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Stereochemistry of ring opening of cyclopropane by platinum(II)

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Abstract

Cyclopropane is opened by treatment with chloroplatinic acid to form a platinacyclobutane. The stereochemistry at both sites of formation of the platinum–carbon bonds was determined by the use of cyclopropane-1,2,3-d_3 in which all three deuterium atoms were on the same side of the ring. The ^{1}H spectrum of the product was A_2X, in which the coupling constant, 10.4 Hz, clearly indicates that the *cis* relationship between the protons had been retained. Therefore, the ring opening occurs with retention at both carbon atoms.

Introduction

Metallacyclobutanes are important intermediates in alkene polymerization and metathesis and in cyclopropane ring opening. Platinacyclobutanes, first described by Tipper [1], have been well characterized by chemical and spectroscopic methods [2]. Without added nucleophiles, platinacyclobutanes are tetrameric. In the presence of good nucleophiles, monomers may be formed. The X-ray crystallographic structure of the monomeric dipyridine adduct of unsubstituted cyclopropane indicates that one C–C bond is entirely cleaved, and the platinacyclobutane has an approximate ring pucker of 168° (the dihedral angle between two three-atom planes) [2].

Determination of the stereochemistry of ring opening has been key to understanding the mechanism. Studies of substituted cyclopropanes have shown that insertion of platinum occurs with retention at both carbons [3]. Even the presence of a single substituent, however, can alter the mechanism of reaction. Thus, in the bromination of cyclopropane, there is a profound mechanistic change between unsubstituted and monosubstituted cyclopropanes [4]. Consequently, we have sought a method to determine the stereochemistry of ring opening by platinum using unsubstituted cyclopropane. We have prepared *cis*-cyclopropane-1,2,3-d_3, in which each carbon atom bears a deuterium atom and all three deuteriums are on the same side of the ring [5]. We have subjected this substrate to platination and report the results herein.

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Results and discussion

The tetramer of 1,1-dichloroplatinacyclobutane (which would be named as a platinetane by the Hantzsch–Widman system) was prepared and isolated according to the Tipper procedure [1]. It is not expected that mechanistic differences would have arisen had another source of platinum, such as Zeise's dimer, been used. The brown solid was dissolved in 4/1 $CDCl_3/CD_3OD$. The ^1H spectrum at 400 MHz consisted of a doublet at δ 2.65 and a multiplet at δ 2.32. The vicinal coupling constant was easily measured to be 10.4 Hz without deuterium decoupling (Fig. 1). This value was confirmed in the ^{195}Pt satellites. Peaks marked with an X were proved to be impurities by proton–proton decoupling experiment: irradiation of the multiplet at δ 2.32 caused the doublet to collapse but left the impurity peaks unchanged.

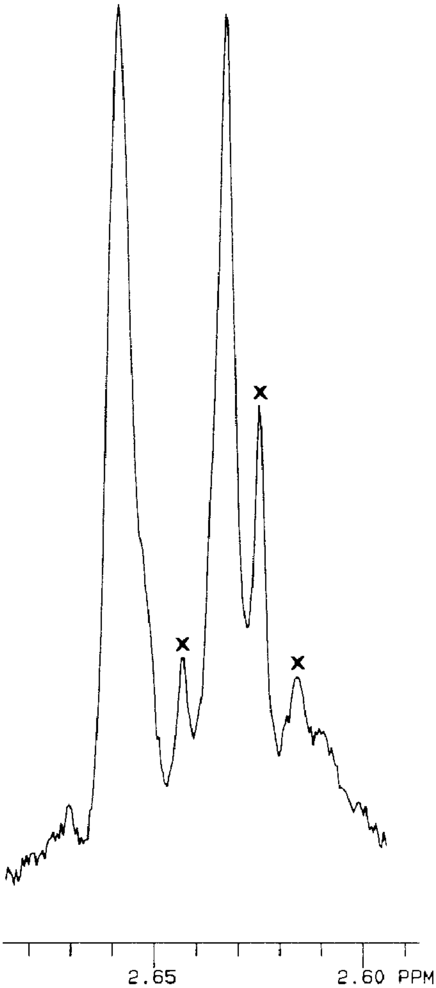
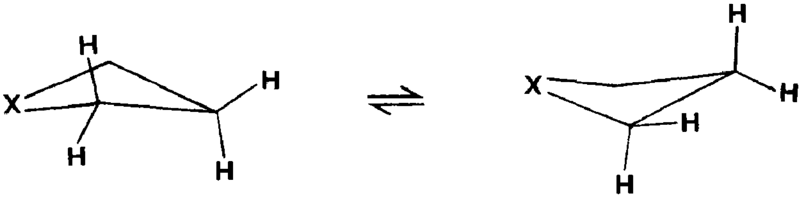


Fig. 1. The 400 MHz proton spectrum of the tetramer of 1,1-dichloroplatinacyclobutane-2,3,4-d_3 in $CDCl_3$. Peaks marked with an X are impurities.

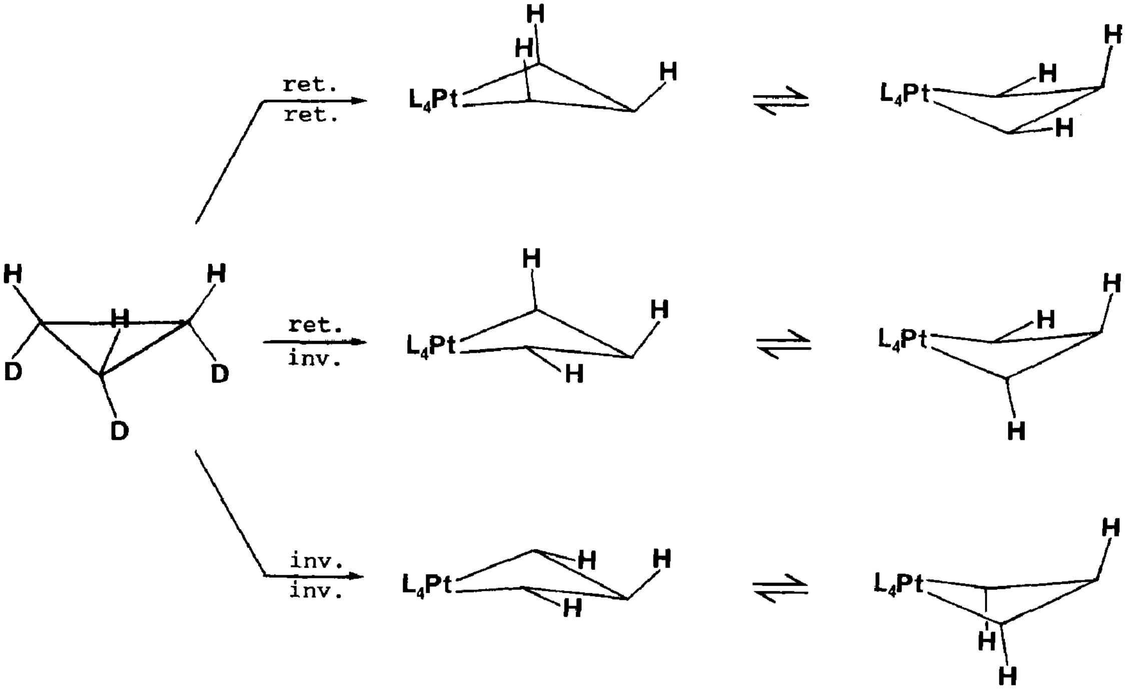
Most saturated four-membered rings are puckered. The angle between the planes (C1–C2–C3 and C3–C4–C1) in cyclobutane is about 150° (180° would be planar) [6], so that the average *cis* and *trans* couplings are quite different, eq. 1 ($X = CH_2$).



(1)

The *cis* coupling (10.4 Hz) is the average through ring flipping of couplings close to the 0° Karplus maximum. Hence it is much larger than the trans coupling (4.9 Hz), which is the average of values well below the Karplus maximum at 180° [7]. Thus in nonplanar four-membered rings, it is easy to distinguish *cis* and *trans* couplings.

The ring pucker angle in platinacyclobutane (168°) is larger than that in cyclobutane, so the relative inequality of the couplings should be maintained or enhanced. Since platinacyclobutane is closer to planarity than cyclobutane, its *cis* coupling should be much larger than the *trans* coupling. In unlabeled platinacyclobutane the spectrum is deceptively simple. Because the protons at the 2 and 4 positions are closely coupled to those at the 3 position, spin state mixing gives rise to observation of only a single averaged coupling constant of 8.0 Hz (which should not be interpreted as equal *cis* and *trans* couplings).



Scheme 1

Our starting cyclopropane has hydrogens that are mutually *cis*. If ring opening occurred with double retention, the large *cis* coupling would be retained (Scheme 1). If inversion occurred at both carbons, the coupling would be transformed into the smaller trans coupling. In the event that retention occurred at one carbon but inversion (or racemization) occurred at the other, an intermediate value would be obtained. The value in the unlabeled compound (8.0 Hz), in fact, is a second-order average of the large *cis* (ca. 11 Hz) and the small trans (ca. 5 Hz) coupling.

The spectrum of the labeled compound is an A_2X pattern (Fig. 1 shows the A portion) and the coupling is 10.4 Hz. This large value is unambiguously a *cis* coupling. No more than a few percent of a *trans* coupling could be admixed. Consequently, we conclude that ring opening of cyclopropane occurs with retention at both carbon atoms, in agreement with conclusions drawn from substituted systems [3].

Experimental

Approximately 0.05 g (1.1 mmol) of *cis*-cyclopropane-1,2,3-d_3 [5] was vacuum-transferred into a 5 mm tube containing 0.05 g of chloroplatinic acid and 0.5 ml of acetic anhydride. The tube was sealed and placed in the dark for 17 h. The tube was opened and the liquid decanted from the brown precipitate. The precipitate was washed twice with $CHCl_3$, dried, transferred to a 5 mm NMR tube, and dissolved in 4/1 $CDCl_3/CD_3OD$. Proton spectra were taken at 400 MHz on a Varian XLA-400.

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