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ISOLATION AND CHARACTERIZATION OF 2-[BIS(PYRIDINE)DICHLOROPLATINA]-1-CYANOBICYCLO[1.1.1]PENTANE DERIVED FROM 1-CYANOBICYCLO-[1.1.0]BUTANE AND Pt(II) COMPLEXES

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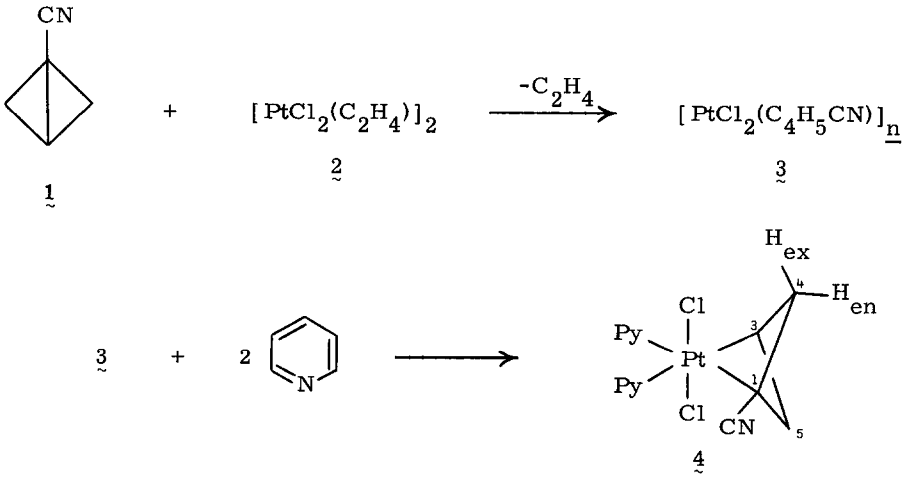
Summary: 2-[Bis(pyridine)dichloroplatina]-1-cyanobicyclo[1.1.1]pentane, obtained by the reaction of 1-cyanobicyclo[1.1.0]butane with di-μ-chlorodichlorobis(ethylene)diplatinum(II) followed by the treatment with pyridine, has been isolated and characterized.

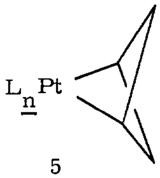
There has been considerable recent interests in transition-metal catalyzed valence isomerizations of highly strained cyclic hydrocarbons.[3] Though many studies have been directed toward the elucidation of the mechanisms of the catalysis, a lot of fundamental problems still remain to be answered. Only a small number of examples have been reported for the detection or isolation of the reactive intermediates.[4] We have been studying the mechanisms of the transition-metal catalyzed reactions of bicyclo[1.1.0]butanes.[3c,d,5] This time we have examined the reaction of 1-cyanobicyclo[1.1.0]butane (1) with Pt(II) species. This paper describes the isolation and characterization of novel 1-substituted 2-platinabicyclo[1.1.1]pentane complexes.

Treatment of a large excess of 1 with di-μ-chlorodichlorobis(ethylene)diplatinum(II) (Zeise's dimer) (2) in acetone at -15 °C resulted in the precipitation of a 1:1 complex 3 as yellow-orange solid in 83% yield, mp 160—170 °C (decomp.). Most of the excess 1 was



recovered unchanged. The IR spectrum of 3 (KBr) showed strong bands at 2210 and 2190 cm^{-1}, assigned to ν (CN), and a weak band at 520 cm^{-1}, assigned to ν (Pt—C). Further structural studies were difficult because of the insolubility of the complex 3 in most common organic solvents. Reaction of 3 with two equiv. of pyridine in methylene chloride at -20 °C proceeded slowly and formed a clear yellow solution, from which the complex 4 was obtained as light brown fine crystals on removal of the solvent. Purification by column chromatography on neutral alumina (Woelm N—Super I, 1:100 methanol—methylene chloride) at -30 °C gave a pure sample of 4 in 43% yield, mp 59—60 °C (decomp.).[6] The complex 4 exhibited a single absorption at 335 cm^{-1} in its IR spectrum, assigned to platinum—halogen stretching vibration,[7] which supports the *trans*-halogen structure.[8] The ^{1}H and ^{13}C NMR spectra of 4 permitted an unambiguous assignment of its structure. The ^{1}H NMR spectrum (CD$_2$Cl$_2$) of 4 exhibited a couple of multiplets at δ 0.8—1.0 (2H) and 1.0—1.2 ppm (2H), which are assigned to H$_{en}$ and H$_{ex}$ at C-4 and C-5. The methine proton at C-3 appeared at δ 2.9—3.1 ppm as a multiplet with a platinum satellite (*J*(Pt-H) 86 Hz). The proton decoupled ^{13}C NMR (^{12}CD$_2$Cl$_2$, -20 °C) contains four kinds of sharp signals occurring at δ 11.9 (C-1, *J*(Pt—C-1) 978 Hz), 16.0 (C-3, *J*(Pt—C-3) 477 Hz), 37.8 (C-4 and C-5), and 123.3 ppm (CN) in addition to those due to the coordinated pyridines (127.6, 141.6, and 155.0 ppm). The gated decoupled spectrum of 4 confirmed a clear-cut assignment of each signal which appeared at δ 11.9 (s, C-1), 16.0 (d, C-3, *J*(C-H) 159 Hz), 37.8 (t, C-4 and C-5, *J*(C-H) 143 Hz), and 123.3 ppm (s, CN). The observed large C-H coupling constants for C-3, C-4, and C-5 are presumably attributed to the fact that 4 has a strained double-puckered conformation, which brings about an increased s character of the C-H bonds and hence large *J* values.[9] This appears to be a common feature in the 2-platinabicyclo[1.1.1]pentane complexes as we reported previously.[5] A large Pt-C coupling constant for C-1 bearing a cyano group can be accounted for by the effect of the electron-withdrawing cyano group on the Pt—C-1 bonding character.[10]

Previously we observed a remarkable temperature dependence of ^{13}C and ^{195}Pt NMR spectra of the complex 5 (L = pyridine and chloride) derived from the parent bicyclo[1.1.0]-butane, which, coupled with the chemical behaviors of 5, implies that there is a rapid interconversion between center-opened type complex 5 and the side-opened type one, 6.[5] In contrast, no apparent line shape change in ^{13}C{^{1}H} NMR of 4 was observed with the temperature



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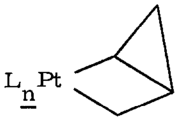

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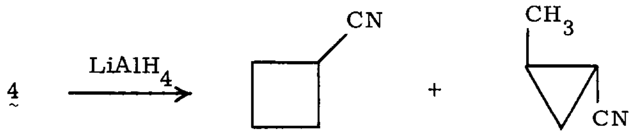
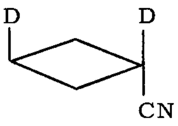
ranging from -80 °C to 20 °C, which indicates that the complex 4 has a rigid structure in solution. The primary reason for such remarkable difference in behaviors between these complexes remains unclear.

The complex 4 was allowed to react with $LiAlH_4$ in THF at 0 °C to afford cyanocyclobutane (7) as a major product accompanied by a small amount of *trans*-1-cyano-2-methylcyclopropane (8).[11] The stereospecific deuterium incorporation was observed on the reduction of 4 with $LiAlD_4$, producing *cis*-1,3-dideuterocyanocyclobutane (9) (78% yield) and 10 (2%).[12]



7 93% 8 2%



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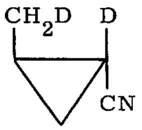

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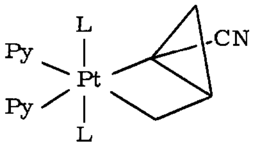

11 L = Cl
12 L = H or D

The above results are compatible with the assigned structure 4. The origin of the cyclopropane derivatives 8 and 10, though produced in low yields, is not clear at present. The complex 4 may contain a compound of the type 11 in an amount within the limit of NMR detection (~2%). An induced rearrangement from 4 to 12 upon replacement of chloride in 4 by hydride might be an alternative possibility. The formation of 4 would involve initial interaction of the central carbon—carbon σ bond of 1 which has high p character with the Pt(II) species followed by oxidative addition of this bond to the platinum.[13] The above results indicate that an electron-withdrawing cyano group at the angular position of bicyclo[1.1.0]-butane exerts considerable influence on the stability and the chemical behaviors of the metallacycle products. We are currently investigating the conversion of 4 to cyanocarbene—platinum complexes, which will be discussed in due course.

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Refernces and Notes

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6. Satisfactory C, H, and N analyses were obtained.
7. IR spectrum of **4** (KBr): 2935 s, 2230 m, 2195 s, 1240 m, 1100 m, 975 m, 880 m, 560 w, and 335 m cm^{-1}. The absorptions relevant to the coordinated pyridine were omitted.
8. S. E. Binns, R. H. Cragg, R. D. Gillard, B. T. Heaton, and M. F. Pilbrow, *J. Chem. Soc.*, (A), 1227 (1969); J. D. Ruddick and B. L. Shaw, *ibid.*, (A), 2801 (1969).
9. K. B. Wiberg, in "Advances in Alicyclic Chemistry," eds. H. Hart and G. J. Karabatsos, Academic Press, New York, 1968, vol. 2, pp. 191—196.
10. Y. Koie, S. Shinoda, and Y. Saito, *Inorg. Chem.*, **20**, 4408 (1981); F. H. Allen and A. Pidcock, *J. Chem. Soc.*, (A), 2700 (1968).
11. All products were isolated by preparative g.l.c. (10% diisodesyl phthalate on Celite 545, 3m, 110 °C) and identified by comparison of NMR and mass spectra with those of the authentic samples.
12. The structure and stereochemistry of **9** and **10** have been assigned by comparison of NMR spectra and mass cracking patterns with those of nondeuterated authentic samples.
13. An extended Hückel calculation showed that introduction of a cyano group at the angular position of bicyclo[1.1.0]butane exerts some influence on the energies of HOMO and LUMO, but alters the symmetric structures of these orbitals only to a small extent.[3d]

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