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REACTIONS OF PLATINUM COMPLEXES WITH SPIRO COMPOUNDS. FORMATION OF PLATINOSPIROALKANES

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Summary

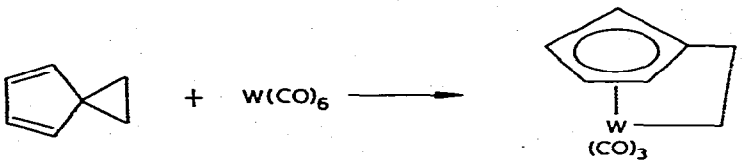
Spiro[2.*n*]alkanes (n = 2, 4, 5) react with platinum complexes to form compounds of composition $PtCl_2$(spiroalkane). These materials have been characterized by infrared and nuclear magnetic resonance spectra, and the point of insertion has been shown to be the cyclopropyl carbon—carbon bond opposite the spiro carbon.

Introduction

Within the past decade there has been an increasing interest in reactions of saturated carbon—carbon bonds promoted by transition metal complexes, an interest motivated at least in part by the attempt to mimic homogeneously reactions which are of great importance heterogeneously. Extensive studies of metal ion catalysis of the symmetry forbidden transformations of strained polycyclic hydrocarbons [1] have demonstrated that metal complexes do indeed participate in carbon—carbon bond cleavage reactions, yet the specific role of the metal remains ambiguous. Reactions of cyclopropanes (and heterocyclopropanes) with platinum-group metal complexes constitute the most thoroughly examined cases of stoichiometric cleavage of carbon—carbon bonds. The resulting insertion products, trimethylenemetal complexes or metallocyclobutanes, have been characterized for a variety of substituted cyclopropanes [2].

Surprisingly, there have been no reports of simple insertion of a metal into a three-membered ring attached directly to another ring system (either fused or spiro), and only limited reports of any interaction of spiroalkanes with metal complexes. Spiropentane reacts with di-μ-chlorodichlorodiethylene)dipalladium to give 2-(2-chloroethyl)-π-allylpalladium chloride, a product in which both three-membered rings have been cleaved [3]. Under similar conditions, neither spiro[2.4]heptane nor spiro[2.5]octane react [4], presumably reflecting the smaller amount of steric strain in these species. The unsaturated spiroalkane

spiro[2.4]hepta-4,6-diene reacts with several metal complexes to form alkylene bridged π-cyclopentadienyl-σ-alkyl compounds [5] (eq. 1). It is apparent that



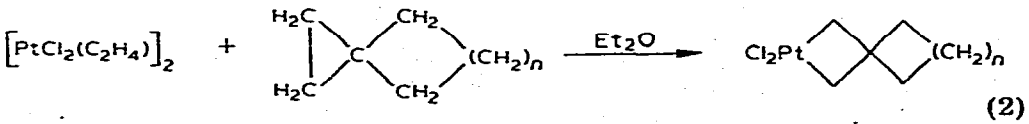
(1)

in these cases part of the driving force, hence the point of cleavage, involves the formation of the aromatic cyclopentadienyl fragment.

We have been examining the diverse reactions which occur between substituted cyclopropanes and platinum complexes [6], and were interested in spiroalkanes for several rasons. First, the added ring strain in the spiro system (relative to cyclopropane itself) should promote the reaction. Secondly, the presence of this strain might be sufficient to alter the normal steric control of the point of insertion. Finally, as we have observed for methyl-substituted cyclopropanes, reactions in acetic anhydride give rise to several acylation products. Should such reactions occur with spiroalkanes they would require cleavage of both rings, and might be expected to lead to a pyrylium ion fused to a cyclobutane ring.

Results and discussion

We previously noted [8] the failure of spiropentane to form a platinocyclobutane upon reaction with Zeise's dimer. Although not pursued, we now believe that the failure to isolate the desired product may be traced to either the specific conditions used, ethanol as solvent and the presence of acid, or, more probably, ready evaporation of spiropentane from the solution. The platinospiroalkane complexes may be prepared by treatment of the spiroalkane with chloroplatinic acid in either acetic anhydride, ethyl acetate, or dichloromethane. However, the most convenient preparation of these insertion products is by direct reaction of the spiroalkane with Zeise's dimer in refluxing ether (eq. 2). The



(2)

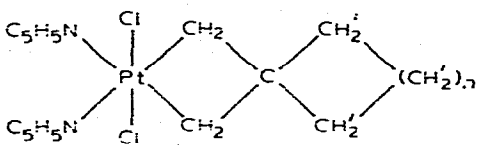
n = 0, 2, 3

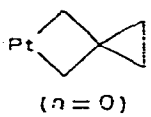
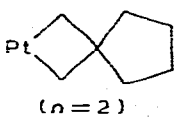
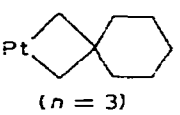
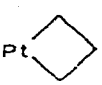
products isolated are generally pure, but are, like the products formed from simple cyclopropanes, insoluble in solvents with which they do not react. More tractable materials are obtained upon formation of the bis-pyridine adducts, which are readily soluble in polar organic solvents.

Infrared spectra of the initially formed complexes, as well as the pyridine adducts, exhibit certain absorptions which are unaffected by variations in the spiroalkane, and which may thus be assigned as characteristic of the platinocyclobutane moiety. A weak absorption near 3010 cm^{-1}, attributable to C—H stretching modes in the heterocyclic ring system, shifts to about 2995 cm^{-1} in the pyridine adducts. A CH_2 deformation mode at 1410 cm^{-1} is unpertubed

TABLE 1

NMR PARAMETERS FOR SPIROALKANE COMPLEXES (Values in parentheses are chemical shifts for comparable protons in the uncomplexed spiroalkanes)



	$\delta(CH_2)$ [a]	$\delta(CH_2')$ [b]	J(Pt—H) (Hz)
 (n = 0)	2.72 (0.75)	0.56 (0.75)	82
 (n = 2)	2.71 (0.42)	1.6 (1.6)	85
 (n = 3)	2.61 (0.22)	1.4 (1.5, 1.3)	84
 [c]	2.60	[2.60]	82

[a] Referred to internal TMS, $CDCl_3$ solutions. [b] For spiroheptane and spirooctane, as well as their platinum complexes, CH_2' absorptions are broad, complex multiplets. [c] There is some variability in NMR parameters for this complex as reported in the literature. We have used the values from ref. 9, which we consider to be the most reliable.

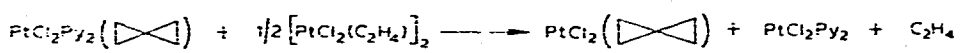
upon adduct formation. An intense absorption near 1090 cm^{-1}, also unperturbed upon formation of the pyridine adduct, appears to be characteristic of the PtC_3 ring system, and is the most useful identifying feature in the infrared spectra of such species.

Table 1 lists pertinent nuclear magnetic resonance data for these complexes, as well as for the unsubstituted cyclopropane complex. These data clearly establish the point of insertion as being the three-membered ring, specifically the carbon—carbon bond remote from the spiro carbon. Previous investigations [2] have shown that the site of reaction is largely sterically controlled, and the results here are consistent with expectations on steric grounds. The near identity of the platinum—hydrogen coupling constants suggests quite similar structural parameters for the platinocyclobutane ring in all of these compounds. The similarity in structural and electronic parameters is also reflected in the small range of chemical shifts observed for the methylene protons adjacent to

platinum. By contrast, the cyclopropyl protons of the spiro[2.*n*]alkanes themselves exhibit chemical shifts ranging from δ 0.75 ppm in the highly strained spiropentane to δ 0.22 ppm in the apparently unstrained (relative to 1,1-dimethylcyclopropane, δ 0.22 ppm) spirooctane.

As has been observed for other complexes resulting from platinum insertion into the three-membered ring, decomposition of $PtCl_2(C_5H_5N)_2(C_5H_8)$ with aqueous KCN leads to the formation of spiropentane only, with no evidence for any rearrangement products. This decomposition reaction, however, is surprisingly slow. The reaction was observed by mixing a saturated solution of KCN in D_2O with a solution of the complex in $CDCl_3$, and monitoring the NMR spectrum of the chloroform layer. The disappearance of signals due to the complex, and the appearance of the free spiropentane signals, was a gradual process with a half-life longer than one day, and after three days small amounts of the complex remained.

Spiropentane contains two potentially active sites for platinum insertion, and we have attempted, without success, to prepare complexes of stoichiometry $(PtCl_2Py_2)_2$(spiro-C_5H_8). The most promising route, involving reaction between $PtCl_2Py_2$(spiro-C_5H_8) and Zeise's dimer in either ether or chloroform, apparently reacts as in eq. 3. and involves pyridine (or spiropentane) transfer.



Experimental

Preparation of complexes.

A. From Zeise's dimer, $[PtCl_2(C_2H_4)]_2$

$PtCl_2$(spiro-C_5H_8). 0.218 g of Zeise's dimer was dissolved in 40 ml anhydrous ether. After cooling in an ice bath, an excess of spiropentane (0.50 g) was added, and the solution heated to reflux for 6 h. The product was filtered and washed with ether, giving 0.20 g (81%) of pale yellow powder. Anal. Found: Pt, 57.90; C, 18.04; H, 2.79. $PtCl_2(C_5H_8)$ calcd.: Pt, 58.39; C, 17.98; H, 2.41%.

$PtCl_2$(spiro-C_7H_{12}). This complex was prepared as above from the reaction of Zeise's dimer and spiro[2.4]heptane, yield 55%. Anal. Found: Pt, 54.01; C, 23,09; H, 3.26. $PtCl_2(C_7H_{12})$ calcd.: Pt, 53.87; C, 23.21; H, 3.34%.

$PtCl_2$(spiro-C_8H_{14}). This complex was prepared as above from the reaction of Zeise's dimer with spiro[2.5]octane, yield 68%. Anal. Found: Pt, 51.78; C, 24.95; H, 3.48. $PtCl_2(C_8H_{14})$ calcd.: Pt, 51.86; C, 25.54; H, 3.75%.

B. From chloroplatinic acid in acetic anhydride

Reaction of chloroplatinic acid with an excess of spiropentane in acetic anhydride led to an insoluble brown powder which defied purification. Although the composition of this material was variable from preparation to preparation, analysis of a typical reaction product indicated a stoichiometry $PtC_{14}H_{16}Cl_3O_4$. Reaction of this product with neat pyridine gave several insoluble materials, as well as a chloroform soluble fraction which, upon isolation, was shown by analysis, infrared, and NMR spectroscopy to be identical to the pyridine adduct of $PtCl_2$(spiro-C_5H_8) as prepared above.

C. From chloroplatinic acid in ethyl acetate or dichloromethane

Reaction of chloroplatinic acid with an excess of either spiropentane or spiroheptane in either ethyl acetate or dichloromethane gave low yields of the appropriate complex, $PtCl_2$(spiroalkane).

D. Conversion of $PtCl_2$(spiroalkane) to $PtCl_2(Py)_2$(spiroalkane)

$PtCl_2(Py)_2$(spiro-C_5H_8). The most facile route to pure complexes was found to be the method of McQuillin and Powell [2]. 0.110 g of $PtCl_2$(spiro-C_5H_8) were suspended in 3 ml of $CHCl_3$. After cooling to 5°C, 0.2 ml of pyridine were added, and the mixture warmed slowly to room temperature. The solution was passed through a short column of silica gel and eluted with chloroform. Evaporation of solvent gave 0.107 g (66%) of product. Anal. Found: Pt, 38.98; C, 36.37; H, 3.59; N, 5.63. $PtCl_2(C_5H_8)(C_5H_5N)_2$ calcd.: Pt, 39.63; C, 36.59; H, 3.68; N, 5.69%.

$PtCl_2(Py)_2$(spiro-C_7H_{12}). This complex prepared in the same fashion as above (68%). Anal. Found: Pt, 37.00; C, 40.10; H, 4.18; N, 4.98. $PtCl_2(C_7H_{12})(C_5H_5N)_2$ calcd.: Pt, 37.47; C, 39.24; H, 4.27; N, 5.38%.

$PtCl_2(Py)_2$(spiro-C_8H_{14}). This complex also was prepared in the same fashion as above (69%). Anal. Found: Pt, 35.97; C, 39.12; H, 4.38; N, 5.21. $PtCl_2(C_5H_5N)_2(C_8H_{14})$ calcd.: Pt, 36.51; C, 40.46; H, 4.53; N, 5.24%.

Spiroalkanes were purchased from Columbia Organic Chemicals, and used as received. Infrared spectra using KBr pellets were obtained on a Beckman IR-20A spectrophotometer. NMR spectra of deuteriochloroform solutions were obtained at 100 MHz using a JEOLCO JNM-MH-100 spectrometer, and at 60 MHz using a JEOL C-60HL high resolution spectrometer. Both TMS and $CHCl_3$ were used as internal references, and all chemical shifts are reported relative to TMS (δ 0.0 ppm).

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