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REACTIONS OF PLATINUM COMPLEXES WITH ALKYL-SUBSTITUTED CYCLOPROPANES. THE FORMATION OF PLATINACYCLOBUTANES

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Summary

Mono-, di-, and tri-alkyl-substituted cyclopropanes react with certain platinum complexes to form platinacyclobutanes, tetrakis[dichloro(substituted-cyclopropane)platinum]. These products result from insertion of platinum into the least-substituted carbon—carbon bond of the cyclopropane ring. Although the stereochemistry of insertion is compatible with steric control of the reaction, evidence is presented for dominant electronic control, with platinum behaving as a nucleophile in the actual insertion step. Formation of these compounds, and their subsequent chemical reactions, appear to be competitive with rearrangement to platinum—olefin complexes.

Introduction

In 1955 Tipper reported [1] that the reaction of cyclopropane with chloroplatinic acid in acetic anhydride produced a complex of empirical composition $PtCl_2(C_3H_6)$. This material was subsequently shown to be tetrameric, and to result from insertion of platinum into a carbon—carbon bond of the cyclopropane ring [2—4]. A number of analogous compounds with hexyl- and phenyl-substituted cyclopropanes have since been prepared, usually from the reaction of the substituted cycloproprane with Zeise's dimer in either dichloromethane or ether [5—7]. In most of these cases the course of the reaction appears to be sterically controlled, so that platinum inserts into the least hindered carbon—carbon bond of the cyclopropane ring. However, Powell and McQuillin showed that electronic factors are also important, since with *p*-tolylcyclopropane platinum inserts into a substituted ring bond [6,7]. Recent work [8] suggests that electronic factors may in fact be dominant. Phenylcyclopropane has been found to give an initial product resulting from insertion at the C(1)—C(2) bond, and this material then undergoes a facile isomerization to the C(2)—C(3) insertion product. In analogous materials derived from Pt^0, elec-

tronic effects are clearly important, and, for example, $Pt(PPh_3)_4$ reacts with 1,1,2,2-tetracyanocyclopropane to give insertion into the tetrasubstituted C(1)—C(2) bond [9].

Surprisingly, there have been no reports of the insertion products derived from simple alkyl-substituted cyclopropanes where the steric requirements of the substituents are likely to be small. Under the preparative conditions used originally by Tipper [1] (i.e., chloroplatinic acid in acetic anhydride) methyl-substituted cyclopropanes yield both pyrylium ion salts [10] and platinum complexes of β,γ-unsaturated ketones [11], but no isolable insertion products. Since the mechanism required to account for the formation of certain of these products involves initial production of the insertion complexes, we have been interested in their isolation. We report here the results of studies on the interaction of simple alkyl-substituted cyclopropanes with platinum complexes under conditions designed to allow the isolation of platinacyclobutanes.

Experimental

All cyclopropanes (Chemical Samples Company or Columbia Organic Chemicals) were used as received. Chloroplatinic acid, of nominal composition $H_2PtCl_6 \cdot 6\ H_2O$, was prepared from metallic platinum. This material was dried by gently heating the acid in a recrystallizing dish so that its actual water content, as determined by titrimetric molecular weight determinations, was from one to three waters of hydration. There appeared, however, to be no dependence of the reactions on the amount of water present. Zeise's salt, $KPtCl_3(C_2H_4) \cdot H_2O$, was converted to the dimer, $[PtCl_2(C_2H_4)]_2$, by dissolution in ethanolic hydrochloric acid, filtration, and removal of solvent. Microanalyses were performed by Dornis und Kolbe, West Germany, and Integral Microanalytical Laboratories, Inc., Raleigh, N.C. Infrared Spectra in the region 4000 to 250 cm^{-1} were obtained on a Beckman IR-20-A Spectrophotometer. ^1H NMR measurements were recorded on a JEOL C-60HL High Resolution 60 MHz Spectrometer and a JEOL JNM-MH-100 100 MHz Spectrometer.

Preparation of complexes

$[PtCl_2(1,1\text{-}Me_2CCH_2CH_2)]_4$. (a) From chloroplatinic acid: 1.42 g of 1,1-dimethylcyclopropane were added to a solution of 0.62 g chloroplatinic acid in 25 ml of ethyl acetate. An oil immediately formed, but after 3 h of stirring at room temperature, the solution was again clear. After stirring for 24 h, a pale yellow powder, IIa, had precipitated from solution. The complex was isolated by filtration. Yield: 0.138 g (34%). Complexes of *trans*-1,2-dimethylcyclopropane and 1,1,2-trimethylcyclopropane were prepared in an analogous fashion.

(b) From Zeise's dimer: 4.0 ml of 1,1-dimethylcyclopropane were added to a suspension of 0.285 g Zeise's dimer in anhydrous diethyl ether (30 ml) which had been cooled in an ice/H_2O bath. The reaction mixture was then refluxed while stirring with a drying tube attached to the condensor. The orange color of the undissolved Zeise's dimer gave way to the pale yellow color of the product after several hours. The product, IIa, was then filtered, washed with $CHCl_3$, followed by washing with ether, and dried in vacuo. Yield: 0.144 g (48%). Complexes of *trans*-1,2-dimethylcyclopropane, 1,1,2-trimethylcyclopropane,

ethylcyclopropane, 1,1-diethylcyclopropane, and isopropylcyclopropane were prepared in an analogous fashion.

$PtCl_2(1,1\text{-}Me_2CCH_2CH_2)(C_5H_5N)_2$. 0.122 g of $[PtCl_2(C_5H_{10})]_4$ (IIa) were suspended in 3 ml of $CHCl_3$ and cooled in an ice/H_2O bath. 0.1 ml of pyridine, also previously cooled in an ice/H_2O bath, was added, and dissolution of the complex occurred within ca. 15 min, yielding a yellow solution which was eluted with $CHCl_3$ through a 1 cm × 5 cm silica gel column. The yellow eluant was evaporated to dryness in vacuo giving a pale yellow powder, IIIa. Yield: 0.113 g (61%). Bis-pyridine adducts of the *trans*-1,2-dimethylcyclopropane, ethylcyclopropane, and isopropylcyclopropane complexes were prepared in an analogous fashion.

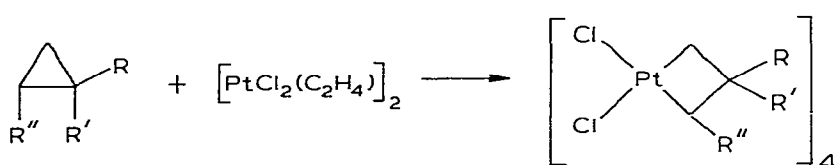
$PtCl_2(2,3\text{-}CH_2CMeCMe_2)(C_5H_5N)$. Attempts to prepare the bis-pyridine adduct of the 1,1,2-trimethylcyclopropane complex by the above procedure gave instead an olefin complex, IV, resulting from cyclopropane isomerization. Yield, 81%. Anal. Found: C, 30.17; H, 3.45; N, 4.30. $C_{11}H_{17}Cl_2NPt$ calcd.: C, 30.80; H, 3.97; N, 3.27%.

$PtCl_2(1,1,2\text{-}Me_2CCMeHCH_2)(C_5H_5N)_2$. 0.077 g of $[PtCl_2(C_6H_{12})]_4$ (IIc) were suspended in 2 ml acetone and cooled in an acetone/dry ice bath. 0.1 ml of pyridine were added and the system was then allowed to slowly warm to room temperature. Complex IIIa was isolated by adding H_2O to the acetone solution, resulting in a gummy, yellow solid. Yield: 0.071 g (62%).

Results and discussion

In the case of 1,1-dimethyl-, *trans*-1,2-dimethyl-, and 1,1,2-trimethyl-cyclopropane, platinacyclobutanes may be prepared by the reaction of the substituted cyclopropane with chloroplatinic acid in ethyl acetate. These conditions approximate those [10,11] which lead to pyrylium ions and β,γ-unsaturated ketones, differing primarily in the absence of an acylating agent. The structures of the platinacyclobutanes which form are those considered to be necessary intermediates in the formation of pyrylium ions, and thus support the proposed mechanistic sequence [10].

The most facile route to the formation of the platinacyclobutanes is reaction of the substituted cyclopropane with Zeise's dimer in refluxing ether, according to eq. 1.



(1)

I a-f

II a-f

Ia, IIa: R = R′ = CH_3; R″ = H

Ib, IIb: R = R″ = CH_3; R′ = H

Ic, IIc: R = R′ = R″ = CH_3

Id, IId: R = CH_2CH_3; R′ = R″ = H

Ie, IIe: R = R′ = CH_2CH_3; R″ = H

If, IIf: R = $CH(CH_3)_2$; R′ = R″ = H

Characterization of these materials as containing the PtC_3 ring follows from analytical data, physical properties, infrared spectra, and NMR spectra. The

complexes are formed as air-stable pale yellow powders which are insoluble in solvents with which they do not react. Analytical data (Table 1) establish the empirical formulas in each case to be $PtCl_2$(substituted-cyclopropane). As expected, the infrared spectra of all these complexes are comparable and contain certain features which appear to be characteristic of the structure. A weak C—H stretch near 3000 cm^{-1}, strong absorptions near 1100 cm^{-1} (which appear to be characteristic of the PtC_3 ring), and a single strong Pt—Cl stretching mode near 320 cm^{-1} support the structural assignment. Conclusive evidence for insertion, and also detailed structural assignments, come from NMR spectra (Table 2). These complexes all dissolve in pyridine-d_5, presumably forming bis-pyridine adducts $PtCl_2Py_2$(substituted-cyclopropane) (vide infra). Although pyridine adducts are isolable in certain cases, characterization of the complexes by NMR in pyridine-d_5 allows all to be compared on a common basis, and furthermore precludes the problems of isomerization [8] which might occur during the synthesis and isolation of the adducts. As has been reported [5] for the pyridine adducts of other substituted platinacyclobutanes, the cyclopropyl protons are shifted significantly downfield compared to the parent cyclopropanes. The presence of ^{195}Pt—^1H spin—spin coupling is particularly useful for structural assignments, with J(PtH) ca. 85 Hz for protons on the α-carbon and J(PtH) ca. 25 Hz for protons on α-methyl substituents. In each case, the data demonstrate that insertion occurs at the least substituted carbon—carbon bond, i.e., insertion is consistent with steric control.

For the insertion products derived from 1,1-dimethyl-, *trans*-1,2-dimethyl-, ethyl-, and isopropyl-cyclopropane, bis-pyridine adducts can be prepared

TABLE 1

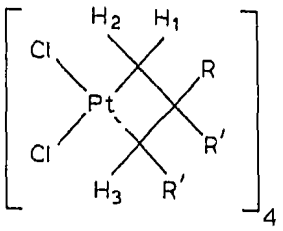
ANALYTICAL DATA FOR CYCLOPROPANE COMPLEXES AND BIS-PYRIDINE ADDUCTS

Cyclopropane precursor	Complex	Empirical formula	Analysis Found (calcd.) (%)		
			C	H	Cl
1,1-Dimethylcyclopropane	IIa	$PtCl_2(C_5H_{10})$	17.90 (17.87)	3.06 (2.99)	21.20 (21.10)
1,2-Dimethylcyclopropane	IIb	$PtCl_2(C_5H_{10})$	17.95 (17.87)	2.88 (2.99)	21.03 (21.10)
1,1,2-Trimethylcyclopropane	IIc	$PtCl_2(C_6H_{12})$	20.64 (20.58)	3.38 (3.43)	20.43 (20.25)
Ethylcyclopropane	IId	$PtCl_2(C_5H_{10})$	17.60 (17.87)	2.86 (2.99)	20.84 (21.10)
Isopropylcyclopropane	IIe	$PtCl_2(C_7H_{14})$	22.34 (23.08)	3.67 (3.85)	— —
	IIf	$PtCl_2(C_6H_{12})$	20.30 (20.58)	3.21 (3.43)	20.27 (20.25)
1,1-Dimethylcyclopropane	IIIa	$PtCl_2(C_5H_{10})(C_5H_5N)_2$	36.10 (36.45)	3.82 (4.05)	14.12 (14.34)
1,2-Dimethylcyclopropane	IIIb	$PtCl_2(C_5H_{10})(C_5H_5N)_2$	35.08 (36.45)	3.71 (4.05)	14.84 (14.34)
Ethylcyclopropane	IIId	$PtCl_2(C_5H_{10})(C_5H_5N)_2$	35.85 (36.45)	3.94 (4.05)	14.62 (14.34)
Isopropylcyclopropane	IIIf	$PtCl_2(C_6H_{12})(C_5H_5N)_2$	37.04 (37.85)	4.29 (4.34)	5.09[a] (5.52)

[a] Nitrogen

TABLE 2

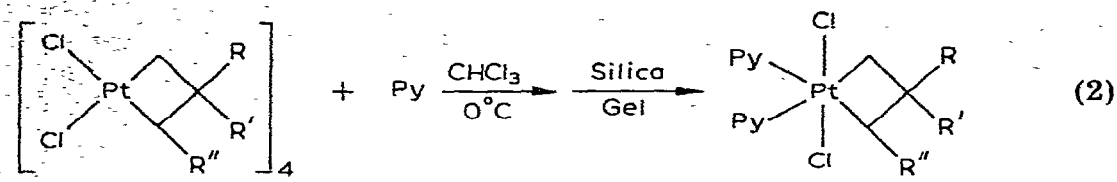
1H NMR SPECTRA (C_5D_5N) OF INSERTION COMPLEXES



Complex	Substituents			Chemical shift (δ, ppm) [a]					
	R	R'	R''	R	R'	R''	H(1)	H(2)	H(3)
IIa	CH_3	CH_3	H	1.39 (s, 6H)	—	2.97 (s, 4H, J(PtH) 86.5)	—	—	—
IIb	CH_3	H	CH_3	1.11 (d, 3H, J(HH) 5.6)	[b]	0.84 (d, 3H, J(HH) 6.4, J(PtH) 25.5)	2.98 (m, 3H, J(PtH) ≃ 85)	—	—
IIc	CH_3	CH_3	CH_3	1.24 (s, 3H)	1.40 (s, 3H)	0.74 (d, 3H, J(HH) 7.5, J(PtH) 27.0)	3.75 (m, 2H)	—	2.95 (m, 1H, J(PtH) 87.0)
IId	CH_2CH_3	H	H	0.88 (t, 3H, J(HH) 7.5) 1.65 (m, 2H)	[b]	2.83 (m, 2H, J(PtH) 86.3)	—	3.13 (m, 2H, J(PtH) 83.3)	—
IIe	CH_2CH_3	CH_2CH_3	H	0.88 (t, 6H, J(HH) 6.75) 1.95 (q, 4H, J(HH) 6.75)	— —	2.90 (s, 4H, J(PtH) 87.0)	—	—	—
IIf	$CH(CH_3)_2$	H	H	0.93 (d, 6H, J(HH) 6.0) 1.9 (m, 1H, broad) [c]	[b]	2.94 (m, 4H, J(PtH) ≃ 90)	—	—	—

[a] TMS 0.00 ppm; d, doublet, t, triplet, q, quartet; m, multiplet; s, singlet; all coupling constants in Hz. [b] Not observed. [c] Tentative assignment for methine proton of isopropyl substituent, which is not distinguishable from R'(=H).

according to eq. 2. The isolated products have been characterized by analytical



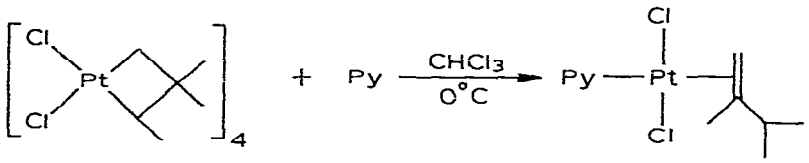
(2)

II III

IIa, IIIa: R = R′ = CH_3, R″ = H
IIb, IIIb: R = R″ = CH_3, R′ = H
IIId, IIId: R = CH_2CH_3, R′ = R″ = H
IIIf, IIIf: R = $CH(CH_3)_2$, R′ = R″ = H

data (Table 1), infrared and NMR spectra using deuteriochloroform as solvent (Table 3). These NMR spectra show upfield shifts relative to the spectra of the insertion complexes in pyridine-d_5, but clearly establish that the structures are identical to those of the initially formed complexes; i.e., that no isomerization has occurred.

As has been reported previously [12], the reaction of IIc (R = R′ = R″ = CH_3) with pyridine in $CHCl_3$ did not give the expected bis-pyridine adduct, but instead produced the isomeric olefin complex IV (eq. 3).



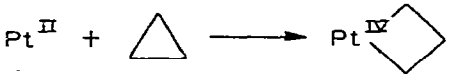
(3)

IIc IV

The authentic bis-pyridine adduct of the trimethylcyclopropane insertion complex has been prepared by performing the above reaction at low (ca. −40°C) temperatures.

Although *trans*-1,2-dimethylcyclopropane undergoes a facile reaction with Zeise's dimer to form a platinacyclobutane, the isomeric *cis*-1,2-dimethylcyclopropane fails to react. This result is consistent with the previous report that *trans*-1-methyl-2-n-butylcyclopropane forms a platinacyclobutane, whereas its *cis*-isomer does not [7]. Similarly, reactions involving either methylcyclopropane or 1,1,2,2-tetramethylcyclopropane produce only minute amounts of product and relative to the other alkyl cyclopropanes, must be considered unreactive.

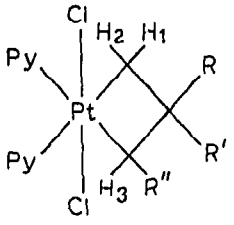
The extent to which electronic factors are important in the formation of platinacyclobutanes has been somewhat ambiguous. The insertion reaction (eq. 4), is formally an oxidative addition. For this reaction, then, platinum is



(4)

TABLE 3

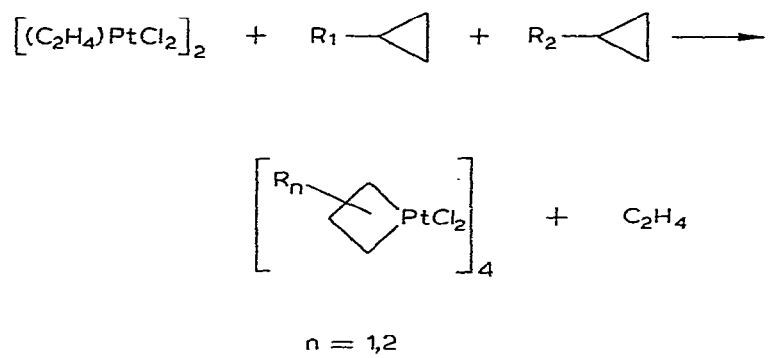
^{1}H NMR SPECTRA ($CDCl_3$) OF BIS-PYRIDINE ADDUCTS



	Substituents			Chemical shift (δ, ppm) [a]					
	R	R'	R''	R	R'	R''	H(1)	H(2)	H(3)
IIIa	CH_3	CH_3	H	1.15 (s, 6H)	—	2.64 (s, 4H *J*(PtH) 85.5)	—	—	—
IIIb	CH_3	H	CH_3	0.98 (d, 3H, *J*(HH) 6.75)	[b]	0.57 (d, 3H, *J*(HH) 6.75, *J*(PtH) 24.0)	2.95 (m, 1H)	2.31 (m, 2H)	—
IIIc	CH_3	CH_3	CH_3	1.03 (s, 3H)	1.13 (s, 3H)	0.47 (d, 3H, *J*(HH) 7.0, *J*(PtH) 24.6)	2.67 (2H, AB pattern)	—	3.45 (m, 1H, *J*(HH) 7.0)
IIId	CH_2CH_3	H	H	0.85 (t, 3H, *J*(HH) 6.5) 1.48 (m, 2H)	[b]	2.49 (m, 2H, *J*(PtH) 78.0)	—	2.80 (m, 2H, *J*(PtH) 78.0)	—
IIIf	$CH(CH_3)_2$	H	H	0.87 (d, 6H, *J*(HH) 6.0) 1.6 (m, 1H, broad) [c]	[b]	2.69 (m, 4H, *J*(PtH) 90.0)	—	—	—

[a] TMS δ 0.00 ppm; d = Doublet, t = Triplet, q = Quartet, m = Multiplet, s = Singlet, coupling constants in Hz. [b] Not observed. [c] Tentative assignment for methine proton of isopropyl substituent, which is not distinguishable from R'(= H).

expected to behave as a nucleophile, and to attack the carbon—carbon bond bearing the most electronegative substituents. In the case of simple alkyl-substituted cyclopropanes this will be the least-substituted bond, and thus electronic and steric factors both favor insertion as observed. In contrast, electronic and steric factors predict different sites of reaction for phenyl-substituted cyclopropanes. Since platinum inserts, at least initially, into the C(1)—C(2) bond of phenyl- [8] and *p*-tolyl-cyclopropane [6], it appears that electronic control is dominant here. This is certainly true as well for the reaction of tetracyanocyclopropane with Pt^0, as platinum inserts into the most highly substituted carbon—carbon bond [9]. Although the stereochemistry of insertion in all of these cases is thus compatible with platinum behaving as a nucleophile, relative reactivities of various cyclopropanes have been interpreted as suggesting that platinum behaves as an electrophile [7]. Competition studies [7] involving reaction 5 led to the conclusion that reactivity decreased in the sequence R =



(5)

n = 1,2

n-C_6H_{13} > $PhCH_2$ > Ph > *o*-$NO_2C_6H_4$. These two contradictory conclusions (i.e., relative reactivity suggesting electrophilic attack by platinum and the stereochemistry of reaction suggesting nucleophilic attack by platinum) are compatible with a two-stage reaction (eq. 6) involving initial formation of an

(6)

edge-bonded "π-complex" [5] * and a subsequent irreversible (or nearly so) insertion step. If k_1 is rate-determining, then the observed reactivity sequence is reasonable, since this edge-complex can be thought of as an acid—base adduct with the basicity of the donor, cyclopropane, being enhanced by the presence of electron-donating substituents on the ring. The stereochemistry of insertion, however, depends only on the second half of this reaction sequence. Presuming that the edge-complex possesses some fluxionality, platinum can then exhibit its nucleophilic character by inserting into the C—C bond of the ring carrying the most electronegative substituents. Recent kinetic studies of the reaction of arylcyclopropanes with either $[PtCl_2(C_2H_4)]_2$ or $[PtCl_2(CH_2CH_2CH_2)]_4$ in tetra-

* It is not our intent to convey structural implications by the use of the term "π-complex", but rather the existence of some as yet unknown type of molecular association between the cyclopropane and the platinum center.

hydrofuran have led Tipper et al. [13] to propose a similar mechanism for these reactions.

Acknowledgement

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