# The Structure of π-Allyl(triphenylphosphine)palladium-trichlorotin

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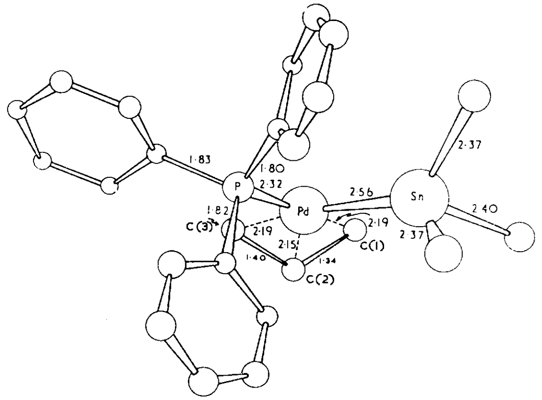
THE preparation of $(\pi\text{-}C_5H_5)Ni(PPh_3)SnCl_3$ results from the reaction of $SnCl_2$ with $(\pi\text{-}C_5H_5)Ni(PPh_3)Cl$.[1] The reaction of the similar compound $(\pi\text{-}C_3H_5)Pd(PPh_3)Cl$,[2] with $SnCl_2$ is reported here. Treatment of $(\pi\text{-}C_3H_5)Pd(PPh_3)Cl$, or a mixture (1 : 2 mole ratio) of the dimer $[(\pi\text{-}C_3H_5)PdCl]_2$ and triphenylphosphine, with $SnCl_2$ in acetone gives a yellow compound (I) in high yield. Analysis indicates that (I) has the formula $(\pi\text{-}C_3H_5)Pd(PPh_3)SnCl_3,\frac{1}{2}Me_2CO$, and conductance measurements show it to be a non-electrolyte in nitrobenzene. Its proton n.m.r. spectrum ($CDCl_3$) shows that a π-allyl group is present. The terminal allylic protons give rise to broad resonances, but the band-widths are unchanged at −40°. This suggests that the broadening is most probably due to coupling with other nuclei, rather than to the exchange phenomena of the type shown by $(\pi\text{-}C_3H_5)Pd(PPh_3)Cl$.[2–5] The n.m.r. spectrum confirms the presence of acetone in the molecule, and this is also shown by the i.r. spectrum (bands at 1710 and 1204 $cm.^{-1}$). In the far-i.r. region, (I) does not show the expected doublet (at 330 $cm.^{-1}$), characteristic of the $SnCl_3^-$ ligand.[6,7] Three strong bands are observed at 329, 302, and 296 $cm.^{-1}$, but these bands have not, as yet, been assigned.

The structure of $(\pi\text{-}C_3H_5)Pd(PPh_3)SnCl_3,\frac{1}{2}Me_2CO$ has been determined by three-dimensional *X*-ray analysis. The crystals are monoclinic, space group $P2_1/c$, $a = 12{\cdot}80$, $b = 22{\cdot}03$, $c = 9{\cdot}44$ Å $\beta = 103{\cdot}2°$, $Z = 4$. For the 2298 independent non-zero reflexions measured on a Pailred automatic diffractometer, with $F_o^2/\sigma(F_o^2) \geqslant 3{\cdot}0$, $R = 0{\cdot}055$. The corresponding e.s.d.'s for the more important bond-lengths shown in the Figure are: 0·002, Pd–Sn; 0·005, Pd–P; 0·02, Pd–C; 0·006, Sn–Cl; 0·02, P–C; 0·03 Å, C–C.



FIGURE

The molecules consists of a palladium atom, bonded to an $SnCl_3^-$ ligand, a triphenylphosphine ligand, and an allyl group in an approximately planar manner. This is the first reported structure of a derivative containing a palladium–tin bond. The atoms C(1) and C(3) are $+0{\cdot}01$ Å and $-0{\cdot}01$ Å respectively from the palladium co-ordination plane (as defined by Pd, Sn, and P), while the central atom of the allyl group, C(2), is $-0{\cdot}62$ Å from this plane: Sn–Pd–P, 99°; Sn–Pd–C(1), 90°; Sn–Pd–C(3), 157°; P–Pd–C(3), 104°; P–Pd–C(1), 171°; C(1)–Pd–C(3), 67°. The average Sn–Cl distance is 2·38 Å while the mean bond-angles Cl–Sn–Cl and Pd–Sn–Cl are 95° and 121° respectively. The mean P–C bond distance is 1·82 Å, compared with 1·81 Å found in ($\pi$-$C_4H_7$)-$Pd(PPh_3)Cl$.[8]

The Pd–Sn distance is 2·56 Å; this is considerably shorter than the distance of 2·80 Å reported for Pt–Sn in $[(C_8H_{12})Pt_3(SnCl_3)_3]$,[9] in which the tin atom is in an octahedral environment, being surrounded by three platinum and three chlorine atoms. The Pd–Sn distance does, however, correspond to the Pt–Sn distance of 2·54 Å reported for the complex $[Ph_3PMe]_3Pt(SnCl_3)_5$,[10] in which the tin is four-co-ordinate. The observed metal–metal bond-length is approximately 0·1 Å less than the sum of covalent radii.

The allyl group is symmetrically bonded to the palladium atom, the Pd–C(terminal) distances being equal within $1{\cdot}5\sigma$; the dihedral angle between the allyl plane and that containing the palladium, tin, and phosphorus atoms is 110°. The Pd–C(terminal) distances are significantly longer (2·19 Å *cf.*, 2·12 Å) than those observed for $[(\pi\text{-}C_3H_5)PdCl]_2$.[11] The equality of the Pd–C(1) and Pd–C(3) bond lengths suggests that the *trans*-directing influence of the $SnCl_3^-$ ligand and the triphenylphosphine group are comparable, in accordance with a previous report,[6] which suggests, on the basis of spectroscopic evidence, that the *trans*-directing influence of the $SnCl_3^-$ ligand lies between the thiocyanate ion and the cyanide ion.

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