur as shown in Scheme II.

## Conclusions

To summarize, there are obvious similarities in the reactions described above with analogous ring expansions in organic systems,[6] but there are also some important differences due to the influence of the platinum center. Most significant is the skeletal isomerization of **6** ⇌ **7** (Scheme II) which leads to the novel selectivity on solvolysis of **3a****. The platinum center has a very large activating effect for ionization of **7** and a smaller, but still significant, effect for ionization of **6**, and this leads to higher rates of solvolysis than in analogous cyclobutylmethyl derivatives although the ring strain in platinacyclobutanes is lower than in cyclobutanes. In the platinum complexes ring expansion appears to be irreversible, and there is no general scrambling of methylene groups as observed in ring expansion of cyclopropylmethyl esters or hydride shifts as observed in ring expansion of cyclobutylmethyl esters.[6]

## Experimental Section

$^1H$ NMR spectra were recorded using a Varian XL100 spectrometer and $^2H$ and $^{13}C$ NMR spectra by using a Varian XL200 spectrometer. The multiplicities in the $^{13}C$ NMR spectra due to $^1J(CH)$ coupling were obtained from the off-resonance-decoupled $^{13}C$ NMR spectra and are indicated by s, d, t, and q for C, CH, $CH_2$, and $CH_3$ groups, respectively. Mass spectra were recorded by using a Varian MAT 311 instrument.

Cyclopropane derivatives were prepared by literature procedures[40-42] or modifications of these and were characterized by their $^1H$ and $^{13}C$ NMR spectra.[43] The $^{13}C$ labeled cyclopropane $C_3H_5{}^{13}CH_2OH$ was prepared by the method of Golding[44] and shown to contain 7.5% $^{13}C$ by MS analysis. The position of the label was determined by the synthetic method[44] and was confirmed by $^{13}C$ and $^1H$ NMR. Deuterium-labeled cyclopropanes were prepared by reduction of the corresponding cyclopropylcarboxylic acid with $LiAlD_4$ by standard methods.[6,8,9] In all cases the label incorporation was better than 98% as determined by MS, and $^{13}C$ analysis showed only $CD_2OH$ groups detectable. The mesylate esters and platinacyclobutane complexes were prepared as for the unlabeled compounds[43] and were characterized by $^1H$ and $^{13}C$ NMR spectroscopy. In this case MS analysis was not possible since the compounds did not give parent ions, but the NMR analysis is also sensitive (see text).

**Synthesis of Platinacyclobutane Pyridine Derivatives.** In a typical synthesis, cyclopropylcarbinyl methanesulfonate (104 mg) was added to a stirred solution of $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2]$ (100 mg) in dry tetrahydrofuran (5 mL). After 16 h at room temperature, the solution was filtered and the solvent was evaporated to give a yellow solid, which was thoroughly washed with dry ether (6 × 0.5 mL) to remove excess cyclopropane derivative. The solid was suspended in $CH_2Cl_2$ (5 mL), and pyridine was added to the stirred solution at 0 °C until a clear solution was obtained. The solvent was evaporated, and the residue was washed with ether and recrystallized from $CH_2Cl_2$–pentane to give the pale yellow product $[py_2Cl_2PtCH_2CH(CH_2OMs)CH_2]$: yield 113 mg (57%); mp 56–59 °C dec. Anal. Calcd for $C_{15}H_{20}Cl_2N_2O_3PtS$: C, 31.4; H, 3.5; N, 4.9. Found: C, 31.8; H, 3.8; N, 4.9. NMR in $CDCl_3$: $^1H$, $\delta$ 2.36 [m, $^2J(PtH^a)$ = 81.5, $^2J(H^aH^b)$ = 4.8, $^3J(H^aH^2)$ = 9 Hz, $PtCH^aH^b$], 2.58 [m, $^2J(PtH^b)$ = 81.5, $^3J(H^bH^2)$ = 7 Hz, $PtCH^aH^b$], 3.04 (m, $H^2$), 4.12 [d, $^3J(HH^2)$ = 7 Hz, $CH_2O$], 2.94 (s, $CH_3S$); $^{13}C$, $\delta$ −13.7 [t, $^1J(PtC)$ = 356 Hz, $C^1$, $C^3$], 42.1 [d, $^2J(PtC)$ = 104 Hz, $C^2$], 73.8 [t, $^3J(PtC)$ = 54 Hz, $CH_2O$], 37.1 (q, $CH_3S$).

Similarly were prepared and purified the following complexes.

**3c**: yield 48%; mp 86–91 °C dec. Anal. Calcd for $C_{16}H_{22}Cl_2N_2O_3PtS$: C, 32.7; H, 3.8; N, 4.8. Found: C, 32.7; H, 3.9; N, 4.8. NMR in $CDCl_3$: $^1H$, $\delta$ 2.36 [m, $^2J(PtH^a)$ = 85, $^2J(H^aH^b)$ = 5.5 Hz, $PtCH^aH^b$], 1.16 (s, $CH_3C$), 4.16 (s, $CH_2O$), 2.98 (s, $CH_3S$); $^{13}C$, $\delta$ −4.9 [t, $^1J(PtC)$ = 361 Hz, $C^1$, $C^3$], 46.9 [s, $^2J(PtC)$ = 95 Hz, $C^2$], 77.4 [t, $^3J(PtC)$ = 28 Hz, $CH_2O$], 25.0 [q, $^3J(PtC)$ = 30 Hz, $CH_3C$], 36.7 (q, $CH_3S$).

**3d**: yield 28%; mp 132–135 °C dec. NMR in $CDCl_3$: $^1H$, $\delta$ 2.95 [m, $^2J(PtH^a)$ = 85, $^2J(H^aH^b)$ = 6 Hz, $PtCH^aH^b$], 3.23 [m, $^2J(PtH^b)$ = 86 Hz, $PtCH^aH^b$], 4.46 (s, $CH_2O$), 2.42 [s, $CH_3S$]; $^{13}C$, $\delta$ −6.7 [t, $^1J(PtC)$ = 367 Hz, $C^1$, $C^3$], 56.0 [s, $^2J(PtC)$ = 90 Hz, $C^2$], 78.4 [t, $^3J(PtC)$ = 22 Hz, $CH_2O$], 36.3 (q, $CH_3S$).

**3f**: yield 55%; mp 151–153 °C dec. Anal. Calcd for $C_{22}H_{23}Cl_2N_3O_4Pt$: C, 40.1; H, 3.5; N, 6.4. Found: C, 40.0; H, 3.6;

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N, 6.2. NMR in $CDCl_3$: $^1H$, $\delta$ 2.2–3.2 (m, PtC$H^aH^b$), 3.04 (m, $CH^2$), 5.08 [m, $^3J$(HH) = 6 Hz, CHO], 1.28 [d, $CH_3$]; $^{13}C$, $\delta$ −11.6 [t, $^1J$(PtC) = 358 Hz, $C^1$], −10.6 [t, $^1J$(PtC) = 355 Hz, $C^2$], 48.5 [d, $^2J$(PtC) = 101 Hz, $C^2$], 77.2 [d, $^3J$(PtC) = 61 Hz, CHO], 16.5 (q, $CH_3C$).

**3g**: yield 67%; mp 92–96 °C dec. Anal. Calcd for $C_{23}H_{25}Cl_2N_3O_4Pt$: C, 41.0; H, 3.7; N, 6.2. Found: C, 39.2; H, 3.7; N, 5.8. NMR in $CDCl_3$: $^1H$, $\delta$ 2.54 [m, $^2J$(PtH$^a$) = 80, $^2J$(H$^a$H$^b$) = 5, $^3J$(H$^a$H$^b$) = 6 Hz, PtC$H^a$H$^b$], 3.02 [m, $^2J$(Pt$H^b$) = 77 Hz, PtCH$^a H^b$], 3.0 (m, $H^2$); 1.54 (s, $CH_3C$); $^{13}C$, $\delta$ −9.8 [t, $^1J$(PtC) = 361 Hz, $C^1$, $C^3$], 54.8 [d, $^2J$(PtC) = 97.5 Hz, $C^2$], 86.0 [s, $^3J$(PtC) = 63 Hz, $CMe_2O$], 21.9 (q, $CH_3C$).

**Synthesis of Platinacyclobutane 2,2′-Bipyridine Derivatives.** 2,2′-Bipyridine (0.21 mmol) was added to a stirred solution of complex **3a** (0.20 mmol) in $CH_2Cl_2$ (2 mL) in the dark. The reaction mixture was cooled to 0 °C, and after 3 h the yellow crystals of the product **3b** were filtered off and washed with ether: yield 71%; mp 195 °C dec. Anal. Calcd for $C_{15}H_{18}Cl_2N_2O_3PtS$: C, 31.5; H, 3.15; N, 4.9. Found: C, 31.9; H, 3.3; N, 5.2. NMR in $CDCl_3$: $^1H$, $\delta$ 2.37 [m, $^2J$(PtH$^a$) = 81.5 Hz, PtC$H^a$H$^b$], 2.61 [m, $^2J$(PtH$^b$) = 85 Hz, PtCH$^a H^b$], 3.06 (m, $H^2$), 3.52 (d, $^3J$(HH) = 6 Hz, $CH_2O$), 1.54 (s, $CH_3S$).

Similarly was prepared complex **3e** from **3d** and bpy; yield 83%; mp 235 °C dec. Anal. Calcd for $C_{21}H_{22}Cl_2N_2O_3PtS$: C, 38.9; H, 3.4; N, 4.3. Found: C, 38.5; H, 3.2; N, 4.7. $^1H$ NMR in $CDCl_3$: $\delta$ 2.96 [m, $^2J$(PtH$^a$) = 86.5, $^2J$(H$^a$H$^b$) = 5 Hz, PtC$H^a$H$^b$], 3.20 [m, $^2J$(PtH$^b$) = 87 Hz, PtCH$^a H^b$], 4.47 (s, $CH_2O$), 2.47 (s, $CH_3S$).

**Synthesis of Platinacyclopentanol Derivatives 4.** A solution of complex **3a** (95 mg) in acetone-$d_6$–$D_2O$ (60% v/v, 2 mL) was allowed to stand in the dark at 36 °C for 24 h. The reaction was monitored by $^1H$ NMR to ensure that all **3a** had reacted. The solvents were evaporated, the residue was dissolved in acetone and $K_2CO_3$ (0.2 g), and water was added. The solvents were removed, and the residue was extracted with $CH_2Cl_2$ (5 × 2 mL). The volume of the $CH_2Cl_2$ extract was reduced to 1 mL, and pentane was added to precipitate the product **4a**: yield 84%; mp 135–140 °C dec. Anal. Calcd for $C_{14}H_{18}Cl_2N_2OPt$: C, 33.9; H, 3.6; N, 5.6. Found: C, 34.0; H, 3.9; N, 5.6%. NMR in $CDCl_3$: $^1H$, $\delta$ 2.7 [m, $^2J$(PtH) = 85 Hz, $C^1H$]; 3.70 [m, $^2J$(PtH) = 85 Hz, $C^1H$], 3.47 (m, $C^2H$]; 1.05 (m, $C^3H$], 1.6 (m, $C^3H$), 2.8 (m, $C^4H$), 3.28 (m, $C^4H$); $^{13}C$, $\delta$ 29.0 [t, $^1J$(PtC) = 538 Hz, $C^1$], 77.0 [d, $^2J$(PtC) = 19.5 Hz, $C^2$]; 41.2 [t, $^2J$(PtC) = 7.4 Hz, $C^3$]; 17.2 [t, $^1J$(PtC) = 496 Hz, $C^4$].

Similarly were prepared and purified the following complexes. **4b** from **3b** (100-h reaction time): yield 83%; mp >200 °C. Anal. Calcd for $C_{14}H_{16}Cl_2N_2OPt$: C, 34.0; H, 3.2; N, 5.7. Found: C, 34.0; H, 3.6; N, 5.6. NMR in $CDCl_3$: $^1H$, $\delta$ 2.80 (m, $C^1H$), 3.33 (m, $C^1H$), 3.45 (m, $C^2H$), 1.10 (m, $C^3H$), 1.60 (m, $C^3H$), 2.95 (m, $C^4H$), 3.45 (m, $C^4H$); $^{13}C$, $\delta$ 33.1 [t, $^1J$(PtC) = 540 Hz, $C^1$], 77.2 (d, $C^2$), 40.7 (t, $C^3$), 20.9 [t, $^1J$(PtC) = 494 Hz, $C^4$].

**4c** from **3c** (30-h reaction time): yield 88%; mp 105–110 °C dec. Anal. Calcd for $C_{15}H_{20}Cl_2N_2OPt$: C, 35.3; H, 3.95; N, 5.5. Found: C, 35.3; H, 4.0; N, 5.5. NMR in $CDCl_3$: $^1H$, $\delta$ 2.60 (m, $C^1H$), 3.95 (m, $C^1H$), 1.36 (s, $C^2CH_3$), 0.61 (m, $C^3H$), 2.05 (m, $C^3H$), 2.60 (m, $C^4H$), 3.60 (m, $C^4H$); $^{13}C$, $\delta$ 34.0 [t, $^1J$(PtC) = 541 Hz, $C^1$], 81.0 [s, $^2J$(PtC) = 15 Hz, $C^2$], 46.9 [t, $^2J$(PtC) = 6 Hz, $C^3$], 18.4 [t, $^1J$(PtC) = 493 Hz, $C^4$], 25.7 [q, $^3J$(PtC) = 34.5 Hz, $CH^3$].

**4e** from **3e** (80% aqueous acetone, 40 °C, 120-h reaction time): yield 46%; mp 175 °C dec. Anal. Calcd for $C_{20}H_{20}Cl_2N_2OPt$: C, 42.1; H, 3.5; N, 4.9. Found: C, 41.4; H, 3.2; N, 5.3. NMR in $CDCl_3$: $^1H$, $\delta$ 2.98 (m, $C^1H$), 4.47 (m, $C^1H$), 0.92 (m, $C^3H$), 1.65 (m, $C^3H$); 2.71 (m, $C^4H$), 3.98 (m, $C^4H$); $^{13}C$, $\delta$ 38.8 [t, $^1J$(PtC) = 549 Hz, $C^1$], 84.4 (s, $C^2$), 46.6 (t, $C^3$), 21.0 [t, $^1J$(PtC) = 492 Hz, $C^4$].

**4f** from **3f** (70% aqueous acetone, 40 °C, 120-h reaction time): yield 65%; mp 125 °C dec. Anal. Calcd for $C_{15}H_{20}Cl_2N_2OPt$: C, 35.3; H, 3.95; N, 5.5. Found: C, 35.7; H, 4.1; N, 5.3. NMR in $CDCl_3$: $^1H$, $\delta$ 3.83 (m, $C^1H$), 0.66 [d, $^3J$(PtH) = 20.5, $^3J$(HH) = 6 Hz $C^1CH_3$]; 3.32 (m, $C^4H$); $^{13}C$, $\delta$ 38.8 [d, $^1J$(PtC) = 546 Hz, $C^1$], 80.8 [d, $^2J$(PtC) = 43 Hz, $C^2$], 39.1 [t, $^2J$(PtC) = 8 Hz, $C^3$], 10.7 [t, $^1J$(PtC) = 487 Hz, $C^4$], 19.3 [q, $^2J$(PtC) = 18, $CH_3$].

**Kinetic Studies.** A stock solution was prepared containing complex **3a** (100 mg) in acetone-$d_6$–$D_2O$ (2.5 mL, 60% v/v). Five NMR samples of 0.5-mL each were dispensed from this solution. Pyridine was added to four of the samples by microsyringe to give a range of pyridine concentrations from 0 to 0.32 M. The samples were kept in a bath at 36 °C, and the reactions were monitored by $^1H$ NMR, following decay of the MeS resonance ($\delta$ 2.94) due to **3a** and growth of the MeS resonance ($\delta$ 2.54) due to $MeSO_3H$. The solvolyses of **3b** and **3c** were monitored in the same way. Plots of ln [**3a**] vs. $t$ gave good first-order plots from which the first-order rate constants were calculated.

**Synthesis of [PtBrMe$_2$(CH$_2$CH$_2$CH=CH$_2$)(bpy)] (10).** [$Pt(CH_3)_2$(bpy)] (200 mg, 0.53 mmol) was dissolved in dry acetone (25 mL), and 4-bromo-1-butene (354 mg, 2.62 mmol) was added to this solution with stirring. The mixture was allowed to react for 24 h, after which time the intense red color had been dispersed leaving a pale yellow solution. The solution was filtered and taken to dryness. The residue was washed with anhydrous ether (2 × 1 mL) and evaporated again. The solid residue was taken up in $CH_2Cl_2$ and precipitated with $n$-pentane to give 250 mg (92% yield) of the light yellow product, mp 202–204 °C. Anal. Calcd for $C_{16}H_{21}BrN_2Pt$: C, 37.2; H, 4.1; N, 5.4; Br, 15.5. Found: C, 37.0; H, 3.7; N, 5.5; Br, 15.0. $^{13}C$ NMR spectrum in $CDCl_3$: $\delta$ −3.8 [q, $^1J$(PtC) = 695 Hz, $CH_3$], 17.9 [t, $^1J$(PtC) = 696 Hz, $CH_2$], 34.4 [t, $^2J$(PtC) = 20 Hz, $CH_2$], 138.5 (d, CH=); 113.2 [t, $^4J$(PtC) = 6 Hz, $=CH_2$]; bpy resonances at $\delta$ 123.5, 126.8, 138.8, 146.9, and 154.9. This compound decolorizes $KMnO_4$ and $CCl_4$ solutions of $Br_2$.

**Reaction of 10 with AgBF$_4$.** [$PtBr(CH_3)_2$($CH_2CH_2CH$=$CH_2$)(bpy)] (80 mg, 0.16 mmol) was dissolved in acetone (10 mL). $AgBF_4$ (29.3 mg, 0.15 mmol) in water (2 mL) was added with stirring, and a precipitate immediately formed. The solution was stirred in the dark for 1 h after which time it was filtered to give a light yellow solution which was evaporated to dryness on a high vacuum. The residue was dried in a desiccator, over $P_2O_5$. The residue was taken up in $CH_2Cl_2$ and precipitated by the addition of $n$-pentane to give 65 mg (92% yield) of [$Pt(CH_3)_2$-($CH_2CH_2CH$=$CH_2$)($OH_2$)(bpy)][$BF_4$], mp 124–127 °C. IR CsI pellet: 1060 cm$^{-1}$ [$\nu(BF_4^-)$]. Anal. Calcd for $C_{16}H_{23}BF_4NOPt$: C, 35.5; H, 4.3; N, 5.2. Found: C, 36.6; H, 4.3; N, 5.4.

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**Registry No.** **1a**, 696-77-5; **1b**, 697-52-9; **1c**, 102261-80-3; **1d**, 18228-38-1; **1g**, 23437-99-2; **3a**, 81875-81-2; **3a***, 102261-75-6; **3a****, 102261-77-8; **3b**, 81875-82-3; **3b***, 102261-76-7; **3b****, 102261-78-9; **3c**, 81875-83-4; **3c****, 102261-79-0; **3d**, 102261-65-4; **3e**, 102261-66-5; **3f**, 102261-67-6; **3g**, 102261-71-2; **4a**, 81875-84-5; **4b**, 81875-85-6; **4c**, 81875-86-7; **4d**, 102261-68-7; **4e**, 102261-69-8; **4f**, 102261-70-1; **10**, 102261-72-3; **11**·$BF_4$, 102261-74-5; $Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2$, 12073-36-8; $Pt(CH_3)_2$(bpy), 52594-52-2; 4-bromo-1-butene, 5162-44-7.