The Crystal and Molecular Structure of $Pd(Ph_3P)_2(CS_2)$

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Recently, in the study of catalytic reactions of Pd- and Pt-phosphine complexes, Hagihara and his co-workers[1] have recognized that these complexes form addition compounds with some simple molecules, such as O_2, SO_2, and CS_2.

Among these, only the $M(Ph_3P)_3O_2$ (M=Pd or Pt) molecule has been considered to be an active intermediate in the catalytic oxygenation. On the contrary, both CS_2 and SO_2 act as poisons to the catalysts. We have undertaken structural analysis of $Pd(Ph_3P)_2(CS_2)$ in order to scrutinize the molecular structure in detail in connection with the mechanism of the catalytic reaction of the complex. The crystals were kindly given by Professor N. Hagihara.

The crystal data are shown in Table 1. Over 4000 reflections were observed from the equi-inclination Weissenberg photographs taken around the c- and a-axes with nickel-filtered Cu$K\alpha$ radiation.

As Fig. 2 shows, there may be a slight difference between the two S-C bond distances in the CS_2 molecule (1.61 and 1.66 Å). The most striking fact, however, is the coordination of CS_2 to the Pd atom: only one of the S atoms coordinates with Pd. The Pd-S_2 distance is 2.31 Å, while Pd-S_1 is 3.44 Å (sum of the covalent radii: 2.36 Å). The S_1-C_1-S_2 bond is not linear, the S_1-C_1-S_2 angle being 140°. The Pd-C_1 distance, 2.02 Å, is a little shorter than the sum of the covalent radii (2.09 Å), and the S_2-Pd-C_1 angle is about 43°. The Pd atom and its neighbors, P_1, P_2, S_2, and C_1, lie approximately on the same plane, the maximum deviation being 0.09 Å. These results suggest that the coordination around the Pd atom is different from the normal four- or six-coordination. The Pd-P distances are 2.32 and 2.41 Å. The longer one may be interpreted as being due to the trans-lengthening effect. The P_1-Pd-P_2 bond angle is 109°. The average C-C distance and bond angle in benzene rings in triphenylphosphine groups are normal, being 1.40 Å and 119.9° respectively.

Very recently, Baird and his co-workers[2] have also given a preliminary report on a similar coordination of CS_2 in $Pt(Ph_3P)_2(CS_2)$.

TABLE 1. CRYSTAL DATA OF $Pd(Ph_3P)_2(CS_2)$

$a = 11.55 \pm 0.03$Å	$P2_1/c$
$b = 19.52 \pm 0.02$	$D_m = 1.547$ g·cm^{-3}
$c = 18.38 \pm 0.03$	$D_x = 1.546$ g·cm^{-3}
$\beta = 128°53' \pm 10'$	$Z = 4$

TABLE 2. ATOMIC PARAMETERS FOR Pd S, P, AND C_1

Atom	x	y	z
Pd	0.0865	0.1043	0.2757
S_1	−0.2125	0.1111	0.2743
S_2	0.0362	0.2051	0.3164
P_1	−0.0115	−0.0025	0.2098
P_2	0.3202	0.1172	0.3042
C_1	−0.0692	0.1362	0.2850

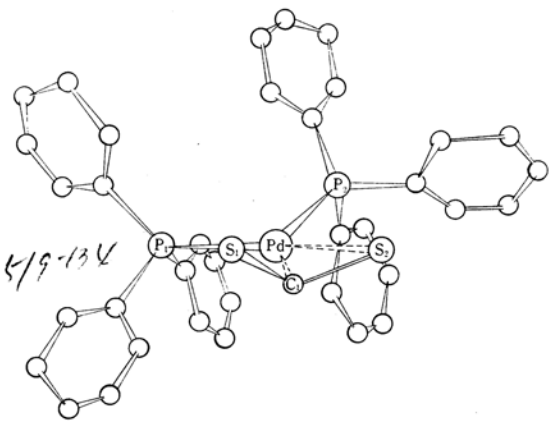

Fig. 1. The molecular structure of $Pd(Ph_3P)_2CS_2$.

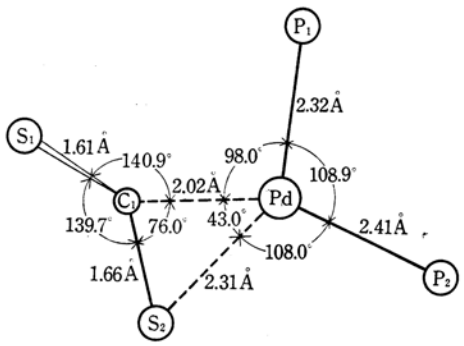

Fig. 2. The geometry around the Pd atom.

1) S. Takahashi and N. Hagihara, This Bulletin, in press.
2) M. Baird, G. Hartwell, Jr., R. Mason, A. I. M. Rae and G. Wilkinson, *Chem. Commun.*, **1967**, 92.