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Structure of bis(triphenylphosphine)diphenylacetyleneplatinum

The structure of bis(triphenylphosphine)diphenylacetyleneplatinum[1] is of interest because of the possible ambiguities in valence states and stereochemical arrangements. For example, the compound could exist as a platinum(0) trigonal complex such as the recently reported tris(triphenylphosphine)platinum(0)[2] with the acetylene occupying one coordination position and π-bonded in a manner similar to ethylene in Zeise's salt, *i.e.*, in valence bond terms, with the electrons of the π_x orbital of the acetylene being donated to an sp^2 hybrid orbital of the metal to form a μ-bond with simultaneous back donation from the filled d_{xz} (or d_{xz} p_z hybrid) orbital of platinum into the π_x^* orbital of the acetylene; or it could be four coordinated platinum(II) with each of the acetylenic carbons σ-bonded to a dsp^2 hybrid of the metal by use of approximately sp^2 orbitals (thereby reducing the triple bond to a double bond). In addition, the planar arrangement could also be described as a trigonal platinum(0) complex with the acetylene forming a μ-bond with the metal sp^2 hybrid orbital with concomitant in-plane back bonding from the metal d_{xy} orbital into the π_x^* of the acetylene. This type of in-plane π-bonding has been suggested as an explanation of the low barrier to rotation of coordinated ethylene[3]. Evidence for these structures has been discussed[1,4,5] and a preliminary report on the X-ray structural determination of bis(triphenylphosphine)di-*p*-bromophenylacetyleneplatinum was mentioned in a book[4] several years ago without further documentation.

We report here our preliminary results.

Bis(triphenylphosphine)diphenylacetyleneplatinum crystallizes in the triclinic space group P$\bar{1}$, having the following cell parameters: a = 11.32 ± .05 Å, b = 15.83 ± .05 Å, c = 13.34 ± .05 Å, $\alpha = 112°51' \pm 20'$, $\beta = 113°26' \pm 20'$, and $\gamma = 83°40' \pm 20'$. The observed density determined by flotation in aqueous zinc chloride is 1.47 ± .06 g/cm^3 and the calculated density assuming two molecules per unit cell is 1.43 g/cm^3.

A total of 3027 intensity data were recorded using the equiinclination Weissenberg method. Approximately two-thirds of these data were measured photometrically and the rest by visual estimation. The solution to the structure has been obtained by

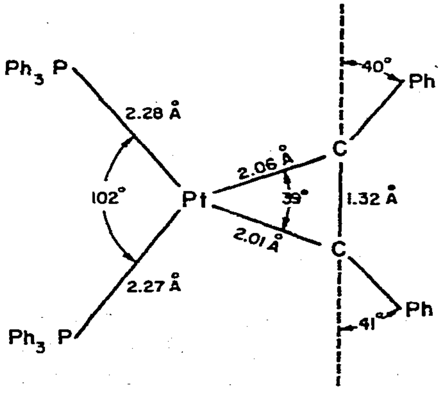

Fig. 1. Structure of bis(triphenylphosphine)diphenylacetyleneplatinum.

a combination of Patterson, Fourier, and difference synthesis methods and partial refinement has been carried out using the block diagonal least squares method of approximation for the matrix of the coefficients of the normal equations (present $R = \Sigma|\Delta F|/\Sigma|Fo| < 0.13$).

The structure in the crystal lies between the two possibilities which have been postulated, but is considerably closer to the planar configuration. The platinum, two phosphorus atoms, and one of the acetylenic carbons lie in a plane with the line of the two acetylenic carbons making approximately a 14° angle with the plane. The salient features of the structure are given in the figure. The fact that the benzene rings of the acetylene are bent at angles of 40° from linear confirms the suggestion made on the basis of dipole moment data of the analogous *p*-substituted-diphenylacetylene-platinum compounds[4]. The carbon–carbon distance is 1.32 ± 0.09 Å.

The phosphorus platinum bond lengths are very similar to those reported earlier for tertiary phosphine platinum compounds: 2.267 ± 0.008 and 2.269 ± 0.008 in hydridochlorobis(diphenylethylphosphine) platinum[6] and 2.26 ± 0.07 in hydridobromobis(triethylphosphine)platinum[7].

The complete detailed structure will be reported at a later date.

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