

strating the pseudo-first-order kinetics. From Figure 3 it is found that  $k_{\psi}$  has the value  $0.25 \text{ hr}^{-1}$  at  $80^{\circ}$ . This result is in agreement with the values obtained by tritium exchange studies on related adenine derivatives.<sup>5,6,11</sup> We find the temperature dependence of  $k_{\psi}$  gives an activation energy of 23 kcal/mol.

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(11) Note: Attention has been drawn previously to the effects of deuterium exchange at 8-C on the Raman spectra of 5'-rIMP by Medeiros and Thomas<sup>10</sup> and by Hartman, Lord, and Thomas.<sup>7</sup> We have been informed that similar observations were also made more recently by Erfurth and Peticolas (S. C. Erfurth and W. L. Peticolas, private communication).

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### Preparation, Structure, and Reactions of an Organometallic [2.2.1] Propellane, the Bis(triphenylphosphine)platinum Complex of $\Delta^{1,4}$ -Bicyclo[2.2.0]hexene<sup>1</sup>

Sir:

The small ring propellanes are of unusual interest with regard to structural and chemical effects at saturated centers.<sup>2-7</sup> In an attempt to prepare a hetero[2.2.1]-propellane, we have examined the reaction of bis(triphenylphosphine)(ethylene)(platinum) (I) with  $\Delta^{1,4}$ -bicyclo[2.2.0]hexene (II); the strained ring olefin II should behave like cyclopropene<sup>8</sup> and displace ethylene from I. The properties of the expected product should show to what extent the presence of platinum modifies structure and reactivity in such small ring propellanes.

The bicyclohexene, II, was prepared as a mixture with 1,2-dimethylenecyclobutane (III) as previously reported.<sup>9</sup> The product mixture was dissolved in toluene and maintained below  $-80^{\circ}$  to avoid a Diels-Alder reaction between II and III. The platinum complex, I, was added to the toluene solution under nitrogen and the temperature was maintained at  $-80^{\circ}$  for 30 min.

(1) This investigation was supported by a grant from the National Science Foundation.

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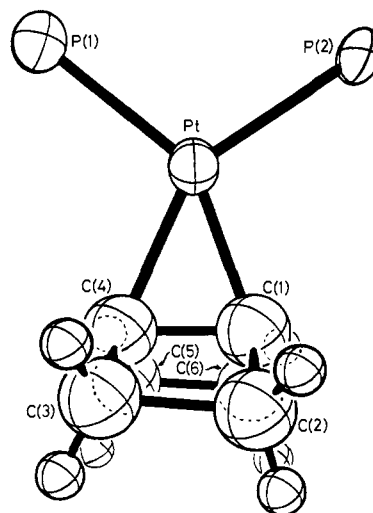
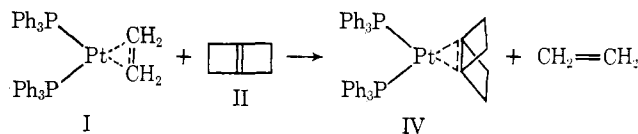


Figure 1.  $\text{Pt}(\text{C}_6\text{H}_5)(\text{PPh}_3)_2$  from a viewpoint normal to the Pt, C(1), C(4) plane and above the platinum atom.

Upon warming to  $-20^{\circ}$ , a clear solution was obtained to which two volumes of ether was added. After filtration, clear light-yellow air-stable crystals of bis(triphenylphosphine) ( $\Delta^{1,4}$ -bicyclo[2.2.0]hexene)platinum (IV) slowly separated.



The structure of IV was determined by X-ray diffraction, intensity data being collected using a Picker four-circle diffractometer. Crystal data for  $\text{Pt}(\text{C}_6\text{H}_5)(\text{PPh}_3)_2$ : orthorhombic;  $P2_12_12_1$ ;  $Z = 8$ ;  $d_{\text{measd}} = 1.54$  (by flotation),  $d_{\text{calcd}} = 1.56 \text{ g/ml}$ ;  $a = 17.726$  (3),  $b = 9.748$  (2),  $c = 19.724$  (3) Å;  $R = 2.8\%$  for 1512 observed reflections. The coordination sphere of platinum and details of the olefin ligand are shown in Figure 1. Important bond lengths (in Å) are: Pt-P(1), 2.29; Pt-P(2), 2.29; Pt-C(1), 2.07; Pt-C(4), 2.14; C(1)-C(4), 1.55; average of other six C-C bond lengths, 1.54. The separation of the olefinic carbon atoms is close to normal for a single  $\sigma$ -bond and the hydrocarbon ligand is significantly bent about the C(1), C(4) vector. The angle between the two four-membered rings is approximately  $123^{\circ}$ .

Formation of IV provides a means of separating II and III by taking advantage of the higher coordinating power of II toward platinum. The stability of IV makes it a convenient way to store II, since a yet stronger ligand should displace II from the complex. A solution of IV in methylene chloride was treated with an excess of carbon disulfide at  $0^{\circ}$  and the volatile product was distilled from the reaction mixture. The  $^1\text{H}$  nmr spectrum of the distillate (in  $\text{CD}_2\text{Cl}_2$  solution) at  $25^{\circ}$  showed a singlet at  $\delta$  3.21 which is characteristic of II.<sup>9</sup> The intensity of this singlet decreased over a period of hours; the cause of this decrease has not been determined as yet, but the product derived from the Diels-Alder reaction of II with 1,2-dimethylene cyclobutane was not found and thus II does not isomerize to III at room temperature. Further proof that the distillate is II was provided by addition of cyclopentadiene; the expected Diels-Alder reaction occurred and the nature

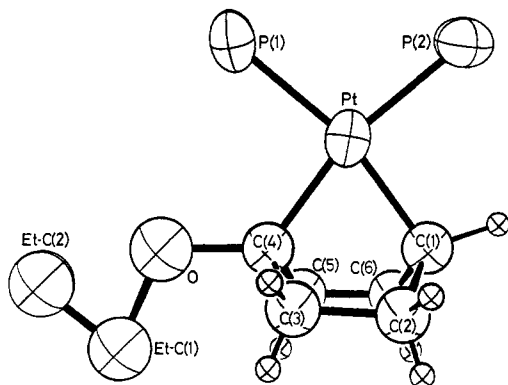
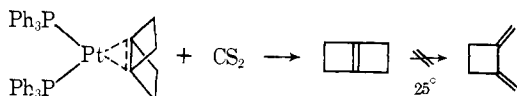


Figure 2.  $\text{Pt}(\text{C}_6\text{H}_9\text{OEt})(\text{PPh}_3)_2$  from a viewpoint normal to the Pt, C(1), C(4) plane and above the platinum atom.

of the product was confirmed by  $^1\text{H}$  nmr and gas chromatography.<sup>9</sup>



The complex, IV, reacted with ethanol at room temperature to form clear, colorless, air-stable crystals of an ethanol adduct, V, in which addition has occurred with cleavage of the C(1)–C(4) bond (rather than the usual type of reaction, release from the metal of the hydrocarbon in its unsaturated form). This choice of reaction pathway appears to be unique and may be due to the strain relief thereby obtained. The reaction is similar to that of [3.2.1]propellane with electrophiles,<sup>4</sup> but the presence of platinum may permit alternative reaction mechanisms.

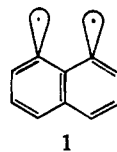
The structure of V was determined by X-ray diffraction. The crystals are monoclinic,  $C2/c$ ,  $d_{\text{measd}} = 1.53$  g/ml (by flotation);  $a = 26.242(8)$  Å,  $b = 12.161(3)$  Å,  $c = 26.744(8)$  Å, and  $\beta = 115.76(2)$ . In addition to eight molecules of  $\text{Pt}(\text{C}_6\text{H}_9\text{OC}_2\text{H}_5)(\text{PPh}_3)_2$  in the unit cell, there are four molecules of an unidentified molecule of crystallization, X. There are two maxima in the electron density map associated with X; these lie on a crystallographic twofold axis of symmetry, are about the height expected for a carbon atom, and are separated by 1.24 Å. Including contributions for X calculated assuming these maxima are carbon atoms, the  $R$  factor converged to 4.4% for 953 observed reflections. The atoms of X are not within bonding distance (2.5 Å) of any atom in the complex platinum molecule, and, since the refined coordinates of the latter molecule do not change significantly after including the contributions of X in the calculations, it can be assumed that the structure of the molecule of interest has been determined. The coordination sphere of platinum and details of the organic ligand are shown in Figure 2. Important bond lengths (in Å) are: Pt–P(1), 2.31; Pt–P(2), 2.28; Pt–C(1) 2.10; Pt–C(4), 2.01. The organic ligand can be considered to have a cyclohexane ring system constrained in the boat conformation by  $\sigma$ -bonds from platinum to C(1) and C(4). The C(1)–C(4) separation is 2.37 Å, indicating that there is no significant residual bonding between them.

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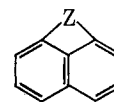
## Single-Atom Peri-Bridged Naphthalenes. Naphtho[1,8-*bc*]thiete

Sir:

In connection with our studies on 1,8-dehydronaphthalene<sup>1</sup> (**1**), we have become interested in compounds in which the peri positions of a naphthalene ring are joined by a single-atom bridge, **2**. Not only might

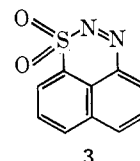


1



2a, Z = CH<sub>2</sub>  
b, Z = CO  
c, Z = NH  
d, Z = O  
e, Z = SO<sub>2</sub>  
f, Z = S  
g, Z = SO

certain compounds of this type serve as precursors of **1** but they should also be of considerable intrinsic chemical interest. Within the carbocyclic domain, the cyclobutane **2a**, the corresponding cyclobutyl radical, anion, cation, and the related cyclobutanone **2b** represent challenging synthetic objectives. No representative of this group of molecules is known,<sup>2</sup> and attempts to prepare nitrogen<sup>3</sup> (**2c**) or oxygen<sup>4</sup> (**2d**) analogs have been unsuccessful. The only report of the isolation of a compound corresponding to the general formula **2** of which we are aware is that of Hoffmann and Sieber,<sup>5</sup> who obtained the sulfone **2e** in 25% yield by irradiation of naphtho[1,8-*de*]1,2,3-thiadiazine 1,1-dioxide (**3**).



3

Their assignment of structure **2e** to this photolysis product was based on its method of preparation, elementary analysis, molecular weight, and ultraviolet and infrared spectra. We now wish to report an efficient synthesis of the parent sulfur-bridged compound, naphtho[1,8-*bc*]thiete (**2f**) and the corresponding sulfoxide, **2g**, as well as some exploratory work on the reactions of these novel heterocycles.

Irradiation through Pyrex of a  $6 \times 10^{-3}$  M solution of naphtho[1,8-*cd*]1,2-dithiole 1,1-dioxide<sup>6</sup> (**4**) in dry, degassed benzene for 9.5 hr under nitrogen resulted in the evolution of sulfur dioxide, detected by a positive zinc nitroprusside test.<sup>7</sup> Evaporation of the solvent and

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