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THE REACTION OF A BRIDGED SPIROPENTANE WITH ZEISE'S DIMER, $[PtCl_2(C_2H_4)]_2$

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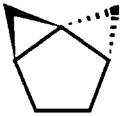
Summary: The products of the reaction of a bridged spiropentane with Zeise's dimer have been studied. Both are formed by insertion into one or the other of the external cyclopropyl C-C bonds. One of them rearranged to a 5-methylenebicyclo[2.1.1]hexane complexed to platinum. The structure of the latter was determined by X-ray crystallography.

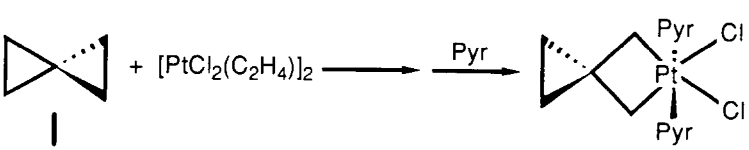
Spiropentane (1) has a strain energy of 63 kcal/mol[1] which is considerably larger than that of two cyclopropane rings. This results from the extra distortion at the central carbon which is forced by symmetry to use sp^3 orbitals. The distortion is easily seen in the angle between the curved bond paths (bent bonds) which is 78° in cyclopropane and increases to 88° for the central carbon of 1.[2] We have studied the bridged spiropentane, 2, which is easily formed by the method of Skattebøl.[3] Here, the strain energy is further increased to 80 kcal/mol as the result of both twisting and bending of the spiropentane unit.[4]

1



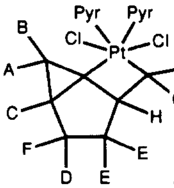
2

We have been interested in the chemical consequence of the increased strain and distortion in 2. Considerable strain would be relieved by cleavage of any of its cyclopropyl C-C bonds. In this connection, reaction with Zeise's dimer was of interest. The reagent normally cleaves cyclopropane rings to form isomerizing platinacyclobutanes which can be trapped and stabilized by the addition of pyridine.[5] The reaction of 1 with Zeise's dimer gives only the product resulting from cleavage of the 2,3-bond, presumably due to steric interactions.[6]



The corresponding reaction of 2 has now been investigated. The reaction was carried out in chloroform at room temperature, and after 2 hr an excess of pyridine was added. The two products were separated by flash column chromatography (1:1 CH_2Cl_2/pentane on Kieselgel 60). The first fraction will be designated as 3 and the second as 4.

The structure of 3 could be determined by its nmr spectra to be one of the expected platinacyclobutanes: ^{1}H nmr (500 MHz, $CDCl_3$): δ 0.25 (m, 1H, J_{PtH} = 42Hz, A), 0.32(m, 1H, B), 0.87(m, 1H, C), 1.32(m, 1H, D), 1.79 (m, 2H, E), 2.18 (m, 1H, F), 2.87 (dd, 1H, J_{PtH} = 80Hz, G), 3.05(m, 1H, H), 3.10(dd, 1H, J_{PtH} = 76Hz, I). ^{13}C nmr: δ 4.63 (CH_2, J_{PtC} = 362Hz), 23.6(CH_2), 27.6(CH), 29.7(C) 30.5(CH_2), 37.3(CH_2), 55.6 (CH, J_{PtC} = 76.8 Hz), and pyridine bands at δ 125.08, 125.16, 137.91, 137.93, 149.39 and 149.8. Homonuclear decoupling showed the coupling pattern given below:

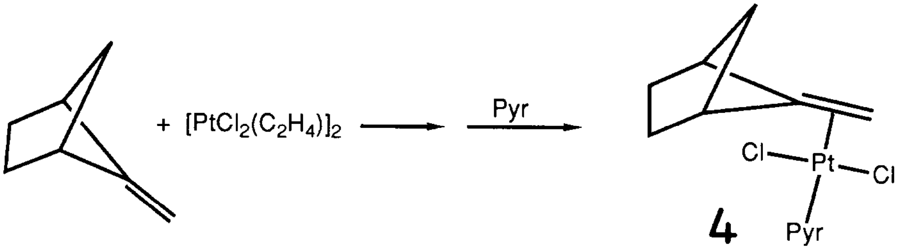


3

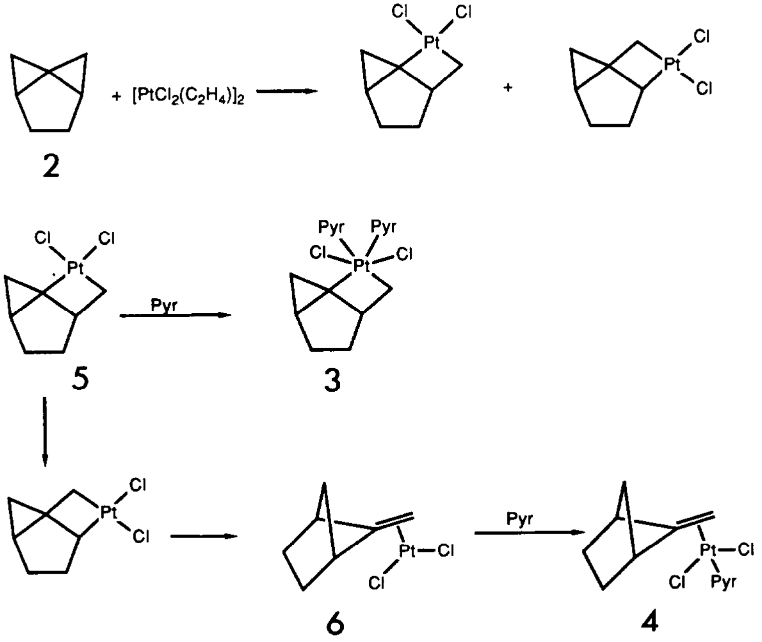
The structure of 4 was determined by X-ray crystallography using a crystal which measured 0.19 x 0.11 x 0.08 mm. Diffraction measurements were made using an Enraf-Nonius CAD-4 fully automated diffractometer using graphite monochromated MoK_α radiation. Preliminary indications of the unit cell based on 25 randomly selected reflections revealed orthorhombic symmetry with the following lattice parameters: a = 6.896(2)Å, b = 8.810(3)Å and c = 23.016(5)Å with $\alpha = \beta = \gamma = 90.0°$. The space group, based on the observed systematic extinctions, could be uniquely assigned as $P2_12_12_1$, Z = 4, with one molecule of composition $PtCl_2C_{12}H_{15}N$ forming the asymmetric unit. The calculated density was 2.095 g/cm³. There were 1152 reflections collected with $2\theta \leq 50°$, 865(75%) of those reflections with $I \geq 3\sigma I$ were taken as observed.

Patterson synthesis revealed the position of the Pt atom. The rest of the structure was found by successive iterations of refinement and difference Fourier syntheses. The absorption coefficient for the compound was μ=105, therefore a numerical absorption correction was performed for the crystal. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated using SDP program HYDRO, and added to the structure calculations. The following full matrix refinement of the non-hydrogen atoms and addition of the hydrogen atoms to the structure factor calculations, without refinement of their positions, resulted in convergence to a standard crystallographic unweighted residual of 0.050, and a weighted residual of 0.033. All intramolecular bond distances and angles are within normal ranges.[7,8]

An ORTEP drawing of the structure is shown in Figure 1 and clearly demonstrates that a rearrangement to a bicyclo[2.1.1]hexane ring system has occurred. This was further confirmed by the formation of 4 from 5-methylenebicyclo[2.1.1]hexane and Zeise's dimer.



When the reaction of 2 with Zeise's dimer was followed by nmr, two adducts, 5 and 6, were initially formed in 1:1 ratio. The ratio changed with time leading to increasing amounts of 6. Upon addition of pyridine shortly after completion of the initial reaction, 3 and 4 were obtained in comparable amounts. However, after the isomerization to 6 had occurred, only 4 was obtained. Thus, the reaction appears to involve insertion of platinum into either of the external cyclopropane C-C bonds. One of the initial adducts, 5, is converted to the other on standing, and the latter undergoes a rearrangement giving 6. This appears to be the first case of Zeise's dimer causing a skeletal rearrangement.



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References

1. Wiberg, K. B. Angew. Chem. 1986, in press.

2. Wiberg, K. B.; Lau, C. D. H.; Bader, R. F. W. to be published. Cf. Bader, R. F. W.; Tang, T.-H., Tal, Y.; Biegler-König, F. W. J. Am. Chem. Soc. 1982, 104, 946.

3. Skattebøl, L. J. Org. Chem. 1966, 31, 2789.

4. Wiberg, K. B. J. Org. Chem. 1985, 50, 5285.

5. Puddephath, R. Coordination Chem. Rev. 1980, 33, 149.

6. Brown, D. B.; Viens, V. A. J. Organomet. Chem. 1977, 142, 117.

7. All data processing was done using a VAX 11/750 and the Enraf Nonius SDP program library (version 18). The plotting and table output programs were written by S. K. Kearsley, Yale, 1985.

8. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, England. Any request should be accompanied by the full literature citation for this communication.

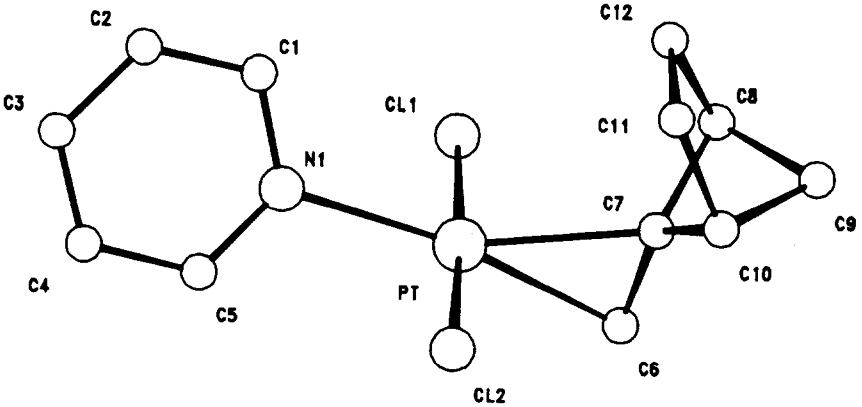

Figure 1

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