

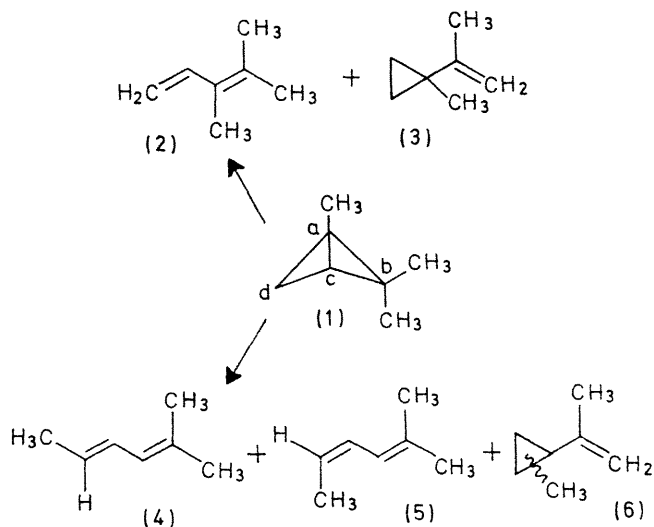
## Ligand Dependency in the Transition-metal-promoted Rearrangements of Derivatives of Bicyclo[1,1,0]butane

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**Summary** The mode of cleavage of 1,2,2-trimethylbicyclo[1,1,0]butane is shown to be dependent on the nature of the ligands attached to the transition-metal catalysts.

THE thermal isomerization of derivatives of bicyclo[1,1,0]butane to derivatives of buta-1,3-diene is generally thought<sup>1</sup> to occur *via* a concerted process at elevated temperatures (150–300°). In contrast are the simple, transition-metal-promoted, rearrangements of derivatives of bicyclo[1,1,0]butane which occur at low temperatures (0–25°) *via* a stepwise process.<sup>2,3</sup> Recent work has demonstrated that different metals promote different modes of cleavage.<sup>2,3</sup> For example, it was shown that (1) yields a mixture of (2) and (3) in the presence of di- $\mu$ -chloro-bis(dicarbonylrhodium)<sup>2</sup> and a mixture of (4), (5), and (6) on exposure to pentafluorophenylcopper tetramer.<sup>4</sup> We now report that the ligands attached to the transition metal are at least as important as the metal itself in controlling the reaction pathway.

When a chloroform solution of (1) was treated with dichlorobis(benzonitrile)-palladium(II) (3 mol %) at 25° for 12 h, a 13:1 mixture of (2):(3) was obtained as the only volatile material. When di- $\mu$ -chloro-bis[ $\pi$ -allylpalladium(II)] (2 mol %) was used as the catalyst, (1) gave 3% (6) and



72% 3:46:41 mixture of (2):(4):(5) after 35 min at 0°. Although both catalysts involved palladium(II), the

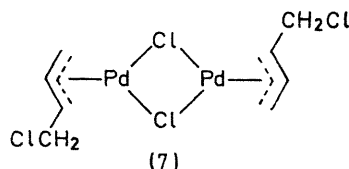
dichlorobis(benzonitrile)palladium(II) gave no (4) and (5), while the  $\pi$ -allylpalladium(II) complex gave only a 2% yield of (2). Suitable control reactions demonstrated that the dienes were not interconverted under the reaction conditions. A complicating factor was that both catalysts slowly promoted polymerization of the product dienes. However, this catalysed disappearance of the dienes could not be used to explain the observed selective isomerizations of (1) since the rates of disappearance of the three different dienes were qualitatively comparable. Hence the observed diene ratios must approximate the initially formed product composition.

The implications of these findings are twofold. First, it is clear that the behaviour of the transition-metal catalysts is critically dependent on the nature of the attached ligand since dichlorobis(benzonitrile)palladium(II) catalysed the cleavage of the a-c and b-c bonds of (1) while di- $\mu$ -chloro-bis[ $\pi$ -allylpalladium(II)] promoted cleavage of the a-b and a-c bonds. Secondly, the observed transformations provided a preliminary indication that there was very little, if any, ligand exchange during the course of the reaction under the conditions described above.

In order to extend the scope of these findings we investigated the properties of the catalyst formed from the use of butadiene as a ligand in place of benzonitrile.<sup>5</sup> This catalyst has structure (7),<sup>6</sup> which is similar to the  $\pi$ -allylpalladium(II) complex. In the presence of (7), (1) gave 3% (6) and 40% 55:26:19 mixture of (2):(4):(5) after 4 h at 25°. Hence (7) was intermediate in catalytic properties between the two palladium(II) catalysts described above.

It was noted above that the results indicated no ligand exchange during the course of the reaction when 2–3 mol % of catalyst was used. This hypothesis was supported by experiments in which the catalyst ratio was decreased 10–100 fold. When 0.2 mol % of dichlorobis(benzonitrile)-palladium(II) was added to a chloroform solution of (1), the

ratio of (2):(4):(5) was (20):(49):(31). This dramatic change in product ratio with catalyst concentration is reasonable if, at the lower catalyst concentrations, the catalyst undergoes ligand exchange to incorporate the diene (2), prior to the complete disappearance of (1). The replacement of benzonitrile by butadiene is a well established type of ligand exchange.<sup>5</sup> When dichlorobis(benzonitrile)palladium(II) was treated with (2) a new palladium complex whose structure is not known was formed. The use of this new complex as a catalyst for the rearrangement of (1) gave results which were qualitatively similar to those observed with other  $\pi$ -allylpalladium(II) type catalysts. Very little (2) was formed and the major products were (4) and (5).



Our results clearly establish the dependency of the mode of cleavage of highly strained polycyclic molecules on the nature of the ligand attached to the transition metal. In addition we have shown that the use of very low catalyst ratios can produce anomalous results if the nature of the catalyst is changed during the course of the reaction due to ligand exchange. Unfortunately, we are not able to offer a satisfactory explanation of how the ligands control the mode of cleavage, at this time.

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