

## Preliminary communication

### The structure of a stable platinum(0) complex of cyclohexyne

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The preparation, properties, and reactions of platinum(0) complexes of small-ring acetylenes (*viz.*, [(cyclohexyne)Pt(PPh<sub>3</sub>)<sub>2</sub>], (I); and [(cycloheptyne)Pt(PPh<sub>3</sub>)<sub>2</sub>], (II)), together with the structure of the cycloheptyne analogue have been reported<sup>1</sup>. In these complexes, the hitherto unobserved<sup>2</sup> cyclohexyne and cycloheptyne groups are stabilized by coordination to a metal ion. We now wish to report the structure of the cyclohexyne derivative (I).

Crystals of I are triclinic, space group  $P\bar{1}$ ,  $a$ , 9.87;  $b$ , 18.14;  $c$ , 10.08 Å;  $\alpha$ , 89.99°;  $\beta$ , 80.68°;  $\gamma$ , 78.28°;  $Z = 2$ . The three-dimensional single crystal X ray structural analysis is based on 5125 unique reflexions collected on a Picker FACS-I automatic diffractometer using crystal monochromated Cu-K $\alpha$  radiation. Only those reflexions for which  $F_0^2/\sigma(F_0^2) \geq 3.0$  were accepted as being statistically significant. Data have yet to be corrected for absorption and extinction effects. Allowing for anisotropic thermal motion of the platinum and phosphorus atoms, and isotropic motion for the carbon atoms, block-diagonal least-squares analysis has converged to a conventional  $R$ -factor of 0.060.

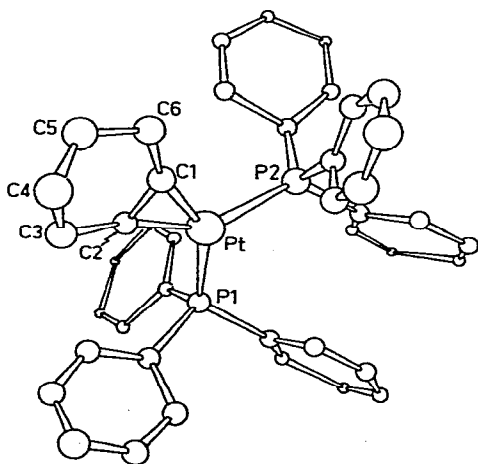


Fig. 1. The overall stereochemistry of (cyclohexyne)Pt(PPh<sub>3</sub>)<sub>2</sub>.

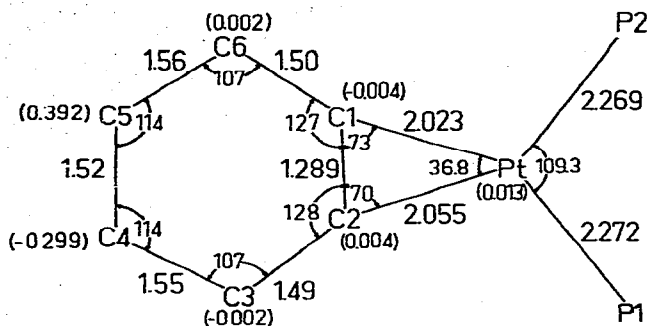


Fig. 2. Important bond lengths (Å) and bond angles (degrees) for (cyclohexyne)Pt(PPh<sub>3</sub>)<sub>2</sub>. Deviations (Å) from the least-squares plane through C(1), C(2), C(3), and C(6) are shown in parentheses.

Bond-distance ESD's at the present stage of refinement are: Pt-P, 0.003; Pt-C, 0.012; P-C, 0.011; C-C, 0.017 Å. The overall stereochemistry of the molecule is shown in Fig. 1, while Fig. 2 shows some detail of the molecular geometry.

The Pt-P distances in the present complex (I) [av. 2.270(3) Å], are within experimental error of those observed for the cycloheptyne complex (II) [av. 2.268(2) Å]<sup>1</sup>, and (PhC≡CPh)Pt(PPh<sub>3</sub>)<sub>2</sub> [av. 2.27 Å]<sup>3</sup>. The agreement between the Pt-C distances and the C-Pt-C angles for I and II is equally good. Thus, the average Pt-C distance in I is 2.04(1) Å [2.05(1) Å for II], and the angle C(1)-Pt-C(2) is 36.8° [36.7° for II]. In contrast, the angle P(1)-Pt-P(2) (109.3°) differs significantly from the corresponding angle in II (102.5°)<sup>1</sup> and in (PhC≡CPh)Pt(PPh<sub>3</sub>)<sub>2</sub> (102°)<sup>3</sup>. The dihedral angle between the planes [Pt,P(1),P(2)] and [Pt,C(1),C(2)] is 3.2°, *cf.*, 8.3° for II, and 14° for the diphenylacetylene derivative.

The alkyne bond distances C(1)-C(2) [I, 1.289 ± 0.017; II, 1.294 ± 0.015 Å] are in excellent agreement. The remaining C-C bond lengths within the cyclohexyne ring are as expected. Thus, the distances C(3)-C(4), C(4)-C(5), and C(5)-C(6) average 1.55 Å, while the bonds adjacent to the alkyne linkage [*viz.*, C(1)-C(6) and C(2)-C(3)] average 1.50 Å. Although not statistically significant, the shortening of these bonds is clearly a consequence of the differing  $\sigma$ -orbital radius of carbon atoms in  $sp$  and  $sp^3$  hybridization states respectively<sup>4</sup>.

The most significant differences between the two coordinated cyclic alkynes are undoubtedly those involving the ring interbond angles. Inspection of the angles at C(3), C(4), C(5), and C(6) in coordinated cyclohexyne shows that, unlike cycloheptyne, there is little, if any, steric strain at these atoms. In accordance with theoretical predictions<sup>5</sup>, the inherent strain associated with the formation of cyclohexyne must, therefore, be relieved almost exclusively at the acetylenic carbon atoms. The average deformation at C(1) and C(2) is 52.5°, *cf.*, 40° predicted for free cyclohexyne<sup>5</sup>. For both I and II the deformation at C(1) and C(2) is *ca.* 12-16° more than that calculated for the free cycloalkyne. This suggests that the increased electron localization at C(1) and C(2), resulting from coordination to platinum(0), is of the same order of magnitude for both I and II. As expected, there is no rotation at the acetylene bond, the atoms C(1), C(2), C(3), and C(6) being coplanar within experimental error.

## REFERENCES

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