complex **1** suggests an anchimric assistance of external exchange. This derivative, being analogous to *p*-xylene rather than toluene, should exchange 6 times slower than the others. It exchanges externally at the same rate, and therefore k_e is accelerated. The slight increase in the internal rate of exchange of **1** with benzene concentration (Table II) could also result from benzene catalysis of internal exchange. However, this might be simple solvent polarity effect of the type shown in Table III. The cause of this intramolecular catalysis of external exchange will be discussed in a subsequent paper.[25]

Acknowledgment. We are grateful to the National Science Foundation, Grant CHE 20612, for support of this research.

(25) Traylor, T. G.; Goldberg, M. J.; Strouse, C. E.; Miksztal, A. M., manuscript in preparation.

Platinacyclobutane Chemistry: Platinacyclobutanes from Bicyclo [*X*.1.0] Hydrocarbons

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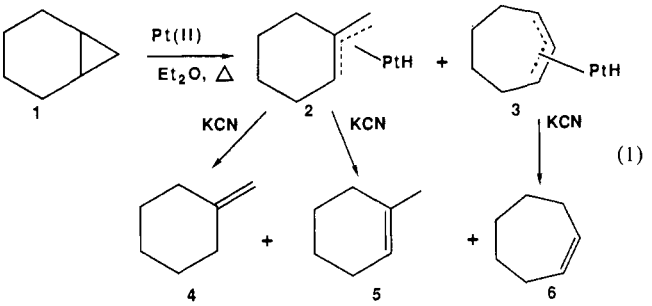
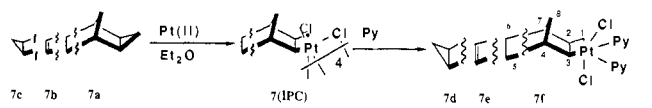
Abstract: Methodologies are now in place for the preparation, isolation, and characterization of platinacyclobutane complexes from ubiquitous substrates such as bicyclo [*X*.1.0] alkanes and alkenes (*X* equals 4 or 6). In the absence of strongly coordinating solvents, the 8-membered-ring complex rearranges to a hydrocarbon mixture containing 1-methylcyclooctene, the exocyclic methylene derivative, and cyclononene. Finally, the platinacyclobutane from bicyclo[6.1.0]nonane, in the presence of 2 equiv of pyridine, rearranges to methylidynylcyclooctane smoothly via an initial α-hydride transfer mechanism rather than a β-hydride transfer mechanism.

Prior to 1982, it was generally accepted that the preparation and isolation of platinacyclobutane complexes from the reaction of Pt(II) with cis-disubstituted cyclopropane derivatives was not possible. Instead, it was proposed that these reactions resulted in the formation of π allylic intermediates which further rearranged as shown in eq 1.[1,2] However, in 1982, we were able to show the cis-disubstituted cyclopropanes which were incorporated in norbornyl systems gave excellent yields of the platinacyclobutanes (eq 2).[3]



(1)



(2)

In this article, we report results on the preparation, isolation, and preliminary chemistry of platinacyclobutane complexes from more common cis-disubstituted cyclopropanes such as those found in bicyclo[*X*.1.0]hydrocarbons.

Results and Discussion

As shown in eq 2, the reaction of Zeise's dimer, Pt(II), with a cyclopropane derivative in ether yields a solid precipitate referred to as the IPC (initially precipitated complex). Previous work on the norbornyl and simple cyclopropane systems by CP/MAS NMR spectroscopy has shown that the hydrocarbon moiety of the IPC was bonded to platinum in the same way as that observed after reaction with pyridine.[4] Further, the IPC was very stable at room temperature. Thus, the strategy to be used for these presumably highly reactive substrates and products was to prepare the IPC, analyze it by solid-state NMR spectroscopy, and then attempt to prepare the mononuclear complex. This could possibly be accomplished with neat pyridine. Initial efforts were placed on the reaction with bicyclo[6.1.0]nonane (**10**) and the results are shown as eq 3.

Preparation and Characterization of Platinacyclobutanes 12 and 15. The solid-state NMR spectrum of **11** is shown in Figure 1 and it is similar to those previously observed for the platinacyclobutane ring in the norbornyl system.[4] The two resonances at 6.9 and 51 ppm are typical of resonances assigned to carbons 1 and 2 in other complexes. The C(3) resonance would be expected to be near 30 ppm but is obviously obscured by resonances of the ring carbons. Resonances in the 140–80-ppm region, which are typical of π-allyl systems,[5] are absent, thus providing further support for a platinacyclobutane complex. Subsequent treatment of **11** with *neat pyridine* gave a stable complex which appears to be the desired and heretofore unknown platinacyclobutane **12** (vide infra). The same procedure was successful in the preparation of **15** (note the difference in reaction temperatures). Although both complexes appear to be infinitely stable in neat pyridine, **15** decomposes faster (2 h) than **12** (6 h) in chloroform solution.

The structures for complexes **12** and **15** were deduced from their NMR spectral resonances which are listed in Table I. Data for

(1) McQuillin, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123.
(2) Cushman, B. M.; Earnest, S. E.; Brown, D. B. *J. Organomet. Chem.* **1978**, *159*, 431.
(3) Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 385.
(4) Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 1370.
(5) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1732.

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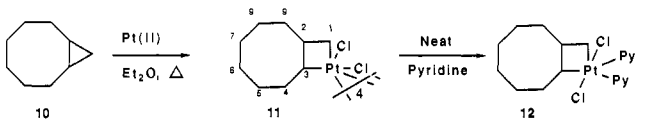
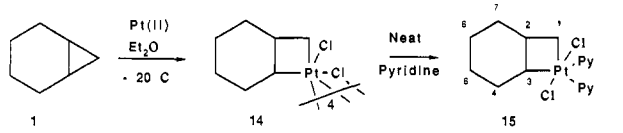


(3)



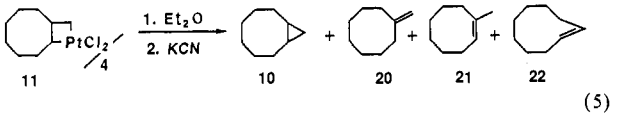
(4)

the established platinacyclobutane complex of tricyclo-[3.2.1.0^{2,4}]octane (**7d**) are also listed for comparison.[3] It is clear that the chemical shift data for carbons 1, 2, and 3 are similar for all three compounds and are typical of platinacyclobutane complexes. Further, the Pt–C coupling constants are indicative of platinum–carbon σ bonds. The fact that C(1) and C(3) are not magnetically equivalent verifies the unsymmetrical substitution pattern for the platinacyclobutane moiety. Finally, the ^{195}Pt resonances in the 3300-ppm region are consistent with known platina(IV)cyclobutane complexes having pyridine ligands.[6]

Preparation of the analogous platinacyclobutane complexes from olefinic substrates was not so facile (Scheme I). Reactions of bicyclo[6.1.0]non-4-ene (**16**) with Zeise's dimer at temperatures between 0 and 60 °C simply resulted in the platinum bound olefin **17**. However, upon treatment with an additional equivalent of Pt(II) and heating in a sealed tube (N_2 purge) at 90 °C for 5–15 min, **17** yielded platinacyclobutane complex **18** which has been previously reported.[7] Its structure was based on NMR and X-ray data. However, since its ^{13}C NMR data have not been previously reported in detail, they are now included in Table I for completeness. It is important to note the magnitude of the Pt–C coupling constant and the resonance frequencies for C-1 and C-3 which indicate both a σ bond and molecular symmetry. Subsequent treatment of **18** with neat pyridine yielded a product whose structure has not been clarified due to its thermal instability, but treatment of this unknown with bipyridine resulted in the well-behaved complex **19**. Again, the carbon NMR data are consistent with an unsymmetrical platinacyclobutane, carbon σ bonds to platinum, an uncomplexed olefin, and a Pt(IV) moiety, all of which are in concert with **19**.

Reactions of Platinacyclobutanes. In the following discussion, results of a brief investigation into the chemical behavior of platinacyclobutanes **11** and **12** shall be presented. The goals of this endeavor were to explore what organic transformations are possible and to compare the results with those from other known platinacyclobutane reactions. In this regard, two avenues are under active investigation: (1) reactions with the tetranuclear IPC (**11**) and (2) reactions with the pyridine derivative (**12**).

Reactions of 11. (1) Thermal Decomposition in Et_2O. On refluxing in ether and subsequent reaction with aqueous KCN, complex **11** yielded four products as shown in eq 5. Each of the



(5)

products was identified by comparing the NMR and GC mass spectra of the mixture with known standards. In a more details set of experiments, **11** was heated in ether for two different time periods (Table II). Further, ^{13}C NMR analysis of the resulting solution revealed a mixture of **20**, **21**, and **22** along with their corresponding platinum π complexes. Hydrocarbon **10** either was not present or was too dilute to be detectable by NMR and mass spectroscopy. However, on treatment of the ethereal solution with KCN, **10** was produced and the platinum complexes released the olefins. Thus, any discussion regarding the product ratios in these types of reactions is contingent upon the heating period and how much of the platinacyclobutane is decomposed.

In this regard, McQuillin[1] had reported the same type of products **4**:**5**:**6** in a ratio of 2:2:1, respectively (eq 1), but the relative ratios were different from those reported herein (**20**:**21**:**22** = 6:4:1). This difference may simply reflect the difference in hydrocarbon substrate, the purity of substrate,[21] or the extent of reaction as stated above.

In light of the fact that reaction 1, which was run without stopping at the intermediate, gave the same products as the reaction shown as eq 5, it is reasonable to conclude that platinacyclobutanes should be considered as intermediates in the reaction of cis-disubstituted cyclopropane derivatives with Zeise's dimer. Scheme II is proposed as the reaction pathway.

(2) Reaction with Dimethyl Sulfoxide. Reaction **7b** and **7c** IPCs with Me_2SO led very cleanly to ring expansion type products **23**

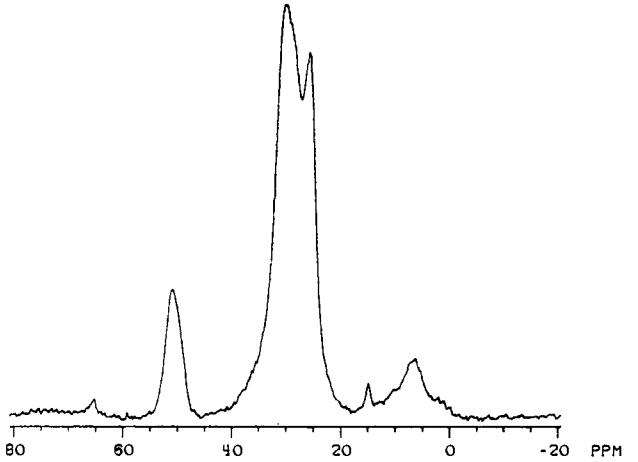
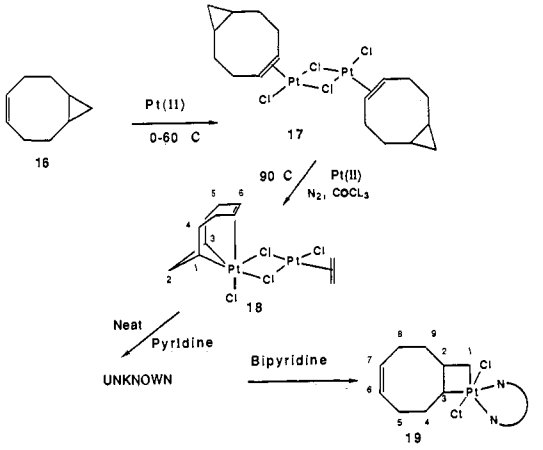
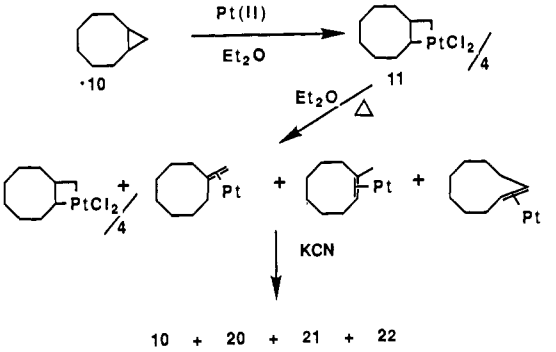


Figure 1. ^{13}C CP/MAS spectrum of platinacyclobutane complex from bicyclo[6.1.0]nonane.

Scheme I



Scheme II



(6) Unpublished results in our laboratory.
(7) Parsons, E. J.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 1793.

Table I. ^{13}C and ^{195}Pt NMR Resonances for Complexes **9a**, **12**, **15**, **18**, and **19**

atom no.	**7d**	**12**	**15**[d]	**18**	**19**
1	−12.1 t [352][b]	−7.2 t [351]	−8.6 t [354]	29.6 d [338]	−6.1 t [361]
2	55.6 d [95]	48.6 d [85]	44.6 d [98]	36.8 t [100]	47.8 d [82]
3	12.4 d [391]	14.2 d [348]	5.8 d [369]	29.6 d [338]	12.5 d [345]
4	40.9 [<10]	31.2[a]	27.2[a]	44.4 and 22.7	34.1[a]
5	29.3 [44]	30.0[a]	20.4[a]	44.4 and 22.7	25.3[a]
6	27.9	25.9[a]	19.9[a]	120.4 [94]	130.4 d[a]
7	41.8 [24]	25.6[a]	25.7[a]	120.4 [94]	131.8 d[a]
8	35.4	29.5[a]			24.9[a]
9		30.8[a]			32.2[a]
Pt	3350[c]	3263	3315	2796 and 2184	3072

[a] Not rigorously assigned. [b] $J_{Pt,C}$. [c] Relative to 1.0 M $Na_2Pt(CN)_4$ in D_2O at 25 °C. [d] Solvent was Py-d_5 in this case.

Table II. Products and Relative Percentages from Reactions with **11**

reagents/products	**10**	**20**	**21**	**22**
1. Et_2O, reflux, 10 h 2. KCN	93.4	3.6	2.4	0.6
1. Et_2O, reflux 46 h 2. KCN	58.4	16.0	20.6	4.9

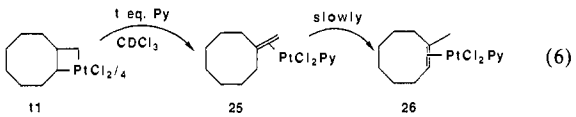
and **24**, respectively.[3,20] Thus, it was anticipated that **11** might yield cyclononene. However, the reaction proceeded by reductive

23 24

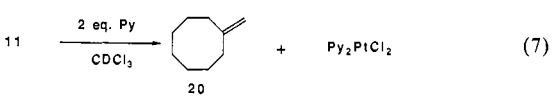
elimination exclusively to yield **10**. This is intriguing in that the same result was obtained from **7a** IPC and from the IPC of phenylcyclopropane. Thus, it appears to be more reasonable to conclude that the bicyclo[*X*.1.0] systems are analogous to simple cyclopropanes and the norbornyl system **7a**. It may then be postulated that bicyclo[*X*.1.0]alkenes may react similarly to substrates **7b** and **7c**.

Reactions of Pyridine Complex 12. (1) Reaction of Complex 11 with Pyridine. As noted in eq 3, complex **12** is best prepared by reacting **11** with neat pyridine. However, the traditional method[8] of preparing **12** by the addition of only 2 equiv of pyridine in $CDCl_3$ led to rearrangement. This prompted us to investigate the rearrangement in more depth.

If only 1 equiv of pyridine was added to **11**, rearrangements occurred as shown in eq 6. Complexes **25** and **26** were identified by comparing their NMR data to those derived from the reaction



(6)

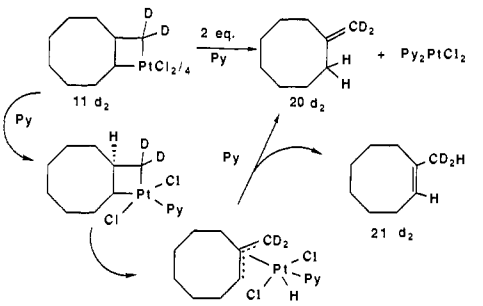


(7)

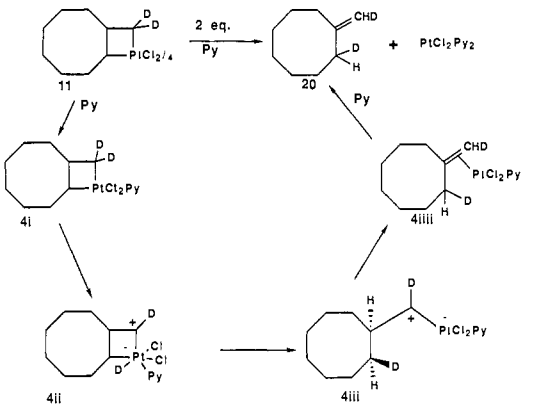
of olefin with Zeise's dimer and pyridine. It is important to note that subsequent reaction of **25** and/or **26** with another equivalent of pyridine released the olefin and yielded Py_2PtCl_2 as a solid precipitate. On the other hand, if 2 equiv of pyridine were used to solubilize **11**, hydrocarbon **20** was generated in nearly quantitative yield (eq 7). It is surmised for this latter reaction that **25** is formed initially and is subsequently decomposed with the extra pyridine to form **20**. These steps must be faster than rearrangement to **26** since the complete conversion to **26** required 25–28 h at room temperature whereas the reaction shown as eq 7 is complete in 6 h.

Finally, there are two pathways commonly accepted for the formation of olefinic products **20** or **25** from **11** and they are diagramed as Schemes III and IV. The path shown as Scheme III has support from the work of Johnson[9] and Brown[10] whereas

Scheme III



Scheme IV



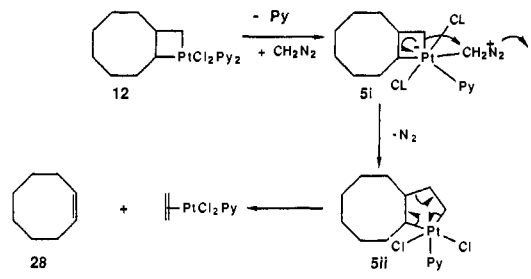
that shown as Scheme IV has been supported by the work of Puddephatt.[11] Obviously, these paths can be distinguished by deuterium-labeling experiments as shown. Complex **11-*d*$_2$** with 87% deuterium per proton at C(1) was prepared with cyclooctene, CD_2N_2, and Rh_2OAc_4 followed by Zeise's dimer. This was verified by ^1H, ^2H, and ^{13}C NMR spectroscopic analyses of **12-*d*$_2$**. Treatment of **11-*d*$_2$** with pyridine in chloroform gave **20** in nearly quantitative yield. Subsequent ^1H and ^2H NMR analyses revealed that one deuterium was located on the exocyclic methylene carbon and one was on the ring carbons adjacent to the olefinic ring carbon. The NMR data for **20-*d*$_2$** are the following: ^1H 4.74 (s, 1 H), 2.18 (m, 3 H), 1.63 (m, 4 H), 1.49 (m, 6 H); ^2H 4.77, 2.17. Thus, the pathway shown as Scheme IV appears to be the major pathway in this organometallic system.

It is important to note in complex **4i** that there are three types of hydrogens available to the platinum: 1-β, 1-α (tertiary), and 2-α (secondary). The actual choice made is one of the secondary protons. One explanation for this behavior might be that steric hindrance from the 8 membered ring carbons forces the platinum moiety to a square-pyramid geometry with chlorine and pyridine in the basal plane. This generates an open coordination site which is available to only one of the secondary hydrogens but trans to

(8) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.

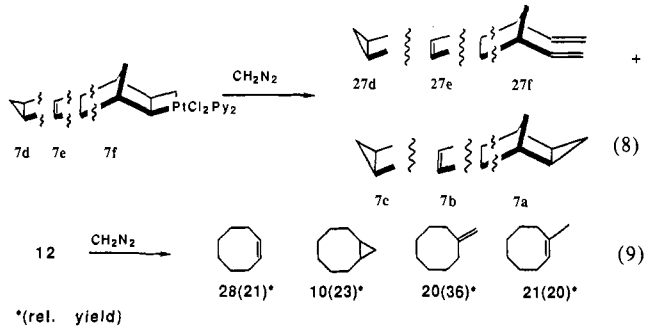
(9) Johnson, T. H.; Cheng, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 5277.
(10) Cushman, B. M.; Brown, D. B. *Inorg. Chem.* **1981**, *20*, 2490.
(11) Puddephatt, R. J.; Al-Essa, R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 45. Puddephatt, R. J.; Ling, S. S. M. *J. Chem. Soc., Chem. Commun.* **1982**, 412.

Scheme V



the other three. Further work is underway on substituted systems to test this hypothesis.

(2) Reaction of 12 with Diazomethane. Previous work in our laboratory has shown that diazomethane reacts with platinacyclobutane complexes to yield dienes as shown in eq 8.[12] The results of a parallel experiment with complex **12** are shown in eq 9.



Although there is no evidence for the production of 1,9-decadiene, which would be analogous with the reaction of **7d**, **7e**, and **7f**, product **28** does reflect a pathway which is similar to that proposed for eq 8 (Scheme V). The difference between this scheme and that proposed for the reaction shown as eq 8 is the structure of intermediate **5ii**. For the norbornyl system, a symmetrical intermediate was proposed to explain products **27d**, **27e**, and **27f**.[12] It is important to note that Scheme V is a proposed scheme and has not been proved.

Summary

A preparative procedure has been described for the synthesis of platinacyclobutanes from cis-disubstituted cyclopropane derivatives. To demonstrate the method, platinacyclobutane derivatives were prepared from bicyclo[4.1.0]heptane (**1**), bicyclo[6.1.0]non-3-ene (**16**), and bicyclo[6.1.0]nonane (**10**). Due to its stability, the platinacyclobutane complex (**12**) has been briefly explored with regard to chemical transformations. Results from heating it in ether suggest that a previously postulated π-allyl intermediate may not be necessary. Treatment of **11** with Me_2SO leads to 100% reductive elimination, a result analogous to that obtained from similar reactions of simple cyclopropane derivatives and the platinacyclobutane complex from tricyclo[3.2.1.$0^{2,4}$]octane. Finally, an excellent method for converting alkenes via cyclopropanes to the exocyclic methylene derivatives was found in the treatment of the IPC with 2 equiv of pyridine in chloroform. Deuterium labeling in this reaction indicates that the transformation occurs by an initial α-hydride transfer rather than an initial β-hydride transfer.

Experimental Section

General. Proton ^{13}C and ^{195}Pt NMR spectra were collected on a Bruker WM 250 spectrometer. MAS/CP spectra were obtained at 37.7 MHz for ^{13}C, and mass spectral data were collected on a VG-16 spectrometer. Pyridine-d_5, Me_2SO-d_6, and $CDCl_3$ were obtained from Stohler, diethyl ether was distilled from calcium hydride prior to use, and diazomethane was prepared from Aldrich Diazald. Zeise's dimer was prepared from K_2PtCl_4 from Johnson-Matthey Corp. Analyses were done by Galbraith Laboratories.

Methylenecyclooctane (20) was prepared by the method of Wittig and Schoellkopf:[13] ^1H NMR ($CDCl_3$) 4.74 (s, 2 H), 2.18 (dd, 4 H), 1.63 (m, 4 H), 1.49 (m, 6 H); ^{13}C NMR;[14a] MS.[14b]

Methylcyclooctene (21) was prepared by addition of methyl Grignard to cyclooctanone with strong acid workup: ^1H NMR ($CDCl_3$) 5.32 (dd, 1 H), 2.11 (dd, 2 H), 2.04 (ddd, 2 H), 1.66 (s, 3 H), 1.44 (m, 8 H); ^{13}C NMR ($CDCl_3$) 137.0 (s), 124.1 (d), 30.3 (t), 30.2 (t), 28.0 (t), 26.6 (t), 26.5 (t), 26.2 (t), 23.5 (q); MS, *m/e* (%) 124 (M^+, 41.5), 109 (15.9), 96 (90.7), 81 (100), 67 (86.8), 55 (52.2), 42 (69.4).

Cyclononene (22) was prepared by LiAlH reduction of cyclononane followed by P_2O_5 dehydration: ^1H NMR ($CDCl_3$) 5.50 (m, 2 H), 2.12 (m, 4 H), 1.46 (m, 8 H); ^{13}C NMR ($CDCl_3$) 130.1 (d), 25.9 (t), 25.7 (t), 25.3 (t), 25.2 (t); MS.[15]

Cyclopropanes 10, 13, and 16. Compounds **10**, **13**, and **16** were prepared from cyclooctene, cyclohexene, and 1,5-cyclooctadiene, respectively, by the method of Rawson and Harrison.[16]

(a) **10**: ^1H NMR;[17a] ^{13}C NMR ($CDCl_3$) 30.0 (t), 27.3 (t), 26.7 (t), 15.5 (d), 9.82 (t); MS.[17b]

(b) **13**: ^1H NMR;[18a] ^{13}C NMR;[18b] MS.[18c]

(c) **16**: ^1H NMR;[19] ^{13}C NMR ($CDCl_3$) 130.3 (d), 29.8 (t), 27.2 (t), 16.5 (d), 12.2 (t); MS, *m/e* (%) 122 (M^+, 3.6), 107 (8.0), 93 (26.3), 80 (100), 67 (68.2), 54 (60.2), 41 (32.8).

Cyclopropane 10-d_2. Cyclooctene was reacted with CD_2N_2 in dry ether in the presence of a catalytic amount of $Rh_2(OAc)_6$. The CD_2N_2 was generated by addition of Aldrich Diazald to 30% NaOD in D_2O with 2-(2-ethoxyethoxy)ethanol-2-*d* as a solvent. **10-d_2** showed 87% deuterium per proton at C(1): ^1H NMR ($CDCl_3$) 1.94 (2 H), 1.65 (2 H), 1.52 (2 H), 1.30 (4 H), 1.86 (2 H), 0.52 (1 H); ^2H NMR (CCl_4) 0.5, 0.3; ^{13}C NMR ($CDCl_3$) deuterium coupling appeared to the resonance at 9.82.

Reaction of 10 and 10-d_2 with Pt(II). In a 5-dram vial was placed 483 μL of **10** or **10-d_2** (0.422 g, 3.40 mmol) and 3 mL of dry ether. Zeise's dimer (0.100 g, 0.34 mmol) was added, and the reaction was stirred at room temperature until the ether turned yellow. The mixture was then further diluted with 10 mL of dry ether, and stirring was continued until all the ether had evaporated. The light orange colored residue was washed with chloroform until the washings were colorless and then was washed once with 10 mL of pentane. The resulting yellow solid was dried under vacuum and yielded 0.120 g of the IPC in 90% yield.

(a) **11**: mp 136–139 °C dec; MAS/CP NMR 51.0, 30.6, 30.4, 29.6, 26.1, 6.9.

Reaction of 13 with Pt(II). In a 5-dram vial was placed 45 μL of **13** (0.033 g, 0.34 mmol) and 2 mL of dry ether. The suspension was cooled to −20 °C, Zeise's dimer (0.050 g, 0.17 mmol) was added, and the mixture was rapidly evaporated to dryness at 0 °C. The solid IPC was not stable and was immediately reacted with pyridine.

Reaction of 11, 11-d_2, and 14 with Pyridine. The pyridine adduct of the IPC was obtained by adding 2 equiv of pyridine to a stirred suspension of the platinum compound in $CHCl_3$. In chloroform, the adduct was unstable and decomposed with time. As a solid, the pyridine adduct also decomposed rapidly. Alternatively, the pyridine adduct could be obtained by placing the IPC directly in neat pyridine and was stable if kept in pyridine solution.

(a) **12**: mp 245 °C dec; ^1H NMR (py-d_5) 3.93 (dd, 1 H, $J_{Pt,H}$ = 95 Hz), 3.00 (m, 1 H), 3.00 (dd, 1 H, J_{Pt}, H = 88 Hz), 2.78 (dd, 1 H, $J_{Pt,H}$ = obsc), 2.50 (m, 1 H), 2.33 (m, 1 H), 1.33–0.99 (m, 10 H); ^{13}C NMR (py-d_5) 49.2 (d, $J_{Pt,C}$ = 100 Hz), 31.9 (t), 31.5 (t), 30.8 (t), 30.0 (t), 26.3 (t), 26.0 (t), 12.9 (d, $J_{Pt,C}$ = 354 Hz), −7.6 (t, $J_{Pt,C}$ = 357 Hz); ^{195}Pt NMR (py-d_5) 3300; ^1H NMR ($CDCl_3$) 3.6 (dd, 1 H, $J_{Pt,H}$ = 96 Hz), 2.7 (m, 1 H), 2.6 (dd, 1 H, $J_{Pt,H}$ = obsc), 2.5 (dd, 1 H, $J_{Pt,H}$ = obsc), 2.2 (m, 2 H), 1.3 (m, 9 H), 0.7 (d, 1 H); ^{13}C NMR ($CDCl_3$) 48.6 (d, $J_{Pt,C}$ = 85 Hz), 31.2 (t), 30.8 (t), 30.0 (t), 29.5 (t), 25.9 (t), 25.6 (t), 14.2 (d, $J_{Pt,C}$ = 348 Hz), −7.2 (t, $J_{Pt,C}$ = 351 Hz), ^{195}Pt NMR ($CDCl_3$) 3263.

(b) **12-d_2**: ^1H NMR (CCl_4) 3.6 (1 H), 2.7 (1 H), 2.2 (2 H), 1.3 (9 H), 0.7 (1 H); ^2H NMR (CCl_4) 2.85, 2.63; ^{13}C NMR ($CDCl_3$) deuterium coupling appeared to the resonance at −7.2.

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(c) The adduct **15** was unstable but the bipyridyl adduct could be isolated: ^{1}H NMR (py-d_5) 3.66 (ddd, 1 H, $J_{Pt,H}$ = 93 Hz), 3.04 (m, 1 H), 3.01 (dd, 1 H, $J_{PT,H}$ = obsc), 2.76 (dd, 1 H, $J_{Pt,H}$ = obsc), 2.14 (m, 2 H), 1.5-1.0 (m, 6 H); ^{13}C NMR (py-d_5) 44.6 (d, $J_{Pt,C}$ = 98 Hz), 27.2 (t), 25.7 (t), 20.4 (t), 19.9 (t), 5.8 (d, $J_{Pt,C}$ = 369 Hz), -8.6 (t, $J_{Pt,C}$ = 354 Hz); ^{195}Pt NMR (py-d_5) 3315.

Reaction of 11 and 14 with 2,2'-Bipyridine. Three to four equivalents of bpy were added to a stirred suspension of **11** or **14** in $CHCl_3$ or pyridine, respectively. Rotoevaporation of the solution yielded a pink or yellow solid which was chromatographed on SiO_2 to give the bpy adduct (87% yield).

(a) Bpy adduct of **11**: mp >300 °C dec. Anal. Calcd for $C_{19}H_{24}N_2Cl_2Pt$: C, 41.76; H, 4.43. Found: C, 41.63; H, 4.42. ^{1}H NMR ($CDCl_3$) 3.5 (dd, 1 H, $J_{Pt,H}$ = 98 Hz), 2.9 (dddd, 1 H), 2.6 (dd, 1 H, $J_{Pt,H}$ = 91 Hz), 2.4 (dd, 1 H, $J_{Pt,H}$ = obsc), 2.2 (m, 1 H), 2.0 (m, 1 H), 1.7-1.5 (m, 9 H), 1.3 (d, 1 H); ^{13}C NMR ($CDCl_3$) 47.4 (d, $J_{Pt,C}$ = 84 Hz), 31.6 (t, $J_{Pt,C}$ ~ 38 Hz), 30.8 (t), 30.5 (t), 29.8 (t), 26.1 (t), 26.0 (t), 13.3 (d, $J_{Pt,C}$ = 341 Hz), -6.6 (t, $J_{Pt,C}$ 364 Hz); ^{195}Pt NMR ($CDCl_3$) 3076.

(b) Bpy adduct of **14**: mp 213 °C dec. Anal. Calcd for $C_{17}H_{20}N_2Cl_2Pt$: C, 39.39; H, 3.89. Found: C, 38.80; H, 3.84. ^{1}H NMR ($CDCl_3$) 3.28 (ddd, 1 H, $J_{Pt,H}$ = 92 Hz), 3.06 (m, 1 H), 2.68 (dd, 1 H, $J_{Pt,H}$ = 84 Hz), 2.46 (dd, 1 H, $J_{Pt,H}$ = 80 Hz), 2.05 (m, 1 H), 1.8-1.3 (m, 7 H); ^{13}C NMR ($CDCl_3$) 42.8 (d, $J_{Pt,C}$ = 91 Hz), 27.4 (t, $J_{Pt,C}$ = 24 Hz), 24.6 (t, $J_{Pt,C}$ = 15 Hz), 20.3 (t, $J_{Pt,C}$ = 42 Hz), 19.4 (t, $J_{Pt,C}$ = 48 Hz), 5.2 (d, $J_{Pt,C}$ = 366 Hz), -7.7 (t, $J_{Pt,C}$ = 341 Hz); ^{195}Pt NMR ($CDCl_3$) 3095.

Formation of 19 from 16. To a stirred solution of **16** (0.042 g, 0.34 mmol) in 10 mL of dry ether was added Zeise's dimer (0.100 g, 0.34 mmol). Complex **17** formed as a yellow precipitate and was isolated by filtration at the end of an hour. This precipitate was placed in 1.5 mL of chloroform, Zeise's dimer (0.100 g, 0.34 mmol) was added, and the mixture was purged with N_2 for 20-30 min. The mixture was then subjected to 3 freeze-thaw cycles and flame sealed in a thick-walled tube under vacuum. The sealed tube was heated to 95 °C for 15 min with frequent agitation. Extraction with chloroform followed by centrifugation and evaporation of the resulting solution yielded **18** as an orange solid. This solid was placed in pyridine solution and 2,2-bipyridine (0.156 g, 1.00 mmol) was added with stirring. Evaporation of the solution yielded a pink solid which was chromatographed on SiO_2 with $CHCl_3$ to give **19** as a white solid: mp 243 °C dec; ^{1}H NMR ($CDCl_3$) 5.73 (m, 2 H), 3.57 (dddd, 1 H, $J_{Pt,H}$ = 95 Hz), 3.15 (m, 1 H), 2.59 (dd, 1 H, $J_{Pt,H}$ = 91 Hz), 2.54-1.82 (m, 8 H), 1.56 (m, 1 H); ^{13}C NMR ($CDCl_3$) 131.8 (d), 130.4 (d), 47.8 (d, $J_{Pt,C}$ = 82 Hz), 34.1 (t), 32.2 (t), 25.3 (t), 24.9 (t), 12.5 (d, $J_{Pt,C}$ = 345 Hz), -6.1 (t, $J_{Pt,C}$ = 361 Hz), ^{195}Pt NMR ($CDCl_3$) 3072.

Reaction of 11 with Me_2SO. Complex **11** (0.100 g, 0.26 mmol) was placed in 2 mL of cold Me_2SO. A green solution formed which was left standing for 12 h. After this time, the only hydrocarbon species in solution was bicyclo[6.1.0]nonane.

Thermal Decomposition of 11 in Et_2O. Complex **11** (0.100 g, 0.26 mmol) in 10 mL of dry ether was refluxed with stirring for 46 h. An aliquot was removed at 10 h. The solid products was rotoevaporated and then were added to stirred solutions of KCN (0.042 g, 0.65 mmol) in 2 mL of H_2O. Stirring was continued until the solid dissolved and then the solution was extracted with $CHCl_3$.

Reaction of 12 with CH_2N_2. Complex **12** was made from **11** with 2 equiv of pyridine in $CHCl_3$ at 0 °C. A large excess of CH_2N_2 was then added to **12** via a stream of dry N_2. Following completion of the reaction, the mixture was distilled under full vacuum to obtain any volatile products. GC/MS and NMR analysis of these products revealed 21% **28**, 23% **10**, 36% **20**, and 20% **21**, by comparison to standards.

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Regioselective Acylation of Secondary Hydroxyl Groups in Sugars Catalyzed by Lipases in Organic Solvents

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Abstract: Several unrelated, commercially available lipases (porcine pancreatic, bacterial, yeast, and fungal) can catalyze transesterification reactions between trichloroethyl butyrate and monosaccharides with blocked C-6 hydroxyl groups (enzymatically acylated or chemically alkylated) in dry organic solvents. Lipases exhibit a remarkable regioselectivity by discriminating among the four available secondary hydroxyl groups in C-6 protected glucose, galactose, and mannose. While some lipases exclusively acylate the C-3 hydroxyl group, others display an overwhelming preference toward the C-2 hydroxyl group. This positional specificity of lipases was used for the preparation of various sugar diesters and, consequently, for either fully enzymatic or chemicoenzymatic preparative synthesis of C-2 or C-3 monoesters of glucose.

Modification of only one out of several identical functional groups in a molecule is a fundamental challenge to organic chemists. An important and synthetically relevant example of this problem is the regioselective acylation of hydroxyl groups in sugars: even discrimination between primary and secondary hydroxyls usually involves multistep procedures, while there is no general basis for the positionally specific acylation of the more abundant, secondary OH groups.[1]

Although enzymes often exhibit a remarkable regioselectivity,[2] enzymatic acylation of sugars in water is thermodynamically unfavorable and hence requires expensive cofactors as a source of free energy. However, enzymes do not have to be used in aqueous solutions and can function as catalysts in organic solvents when certain straightforward rules are followed.[3] In organic media enzymes retain their inherent keen specificity; in addition, they catalyze reactions that are practically impossible in water.[3] For instance, lipases regioselectivity[4] and stereoselectivity[5] acylate alcohols in organic solvents in a quantitative fashion, whereas in

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