The Preparation and Structure of an Azobenzene Complex of Palladium(II) containing a Metal–Carbon σ-Bond

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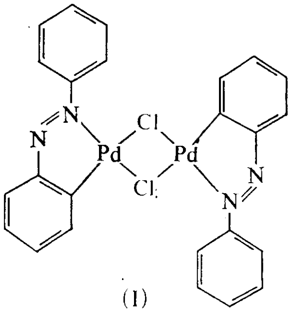
AZOBENZENE undergoes a variety of reactions with transition metals. In the case of the complex formed with di-iron enneacarbonyl, rearrangement to an *o*-semidine skeleton[1] occurs, while carbonylation in the presence of cobalt octacarbonyl causes the formation of 2-phenyl-1*H*-indazolone.[2] Many complexes, however, are thought to involve azobenzene acting as a bidentate ligand,[3] for example, the compound (I), which when treated with four equivalents of triethylphosphine forms the complex $Pd(PEt_3)_2(C_{12}H_9N_2)Cl$ (II).† It was of interest to determine the mode of co-ordination of azobenzene in this complex.

Crystals of (II), *trans*-$Pd(PEt_3)(C_{12}H_9N_2)Cl$, form as orange parallelepipeds in the monoclinic space group, $P2_1/c$, $a = 19{\cdot}521$, $b = 16{\cdot}695$, $c = 17{\cdot}445$, $\beta = 105{\cdot}70°$. There are 8 molecules in the unit cell and the structure analysis therefore required the determination of two independent molecules or a total of 60 atoms excluding hydrogen. Complete three-dimensional data were collected up to $\theta = 21°$ for Mo-K_α on a G.E. automated diffractometer by the "moving crystal, moving counter" technique. The structure was solved by the conventional Patterson, Fourier, and least-squares refinement methods. At present the discrepancy index is $R = 9{\cdot}1\%$ for the 2862 independent reflections above background.



(I)

The two independent molecules in the asymmetric unit have identical configurations within experimental error and the overall geometry around the palladium atom is shown in the Figure. Two *trans*-phosphorus atoms, a chlorine and a σ-bonded azobenzene surround the palladium

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† Bis(triethylphosphine)azobenzene–metal complexes of this type have been previously prepared by J. Bowers and A. C. Cope (private communication).

atom in an approximately square-planar fashion. A mean value of 2·308 ± 0·004 Å was found for the four palladium–phosphorus distances which compares favourably with those found in *trans*-$Pt(PEt_3)_2Cl_2$[4] and *trans*-$Pt[PPh_2Et](H)Cl$.[5] The mean value of the palladium–chlorine bond length *trans* to the σ-bonded carbon atom is 2·381 ± 0·005 Å, longer than the 2·30 Å calculated from the sum of the covalent radius[6] of 1·31 Å for Pd^{II} and 0·99 Å for chlorine. This lengthening is analogous to that found for other metal–ligand bonds *trans* to a σ-bonded carbon atom. For example, in $Ir(C_{15}H_{13}O)(Me_2SO)_2Cl$ [7] the *cis* and *trans* Ir–Cl bond lengths differ by 0·09 Å, in $KPt(acac)_2Cl$ [8] the *cis* and *trans* Pt–O bonds differ by 0·12 Å, and in $Ir_2Cl_4Me_2(CO)_4$ [9] the *cis* and *trans* Ir–Cl bonds involved in a bridging system differ by 0·14 Å.

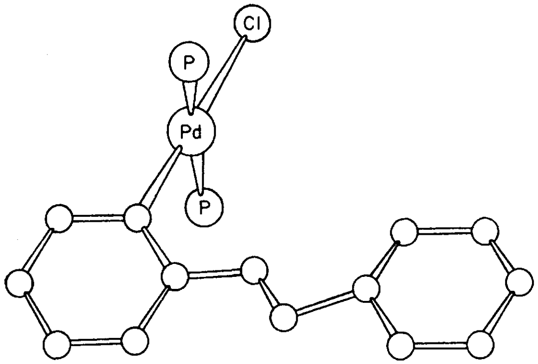

FIGURE. *Ethyl groups of the triethylphosphine ligands are not shown.*

Perhaps the most interesting aspect of this structure is that the potentially bidentate ligand, azobenzene, forms instead a stable, single σ-bond to the metal and thus maintains a square-planar configuration around the palladium atom. The closest distance of approach of either nitrogen to the palladium atom is 3·12 Å. An average palladium–carbon distance of 1·998 ± 0·013 Å was found which is slightly shorter (4σ) than the 2·05 Å predicted for the sum of the Pd^{II}–$C(sp^2)$ σ-bonded covalent radii. It is not possible to assess the importance of π-bonding effects from this relatively small difference. The co-ordinated azobenzene ligand assumes a *trans*-planar configuration and has bond lengths and angles comparable to those of to azobenzene[10] itself.

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