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Preliminary communication

# EVIDENCE FOR THE DIRECT ISOMERIZATION OF A PLATINOCYCLOBUTANE TO AN OLEFIN COMPLEX

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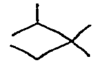
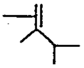
## Summary

Dichloro-2,3,3-trimethyl-1-platinocyclobutane, (I, [$Cl_2$Pt  ]$_4$), prepared by the metathetical reaction of Zeise's dimer and 1,1,2-trimethylcyclopropane, reacts with pyridine in chloroform to produce a platinum complex of 2,3-dimethyl-1-butene (II,$P_y Cl_2$Pt  ). Reaction of I with pyridine at low temperatures (ca. −40° C) leads to a pyridine addition compound (III) in which the platinocyclobutane ring remains intact. The thermal isomerization of III, which may be conveniently studied using NMR, produces a mixture of II and the free olefin.

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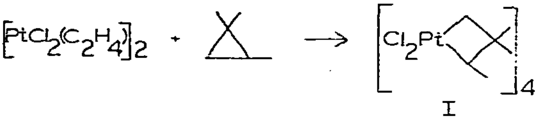
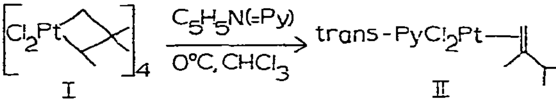
There have been several reports describing the isomerization of cyclopropanes to olefins in the presence of metal complexes, but there has been no direct evidence for the intermediate transformation of a metallocyclobutane to a metal—olefin complex. The reaction of certain cyclopropanes with metal complexes leads to olefins and olefin complexes [1—4], but the intermediacy of metallocyclobutanes has not been demonstrated. On the other hand, platinocyclobutane complexes decompose thermally, both in the solid state [5] and in solution [6], and photochemically in solution [7] to give mixtures of olefin and cyclopropane, but no evidence has been presented for the intermediate formation of metal—olefin complexes. Several other reactions, such as the formation of $\beta,\gamma$-unsaturated ketones from cyclopropanes [8], the oxidation of cyclopropanes in the presence of metal complexes [9, 10], and the reactions of metal—neopentylidene complexes with olefins [11], give products which are explicable only if a cyclopropane-to-olefin isomerization step is involved, but again no direct observation of the isomerization has been made. We report here the isomerization of a platinocyclobutane to a platinum—olefin complex, an observation which thus lends credence to previous claims for such a process.

We have been investigating the reaction of alkyl-substituted cyclopropanes with platinum complexes in an effort to determine the fundamental bases for the carbon—carbon bond cleavage reaction. As is true of many alkylcyclopropanes, 1,1,2-trimethylcyclopropane undergoes a metathetical reaction with Zeise's dimer to produce an insoluble yellow complex which, on the basis of analytical data, infrared spectra in KBr pellets, and $^1$H NMR spectra (vide infra) we believe to be the insertion, I (eq.1).



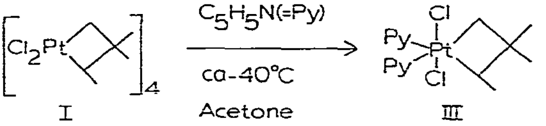
(1)

Because the platinocyclobutanes are apparently insoluble in solvents with which they do not react, they are most conveniently characterized following transformation to the soluble bis(pyridine) adducts. However, under the synthetic conditions commonly used, I reacts to form a platinum complex of 2,3-dimethyl-1-butene (II) derived by isomerization of the cyclopropane (eq.2). This material has been identified by analytical data, by infrared absorptions at 1515 cm$^{-1}$ (coordinated C=C) and in the 300—400 cm$^{-1}$ region, as well as by NMR spectra. In addition to the pyridine signals, the $^1$H NMR spectrum (CDCl$_3$) includes two doublets at δ 1.14 (3H, $J$(HH) 6.0 Hz) and 1.54 ppm (3H, $J$(HH) 6.0 Hz) which correspond to the two magnetically non-equivalent methyl groups of the isopropyl substituent, as well as a multiplet at δ 3.12 ppm (1H) due to the methine proton, a singlet at δ 1.96 ppm (3H $J$(Pt—H) 42 Hz) due to the methyl substituent on the olefin, and a singlet at δ 4.87 ppm (2H, $J$(Pt—H) 64 Hz) due to the olefinic protons. This compound has infrared and NMR spectra identical to an authentic sample of II prepared by the metathetical reaction between Zeise's dimer and 2,3-dimethyl-1-butene followed by pyridine addition.



(2)

In order to preclude the isomerization indicated in eq.2, the addition of pyridine to I suspended in acetone was carried out at low temperature in an acetone/dry ice bath, and the system was then allowed to slowly warm to room temperature (eq.3).



(3)

Complex III was isolated by adding water to the acetone solution resulting in a gummy, yellow solid. The $^1$H NMR spectrum of III in CDCl$_3$ (δ 1.03 (s, 3H), 1.13 (s, 3H), 0.47 (d, 3H, $J$(HH) 7.0 Hz, $J$(PtH) 24.5 Hz), 2.67 (2H, AB pattern, $J$(HH) 7.5 Hz, 3.45 ppm (q, 1H, $J$(HH) 7.0 Hz)) shows only the platinocyclobutane complex, III*. Heating this CDCl$_3$ solution in a 50° C water bath for 1 h re-

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*The observation of $^{195}$Pt coupling to the methyl doublet, and the absence of such coupling to the two methyl singlets rules out the two isomeric platinocyclobutane structures.

sulted in isomerization of III to a mixture of II and uncomplexed 2,3-dimethyl-1-butene (in addition to the peaks reported above for II, $\delta$ 1.04 (d, 6H, $J$(HH) 6.8 Hz), 1.75 (s, 3H), 2.30 (m, 1H), 4.73 ppm (s, 2H)) and was accompanied by the formation of a crystalline yellow precipitate. There was no evidence in the NMR spectrum for any unreacted III. Presumably, the mixture arises from first the isomerization of III to II, followed by decomposition of II producing the free olefin and the precipitate. Substantiating this, we have also observed that authentic II decomposes slowly at room temperature in $CDCl_3$ and more quickly at 50° C to produce free 2,3-dimethyl-1-butene and a yellow precipitate.

The results discussed here provide clear documentation of the transformation of a platinocyclobutane to a platinum—olefin complex, and suggest that such reactions are plausible pathways in the metal-induced reactions of small-ring compounds. The mechanism of this isomerization is currently under investigation. We can postulate at least three possible mechanisms, involving either a direct 1,2-methyl migration, or else a prior rearrangement to an isomeric platinocyclobutane which then isomerizes to the olefin via a hydride shift. The appropriate isomeric platinocyclobutane would be available by either an insertion—deinsertion sequence or else by a reversible isomerization to a metal—carbene/metal—olefin complex. This latter possibility has a clear bearing on the mechanism of the olefin metathesis reaction.

We have obtained preliminary evidence that the isomerization of platinocyclobutanes to olefin complexes may be a fairly general reaction, occurring for many of the complexes derived from alkyl cyclopropanes, and will report more fully on the details of these reactions at a later date.

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