

Preliminary Communication

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Cyclopropane Ring-Opening of Methylene-cyclopropane

Derivatives by Platinum(II) Hydrides

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Summary

The reactions of the trans- and cis- dimethyl esters and the cis-anhydride of Feist's acid with both cationic and neutral platinum(II) hydrides afford a variety of organoplatinum complexes formed by either 1) cleavage of a cyclopropyl bond, 2) addition of Pt-H across the exocyclic double bond of the methylenecyclopropane derivative, or 3) reductive elimination of the Pt-H hydrogen as a proton.

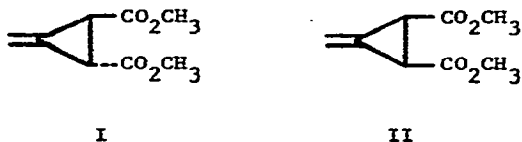
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Considerable interest has been recently evidenced in the transition metal-promoted opening of cyclopropane rings.  $1,2,3$ -Allyl<sup>3,4</sup>, trimethylene-methane<sup>5</sup>,  $\eta^2$ -methylene-cyclopropane<sup>6</sup>, and but-3-enyl<sup>6</sup> derivatives have been isolated from the reactions of zerovalent and divalent complexes of platinum and palladium with methylenecyclopropane derivatives.

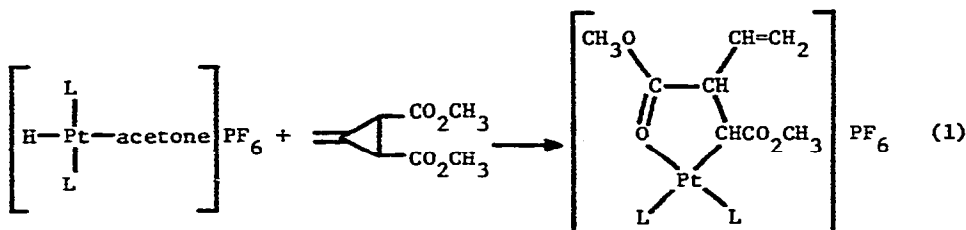
Our studies of the reactions of methylenecyclopropane derivatives and platinum(II) hydrides indicate that a variety of organoplatinum complexes are isolated from these reactions in high yields. Complexes formed by the cleavage of the 1,2-bond of the cyclopropane ring, by 1,2-addition of the Pt-H bond across the exocyclic double bond of the methylenecyclopropane, and by reductive elimination of the Pt-H hydrogen as a proton have been isolated. The formation of these products is dependent upon both the methylenecyclopropane derivative and the particular platinum hydride.

The reaction of the cationic platinum(II) hydrides,  $[\text{trans-PtH}(\text{acetone})\text{L}_2]\text{PF}_6$ ,  $\text{L}=\text{PEt}_3$  and  $\text{PPh}_3$ , and the trans- and cis-

dimethyl esters of Feist's acid, I and II, in  $\text{CH}_2\text{Cl}_2$  at room temperature leads to the formation of the but-3-enylplatinum(II) complexes,



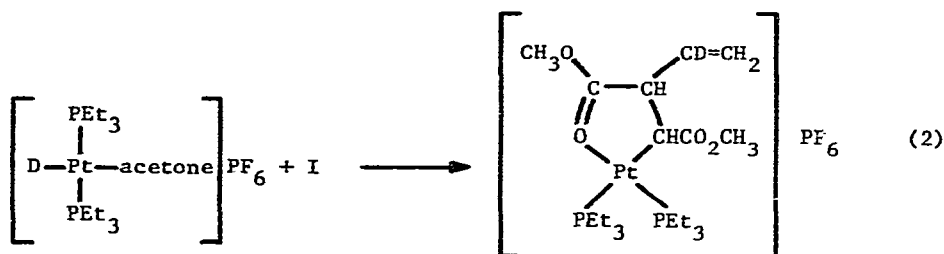
$[\text{Pt}\{\text{CH}(\text{COOCH}_3)\text{CH}(\text{COOCH}_3)(\text{CH}=\text{CH}_2)\}\text{L}_2]\text{PF}_6$ , III and IV, in greater than 75% yield as shown in eq. 1. Cyclopropane ring-opening occurs by 1,2-addition of the Pt-H bond across the 1,2-bond of the cyclopropane ring.



<u>L</u>	<u>Olefin</u>	<u>Product</u>
$\text{PEt}_3$	I	IIIa
$\text{PEt}_3$	II	IIIb
$\text{PPh}_3$	I	IVa
$\text{PPh}_3$	II	IVb

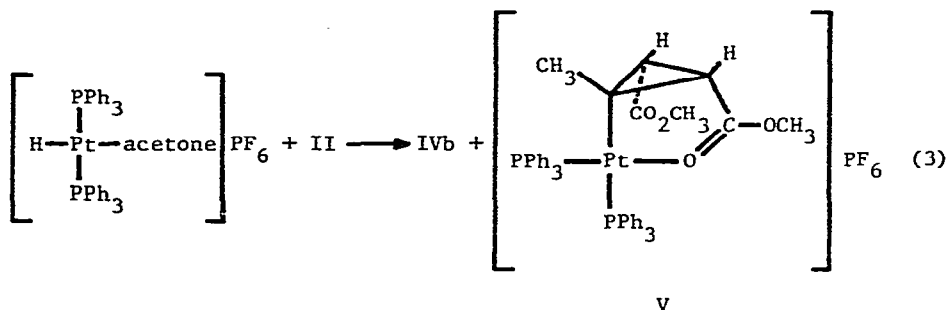
The structures of III and IV have been assigned on the basis of infrared, NMR spectroscopy, and elemental analyses. Both the infrared (Nujol mull) and the NMR spectra (in  $\text{CDCl}_3$ ) show that the ester carbonyl on the  $\beta$ -carbon rather than the  $\text{C}=\text{C}$  bond of the but-3-enyl group is coordinated to the platinum. A  $\nu(\text{CO})$  band between  $1675\text{--}1680\text{ cm}^{-1}$  is assigned to the uncoordinated carbonyl on the  $\alpha$ -carbon and a  $\nu(\text{CO})$  band between  $1590\text{--}1600\text{ cm}^{-1}$  is assigned to the coordinated carbonyl. The NMR spectra have the typical pattern for a vinyl group between 3.5 and 5.0 ppm indicative of the free, uncoordinated vinyl group of the but-3-enyl ligand. The reactions of I and II with  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  also cleave the cyclopropane ring to give a but-3-enyl group; however, the  $\text{C}=\text{C}$  bond rather than the carbonyl of the but-2-enyl ligand is coordinated to the palladium.<sup>7</sup>

The reaction of the corresponding deuteride,  $[\text{trans-PtD}(\text{acetone})\text{-(PEt}_3)_2]\text{PF}_6$ , and I demonstrate that the 1,2-bond of the 2,3-dicarbomethoxy-1-methylenecyclopropane is cleaved and that the deuterium is located exclusively on the 3-carbon of the but-3-enyl group.



The formation of IIIa and IIIb, as well as IVa and IVb, occurs stereospecifically. IIIa and IIIb are diastereomers due to the presence of two chiral carbons at the 1- and 2-positions of the but-3-enyl group and have different NMR spectra. Thus it is possible to determine the stereospecificity of these reactions by NMR spectroscopy. Since no IIIb or IVb is formed in the reactions of I and no IIIa or IVa is formed in the reactions of II, one can conclude that these reactions are stereospecific. Green *et. al.*<sup>8</sup> have shown that the formation of but-3-enylpalladium(II) derivatives by cleavage of the 1,2 bond of the diesters of Feist's acid occurs stereospecifically with retention of configuration at the  $\alpha$ -carbon.

The reaction of [*trans*-PtH(acetone)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>X, X = PF<sub>6</sub> or BF<sub>4</sub>, and II leads to the formation of a second product in equimolar amounts to IVb. The IR and NMR spectra suggest that this compound is the 1-methylcyclopropylplatinum(II) complex, V. Complex V is formed by the 1,2-addition of the Pt-H bond across the exocyclic double bond of II. A product analogous to V is not observed in the reactions of I.

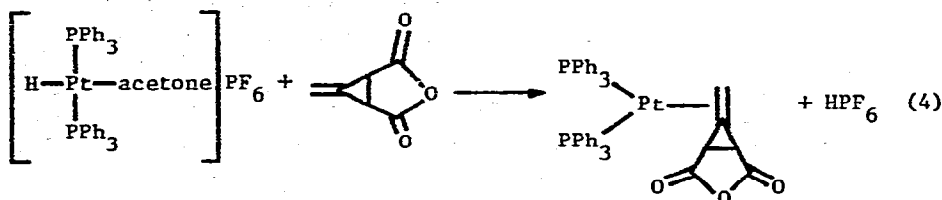


The infrared spectra in both the solid state and in CH<sub>2</sub>Cl<sub>2</sub> solution indicate that one of the ester carbonyls is coordinated to the platinum. However, the ester groups are equivalent in both the <sup>1</sup>H and <sup>13</sup>C NMR spectra at ambient temperature in CD<sub>2</sub>Cl<sub>2</sub>. At low temperatures the ester groups are non-equivalent in both the <sup>1</sup>H and <sup>13</sup>C NMR spectra. The collapse of the singlet assigned to the 2- and 3-carbons of the cyclopropane ring and of the two singlets of the carbons of the COOCH<sub>3</sub> group

in the  $^{13}\text{C}$  spectrum demonstrate the non-equivalence of the two halves of the cyclopropane ring. The rapid dissociation of the coordinated carbonyl from the platinum is consistent with the observed IR and NMR data.

The reaction of trans-PtHCl(PEt<sub>3</sub>)<sub>2</sub> and II yields the but-3-enylplatinum complex, cis-PtCl[CH(COOCH<sub>3</sub>)CH(COOCH<sub>3</sub>)(CH=CH<sub>2</sub>)](PEt<sub>3</sub>)<sub>2</sub>, in which neither but-3-enyl carbonyl is coordinated to the platinum. Presumably, the presence of the coordinating chloride ligand does not require coordination of a carbonyl to obtain the square planar 4-coordinate geometry preferred by platinum(II). Attempts to dissociate the coordinated carbonyl of IIIa and IVa by addition of neutral ligands lead to the isomerization of the but-3-enylplatinum(II) complexes to the isomeric  $\eta^3$ -allylplatinum(II) complexes.<sup>9</sup>

In some cases platinum(0) olefin complexes are the only product isolated from these reactions. This particular reaction type is observed in the reaction of [trans-PtH(acetone)(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> and cis-1-methylenecyclopropane-2,3-dicarboxylic anhydride.



This  $\eta^2$ -methylenecyclopropane derivative is formed by reductive elimination of the Pt-H hydrogen as a proton to give the platinum(0) olefin complex and HPF<sub>6</sub>. This type of reaction may in fact be a general type of reaction in all of the above reactions and is currently under further investigation.

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