Structure and Bonding in Tris(dibenzylideneacetone)dipalladium(0)

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Summary The pentadienone complex of palladium(0), tris(dibenzylideneacetone)dipalladium(0), has been isolated and its molecular structure determined crystallographically.

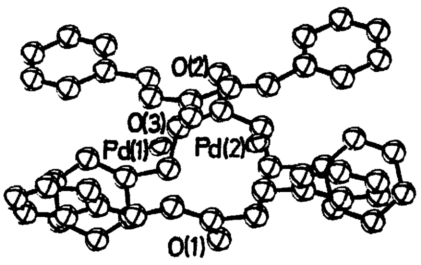
Complexes of zerovalent nickel, palladium, and platinum have been found to be stabilized by π-acceptor ligands.[1] Oxidative reactions of these compounds with unsaturated organic molecules have made them of considerable interest as homogeneous catalysts.[2] Takahashi, *et al.*,[3] have recently reported the unusual bis palladium(0) complex of dibenzylideneacetone (dba). The tris-complex Pt(dba)$_3$ has also been reported.[4] Investigations concerning the catalytic activity of the palladium complex have indicated that it can be used to oligomerize alkynes[5] and may be of potential use as a hydrogenation catalyst.[3]

I.r. data on the palladium complex included with the initial reports was interpreted to indicate bonding to the metal through the olefin groups of the pentadienone moiety. Moseley, *et al.*, however, have reported quite different i.r. data for the palladium complex together with n.m.r. and electronic spectral evidence interpreted to indicate co-ordination through the carbonyl group of the pentadienone.[4] We have found the composition of the palladium complex to be dependent on the solvent medium from which the compound is isolated.

A sample of the complex Pd(dba)$_2$ was prepared by the technique outlined by Takahashi.[3] On recrystallization from methylene chloride or chloroform crystals similar to Pd(dba)$_2$ in colour with the composition [Pd$_2$(dba)$_3$·solvent] were obtained. The i.r. spectrum of the initial complex Pd(dba)$_2$ resembled the spectrum reported by Moseley, *et al.*[4] However, the spectrum of Pd$_2$(dba)$_3$ closely resembled the spectrum reported by Takahashi[3] with ν (C=O) at 1618 cm^{-1} and olefin bands at 1580, 1548, and 1541 cm^{-1}. To help resolve questions concerning the bonding and geometries of these complexes the molecular structure of Pd$_2$(dba)$_3$ has been determined crystallographically.

A crystal of Pd$_2$(dba)$_3$ suitable for *X*-ray work was grown from a methylene chloride–ethanol solution. On the basis of Weissenberg and precession photographs the complex was found to crystallize in space group $P\bar{1}$ of the triclinic system with a unit cell of refined dimensions $a = 12{\cdot}400(5)$, $b = 15{\cdot}149(5)$, $c = 12{\cdot}956(5)$ Å, $\alpha = 115{\cdot}01(5)^\circ$, $\beta = 95{\cdot}23(5)^\circ$, $\gamma = 97{\cdot}30(5)^\circ$. An experimental density of 1·53(1) g cm^{-3} is in agreement with a calculated density of 1·54 g cm^{3} for two formula weights of composition Pd$_2$(C$_{17}$OH$_{14}$)$_3$·CH$_2$Cl$_2$ per unit cell.

The intensities of 4605 reflections were measured on a Picker automatic diffractometer using Mo-K_α radiation. Of the reflections measured 2911 were observed and have been included in the refinement. The structure was solved by standard Patterson and Fourier methods. A least squares procedure in which individual atoms were assigned anisotropic thermal parameters and phenyl rings refined as rigid groups was used to refine the structure. The conventional and weighted *R* factors on convergence of the refinement were 0·068 and 0·072.



(I)

The structure consists of discrete Pd$_2$(dba)$_3$ molecules and methylene chloride molecules of crystallization. The co-ordination geometry about each metal atom is trigonal, three co-ordinate, with the metal bonding to three olefin groups of bridging dibenzylideneacetone ligands (I). This co-ordination geometry has only been observed previously for the metals Pd^0 and Pt^0 with tertiary phosphine ligands.[6] The angles formed about each metal by the centres of the co-ordinated olefin groups average 121(2)° for Pd(1) and 120(2)° for Pd(2). The conformations of the three (dba) groups are different with one in the symmetric *syn, syn* configuration and the other two in the asymmetric *syn, trans* conformation. Chemically equivalent bond distances and angles within each of the pentadienone groups are not significantly different and are approximately equivalent to values expected for unco-ordinated dibenzylideneacetone. The C=C distances for the six olefin groups are slightly elongated on co-ordination to an average value of 1·39(2) Å. The Pd–olefin–carbon distances range from 2·19(1) to 2·28(1), within the range of distances found previously in palladium–olefin complexes.[7] However, these distances are longer than Pt–olefin distances of 2·11 Å found for [P(C$_6$H$_5$)$_3$]$_2$Pt(C$_2$H$_4$), where a near-planar configuration is observed for the olefin and phosphine ligands about the metal.[8] The Pd(1)–Pd(2) distance of 3·240(2) A is the shortest nonbonding Pd–Pd distance yet reported.[7] Each metal atom in the molecule is co-ordinatively unsaturated.

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