Platina(IV)cyclopentanes. Stereoselective Synthesis and Structural Characterization of Trisubstituted Platinacyclopentanes

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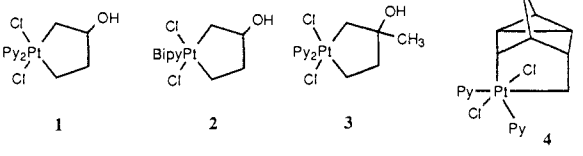
Abstract: In this report, it has been shown that Pt(II) readily oxidatively adds 1,2,3-trisubstituted cyclopropanes with kinetic preference for the syn isomer effecting an epimeric separation. Subsequent acid-catalyzed hydrolysis of the 2-(hydroxymethyl)platina(IV)cyclobutane yields the platina(IV)cyclopentane complex with regio- and stereospecificity. Finally, 3-hydroxyplatina(IV)cyclopentane was oxidized to the corresponding ketone, forming the carbon-bound platinum(IV) enolate complex.

Metallacyclopentane complexes are considered to be important as reaction intermediates in catalytic processes and as organic transformation reagents.[1-3] Among these cyclic complexes, the platinum analogues offer unique features such as thermal stability, various oxidation states, and a nuclear spin of $^1/_2$ to aid NMR characterization. Further, synthetic methodologies leading to a variety of metallacyclopentane derivatives with desired substitution patterns may provide investigators with an opportunity to study mechanisms of reaction as well as new organic and organometallic transformations.

There are only a few references to platina(IV)cyclopentanes engendered basically from oxidative addition to the Pt(II) analogue.[4] Two alternative preparative routes involve carbocyclic rearrangements from platina(IV)cyclobutane derivatives. Puddephatt[5] has cleverly prepared complexes **1–3** by ring enlargement

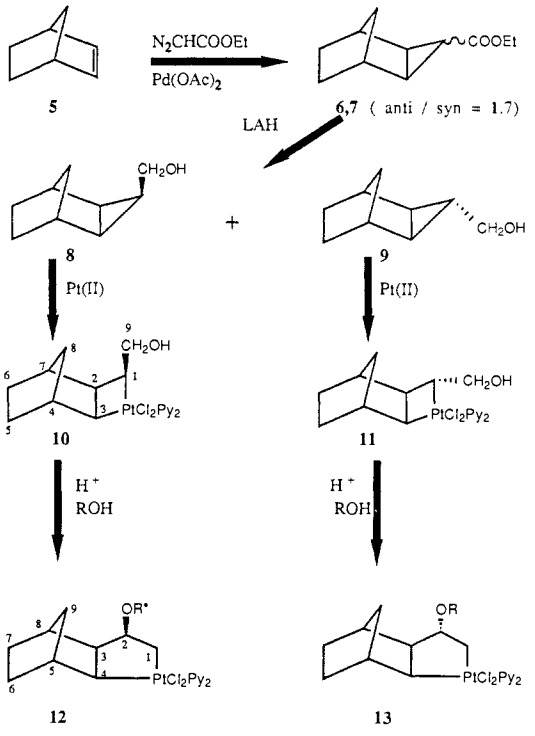


of the mesylate esters of platina(IV)cyclobutanes under solvolysis conditions. In 1983, we reported[6] the formation of **4** by a platinum(II)-facilitated rearrangement of *endo*-tricyclo[3.2.1.$0^{2,4}$]-oct-6-ene.

In this report, we show that trisubstituted platina(IV)cyclopentane complexes can be readily prepared stereospecifically in excellent yield by ring expansion from the platinacyclobutanes. In addition, a crystal structure of one of the cyclopentane complexes is presented to unambiguously establish its structure and stereochemistry.

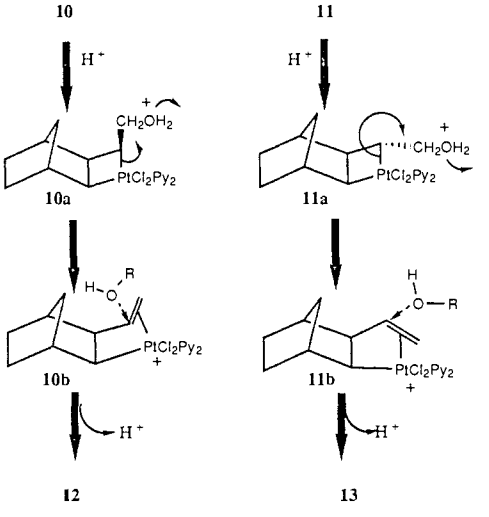
The reaction sequence elaborated in this study is shown in Scheme I. Reduction of the carboethoxy moiety is necessary as Pt(II) will not oxidatively add to cyclopropanes containing an

Scheme I[a]



[a] Asterisk indicates R = H, CH_3, and CH_2CH_2OH.

Scheme II



electron-withdrawing functionality. Separation of epimers **8** and **9** is effected by advantaging their reaction rate difference with

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Table I. ^{13}C NMR Chemical Shift Data for Platinacyclic Complexes (J_{Pt-C})

C no.	10	11	12 (R = CH_3)	13 (R = CH_3)	12 (R = H)	13 (R = H)	12 (R = CH_2CH_2OH)	13 (R = CH_2CH_2OH)	14
1	6.4 (370)	4.0 (370)	21.2 (551)	21.9 (544)	25.9 (548)	25.4 (544)	21.5 (554)	22 (544)	28.9 (586)
2	56.7 (98)	59 (98)	82.9 (56.4)	86.6 (52)	77.1 (45)[c]	78.3 (56)	81.9 (56)	85.95 (59)	219.5 (38)
3	13.0 (394)	14.4 (398)	52.5	56.4	55.9	60.1	53	57.4	60.9
4	40.1 (10)	41.3 (28)	41.8 (531)	36.6 (523)	44.5 (537)	37 (523)	42.2 (530)	36.3 (524)	33.8 (509)
5	28.6	29.2 (41)	44.2	39.8	43.4	39.6	44.5	39.7	41.1
6	28.9	27.4	29.3 (32)	32.2	30.9	32.2	29.9 (31)	32.2 (26)	30.9 (28)
7	37.8	40.7	30.8	28.2	30.8	28.3	31.1	28.2	28.7
8	37.5	35.6	37.3	43.0	37.9	43	37.2	43	43.7
9	63.7 (24)	67 (28)	36.8	36.4	37.9	36.3	38.1	36.3	37.0
10			57.1[a]	57.6[a]			62[b]	62.1[b]	
11							70.4[b]	69.5[b]	

[a] $-CH_3$. [b] $-C(10)-C(11)-OH$. [c] Obtained in pyridine-d_5.

Pt(II). Thus, in a reaction where the Pt(II) is limited to the [**8**], only **10** is formed. Filtration of **10** leaves a solution of **9**, which when reacted with additional Pt(II) yields **11**. Subsequent reaction of either **10** or **11** with 3 drops of H_2SO_4 in ROH yields the platinacyclopentane with both regio- and stereospecificity (Scheme II). The regiochemistry argument comes from the proposed intermediates **10b** and **11b** in the reaction sequences in which the cyclopentane derivative is clearly favored over the cyclobutane complex.[7] The stereospecificity is proposed to be derived from nucleophilic attack at C(2) on the olefinic face, which is anti to the platinum functionality. Subsequent ring closure at the C(1) terminus yields **12** and **13**. Apparently there is no equilibrium between **10b** and **11b**.

Structural Characteristics. Both NMR spectroscopy and X-ray crystallography were used in this endeavor to provide readily identifiable features for future investigations and to ensure the stereochemical assignments.

The ^{13}C NMR data for the platinacyclobutanes (**10** and **11**) and six new platina(IV)cyclopentanes are listed in Table I. Carbons directly attached to ^{195}Pt show typically large coupling constants such as those shown for C(1) and C(3) in the cyclobutanes and C(1) and C(4) in the cyclopentanes.[5,6,8] It is important to note that the $^1J_{Pt-C}$ coupling constants for the cyclopentane complexes are larger than those observed for the cyclobutane derivatives, clearly indicating an increase in the s character of the Pt–C bond in going to the five-membered ring.

Crystals of the anti isomer **13** (R = CH_3) were isolated from a chloroform–heptane mixture and analyzed on a Nicolet R3mE diffractometer.[9] The structure shown in Figure 1 unambiguously establishes the stereochemistry for this isomer and, by inference, all of the others. Selected bond angles and distances are shown in Table II.

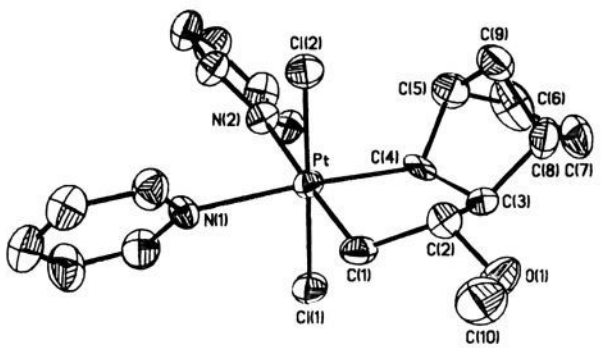
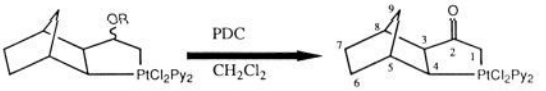


Figure 1. Thermal ellipsoid (50% probability) of **13** (R = CH_3) with labeling scheme.

Table II. Selected Bond Angles (deg) and Distances (Å) for **13** (R = CH_3)

	Angles		
Pt–C(1)–C(2)	110 (1)	Cl(1)–Pt–Cl(2)	178.6 (1)
C(1)–C(2)–C(3)	111 (1)	N(1)–Pt–N(2)	87.5 (4)
C(2)–C(3)–C(4)	110 (1)	C(4)–Pt–N(1)	175.9 (4)
C(3)–C(4)–Pt	111 (1)	C(1)–Pt–N(2)	178.2 (4)
C(4)–Pt–C(1)	83.6 (5)		
	Distances		
Pt–C(1)	2.04 (1)	Pt–Cl(2)	2.325 (4)
Pt–C(4)	2.08 (1)	Pt–N(1)	2.26 (1)
Pt–Cl(1)	2.319 (3)	Pt–N(2)	2.24 (1)

Finally, we report on the oxidation of complexes **12** and **13**, R = H (eq 1). The significance here is that it is not known what types of reactions platinum derivatives can tolerate. Clearly, in



(1)

12 or 13(R = H) 14

this case with 60–70% yields, the complex is reasonably stable. Further work is underway to explore its chemistry. Finally, the key ^{13}C NMR data for **14** is the following: C(1), 28.9 ppm (J_{Pt-C} = 586 Hz); C(2), 219.5; C(3), 60.9; C(4), 33.8 (J_{Pt-C} = 509 Hz). The complete data are listed in Table I. The CO stretch was observed at 1694 cm^{-1}, indicating a reduction of double-bond character.

Summary. In summary, there are several significant results in this report: (a) Platinum(II) will oxidatively add to trisubstituted cyclopropanes, which has never been observed previously. (b) The syn isomer reacts faster with Pt(II) than does the anti isomer. (c) Ring expansion to the cyclopentane complex is facile, regiospecific, and stereospecific. (d) Oxidation of the 3-hydroxyplatinacyclopentane complex proceeds reasonably well, with the platinacyclopentane moiety surviving the reaction conditions to form a platinum(IV) enolate.

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(9) X-ray structure determination of **13** (R = CH_3): Tan-colored crystals of **13** were grown by vapor diffusion of heptane into a chloroform solution. A suitable specimen (approximately 0.18 × 0.52 × 0.54 mm) was mounted on a glass fiber for data collection on a Nicolet R3mE automated diffractometer at 25 °C with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Axial photographs showed orthorhombic symmetry, and systematic absences defined the space group as *Pbac*. Unit cell dimensions of a = 14.591 (4), b = 15.585 (4), and c = 18.329 (3) Å were determined by least-squares refinement with 25 centered reflections in the range 25° < 2θ < 34°. Data collection was by $\theta/2\theta$ scans for 7592 unique reflections in the range 3° < 2θ < 65°. Data reduction, including corrections for Lorentz and polarization effects gave 3131 reflections with $I > 3\sigma(I)$, which were used for structure solution and refinement. The platinum position was obtained from a Patterson synthesis, and difference maps gave the remaining non-hydrogen positions. Calculated density for $C_{20}H_{26}N_2OCl_2Pt$, Z = 8, is 1.84 gm/cm^3 (F(000) = 2240). Absorption corrections were calculated by Gaussian integration using crystal dimensions and indices for crystal faces, μ = 73.5 cm^{-1}; transmission factor range was 0.056–0.330. All atoms were refined with anisotropic thermal parameters, except hydrogens, which were assigned to idealized positions with a common refined isotropic thermal parameter. The orientation of the methyl group was taken from a difference map. Statistical weighting was used, and no corrections for extinction were needed. Refinement of 236 parameters gave a final R value of 0.0568 (R_w = 0.0692). All calculations were performed on a Data General Eclipse computer with the SHELXTL program package by G. M. Sheldrick, Nicolet Instrument Corp., Madison, WI.

Experimental Section

General Procedures. All reactions were run under ambient air conditions, and all products were stable to air. Diethyl ether (Baker) was distilled from CaH_2 and stored over molecular sieves prior to use. Zeise's dimer was prepared from K_2PtCl_4 by the method of Littlecott.[10] The epimeric hydrocarbon mixture was prepared from the reaction of norbornene with ethyl diazoacetate in the presence of Rh(II) acetate.[11] All other solvents and reagents were reagent grade and used without further purification. Electron impact mass spectra were determined with a VG Analytical, Inc., MM16F spectrometer. The mass spectra were analyzed for molecular ion peaks only. NMR spectra were recorded on a Bruker WM250 (250-MHz) spectrometer and are reported in units of parts per million with residual protons in the solvent as an internal standard (deuteriochloroform, 7.24).

Reduction of 6 and 7. A solution of the epimeric hydrocarbons **6** and **7** (10 g, 0.056 mol) in diethyl ether (75 mL) was added dropwise to a stirred solution of lithium aluminum hydride (LAH, 8.5 g, 0.224 mol) in diethyl ether (50 mL). The reaction was allowed to stir at room temperature for 4 h after which time water (40 mL) was slowly added and the mixture stirred for 1 h. The aqueous phase was extracted four times with diethyl ether. The organic phases were combined, and the solvent was removed by rotoevaporation to give the epimeric alcohols **8** and **9** as a light yellow oil: 70% yield; MS *m/e* 138 (M^+); ^1H NMR ($CDCl_3$) δ 3.72 (d, 2 H, *syn*-CH_2OH), 3.21 (d, 2 H, *anti*-CH_2OH), 2.33 (br s, 2 H), 2.19 (br s, 2 H) 1.5–0.5 (overlapping m, 16 H); ^{13}C NMR ($CDCl_3$) (syn) δ 64.9, 35.9, 30.4, 29.8, 21.5, 16.2; (anti) δ 60.4, 35.4, 29.2, 28.3, 20.6, 16.2.

Platinum Complex 10. The integratable ^1H NMR spectrum of the mixture of epimeric hydrocarbons **8** and **9** showed the ratio (syn to anti) to be 1:1.7. Zeise's dimer (154 mg, 0.262 mmol) was added to a stirred solution of the epimeric mixture (0.22 g, 0.56 mmol of **8** and 0.96 mmol of **9**) in diethyl ether (5 mL). The reaction was allowed to gently reflux for 1 h after which time the ether was removed and the yellow product washed and triturated with pentane. The pentane washings were combined and rotoevaporated to yield pure **9** as determined by ^1H NMR. Diethyl ether (5 mL) was then added to the yellow precipitated platinum complex and 2 equiv of pyridine added to the stirred suspension, giving a clear yellow solution. Rotoevporation of the solvent yielded a yellow oil, which solidified to a yellow powder upon repeated trituration with pentane. Yields of 92–96% were obtained: ^1H NMR ($CDCl_3$) δ 3.82 (m, 1 H), 3.59 (m, 1 H), 2.98–2.6 (overlapping m, 4 H), 2.39 (d, 1 H), 2.18 (d, 1 H), 1.7–0.98 (overlapping m, 5 H).

Platinum Complex 11. To a stirred solution of **9** (obtained in pure form in the preparation of **10**) (0.059 g, 0.425 mmol) in ether (5 mL) was added Zeise's dimer (125 mg, 0.213 mmol). The mixture was allowed to gently reflux for 1 h after which time the volume of ether was reduced and the product precipitated by the addition of pentane. Following repeated trituration with pentane, the solid platinum complex was placed in ether (5 mL) and 2 equiv of pyridine was added to the stirred suspension giving a yellow solution. The ether was subsequently removed by rotoevaporation to yield a yellow oil, which solidified upon repeated trituration with pentane: ^1H NMR ($CDCl_3$) δ 3.5–3.0 (overlapping m, 4 H), 2.75 (dd, 1 H), 2.63 (d, 1 H), 2.08 (br s, 1 H), 2.15 (br s, 1 H), 1.55–1.0 (overlapping m, 5 H).

Ring Expansion of 10 To Yield 12 (R = H). In a 50-mL round-bottomed flask equipped with stir bar and condenser were placed complex **10** (124 mg, 0.22 mmol), 10 mL of a 60% (v/v) acetone–water mixture, and 4 drops of concentrated H_2SO_4. The reaction was allowed to stir for 12 h at room temperature after which the acetone was removed from the mixture by rotoevaporation and the product extracted from the acidic water with 3 × 5 mL portions of $CHCl_3$. The organic phases were combined and rotoevaporated to yield a dark yellow oil, which solidified upon repeated trituration with pentane. Yields of 85–95% were obtained: ^1H NMR ($CDCl_3$) δ 4.18 (dd, 1 H), 3.79 (dd, 1 H), 3.26 (d, 2 H), 2.29 (d, 1 H), 2.13 (d, 1 H), 1.95 (d, 1 H), 1.81 (m, 2 H), 1.51 (overlapping m, 2 H), 1.35–1.0 (overlapping m, 2 H).

Ring Expansion of 10 To Give 12 (R = Me). In a 50-mL round-bottomed flask equipped with stir bar and condenser were placed platinum complex **10** (124 mg, 0.22 mmol), absolute methanol (Baker, 10 mL), and 4 drops of concentrated H_2SO_4. The reaction was allowed to stir at room temperature for 12 h after which the reaction mixture was decanted into a 125-mL separatory funnel and 15 mL of $CHCl_3$ added. The solution was then washed with 4 × 50 mL portions of H_2O. The organic phase was then separated and rotoevaporated to yield a yellow oil, which solidified to a yellow powder upon trituration with pentane. Yields of 85–95% were obtained: ^1H NMR ($CDCl_3$) δ 4.18 (dt, 1 H), 3.91 (dd, 1 H), 3.38 (s, 3 H), 3.31 (dd, 1 H), 2.39 (dd, 1 H), 2.29 (d, 2 H), 2.08 (d, 1 H), 1.81 (dd, 1 H), 1.6–1.03 (overlapping m, 5 H).

Ring Expansion of 10 To Yield 12 (R = CH_2CH_2OH). This procedure is analogous to the preparation of **12** (R = Me) except that ethylene glycol (100%, 10 mL) was used in place of absolute methanol: ^1H NMR ($CDCl_3$) δ 4.29 (dd, 1 H) 3.92 (dd, 1 H), 3.76 (m, 2 H), 3.61 (m, 2 H), 3.32 (dd, 1 H), 2.5–2.18 (overlapping m, 3 H), 2.11 (d, 1 H), 1.92 (dd, 1 H), 1.6–1.0 (overlapping m, 5 H).

Ring Expansion of 11 To Yield 13 (R = H). This procedure is directly analogous to the preparation of **12** (R = H), using platinum complex **11** (124 mg, 0.22 mmol) in place of platinum complex **10**: ^1H NMR ($CDCl_3$) δ 4.13 (br m, 1 H), 3.79 (br d, 1 H), 3.68 (dd, 1 H), 2.58 (dd, 1 H), 2.29 (br s, 1 H), 1.84 (br m, 1 H), 1.50 (overlapping m, 2 H), 1.4–1.0 (overlapping m, 4 H).

Ring Expansion of 11 To Yield 13 (R = Me) and 13 (R = CH_2CH_2OH). These procedures are directly analogous to those given for **12** using platinum complex **11** (124 mg, 0.22 mmol) in place of complex **10**: ^1H NMR ($CDCl_3$) (**13**, R = Me) δ 3.87–3.64 (overlapping m, 2 H), 3.39 (s, 3 H), 3.31 (dd, 1 H), 2.54 (dd, 1 H), 2.26 (d, 1 H), 2.12 (d, 2 H), 1.94 (dd, 1 H), 1.6–1.0 (overlapping m, 5 H) (**13**, R = CH_2CH_2OH) δ 4.1–3.49 (overlapping m, 7 H), 2.51 (dd, 1 H), 2.4–2.08 (overlapping m, 3 H), 1.98 (dd, 1 H), 1.6–1.36 (overlapping m, 2 H), 1.3–1.0 (overlapping m, 3 H).

Oxidation of 12 or 13 (R = H) To Give 14. In a 50-mL round-bottomed flask equipped with stir bar and condenser were placed complex **12** (R = H) or **13** (R = H) (150 mg, 0.267 mmol), methylene chloride (25 mL), and pyridinium dichromate (PDC; 0.4 g, 1.067 mmol). The reaction was allowed to stir at room temperature for 24 h after which the volume of CH_2Cl_2 was reduced by rotoevaporation and the reaction mixture then chromatographed on short Florisil column using CH_2Cl_2 as the eluent. The CH_2Cl_2 was then removed by rotoevaproation to yield a light yellow oil, which solidified upon trituration with pentane. Yields of 60–70% were obtained: ^1H NMR ($CDCl_3$) δ 3.94 (d, 1 H), 3.73 (d, 1 H), 3.51 (d, 1 H), 2.42 (d, 1 H), 2.35 (d, 1 H), 2.12 (d, 1 H), 1.92 (d, 1 H), 1.54 (dd, 1 H), 1.51 (dd, 1 H), 1.4–1.0 (overlapping m, 3 H).

Registry No. **6**, 16529-68-3; **7**, 16545-17-8; **8**, 114129-02-1; **9**, 16529-71-8; **10**, 114033-58-8; **11**, 114129-05-4; **12** (R = Me), 117497-47-9; **12** (R = CH_2CH_2OH), 117497-48-0; **12** (R = H), 117603-73-3; **13** (R = CH_2CH_2OH), 117603-72-2; **13** (R = H), 117497-49-1; **13** (R = Me), 117603-74-4; **14**, 117497-50-4; Zeise's dimer, 12073-36-8.

Supplementary Material Available: Listings of atomic coordinates, bond lengths and angles, and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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