Crystal Structure of the Complex of Palladium with Biacetyl-bis(*N*-methyl,*N*-phenyl)osazone

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Summary In the title compound, the biacetyl bis-(*N*-methyl,*N*-phenyl)osazone acts as a tridentate ligand, the nitrogen atoms bonding *via* the lone pairs.

PALLADIUM(II) complexes with osazones have been prepared and characterized.[1] The complexes of the type $Pd(L)Cl_2$, when L = cyclohexane-1,2-dione bisphenylhydrazone and biacetyl bisphenylhydrazone, undergo hydrogen chloride elimination when passed down a silica-gel column, producing dimers of the type $Pd_2(L–H)_2Cl_2$, containing Pd–N covalent bonds. It is therefore surprising that the complex with biacetyl bis-(*N*-methyl,*N*-phenyl)hydrazone, which does not contain an N–H group, undergoes hydrogen chloride elimination under the same experimental conditions. The complex $Pd(L)Cl_2$, prepared as described previously was dissolved in CH_2Cl_2 and passed down a silica gel column, and eluted with $CHCl_3$. A red crystalline compound was obtained by crystallization from CH_2Cl_2–cyclohexane and the elemental analysis corresponds to the formula Pd(L–H)Cl.

The complex crystallises in the orthorhombic system, space group $P2_12_12_1$ with $a = 24{\cdot}88(1)$, $b = 7{\cdot}69(1)$, $c = 9{\cdot}47(1)$ Å, $D_m = 1{\cdot}67$, $D_x = 1{\cdot}68$ g cm^{-3} and $Z = 4$. A total of 1117 independent reflections measured out to a value of $\theta = 60°$, only 788 of which had intensities significantly above background, were recorded on a Siemens A.E.D. using a 5-point measuring routine. The structure was solved by the heavy-atom method. Least-squares refinement with anisotropic temperature factors for Pd and Cl atoms and isotropic temperature factors for all other non-hydrogen atoms has reached a conventional *R* factor of 0·083. The stereochemistry of the complex and some bond-length and bond-angle data are shown in the Figure. Mean standard deviations for bond distances between light atoms are 0·03 Å.

The palladium atom lies in a slightly distorted square-planar environment and bonds to the ligand biacetyl bis-(*N*-methyl,*N*-phenyl)osazone, which acts as a tridentate ligand, with the metal bonded to an *ortho*-carbon of one phenyl group and with two further nitrogens, thus forming two adjacent five-membered rings. The structure confirms that the nitrogen atoms bond through the lone pair as found for the azoarene complexes[2] rather than through the π-electron system as previously suggested.[3] The length of the Pd–N(3) bond, which is *trans* to the σ-bonded aryl, is significantly greater than that *trans* to the chlorine. This is probably a consequence of the large *trans* influence of a σ-bonded carbon atom.

Apart from the unchelated phenyl group and the methyl group linked to N(4), the molecule is nearly planar. This favours a mesomeric effect extended to the entire system, resulting from the short N–N, N–C, and C–C distances. With regard to the metal–carbon bond [1·94(2) Å], a partial π-contribution in addition to the σ-character should not be excluded, on account of the possibility of overlap between the *d*(filled) metal orbitals and the π-electron cloud of the aromatic ring.

Preliminary results of a parallel investigation on the physicochemical properties of the complex are consistent with the structure shown. In fact, i.r. data indicate the presence of only one Pd–Cl stretching vibration; ^{1}H n.m.r. data indicate the presence in the molecule of only nine aromatic hydrogens. The molecular weight is that of a monomeric species. Moreover the reaction with PPh_3 does not result in the displacement of the original ligand L.

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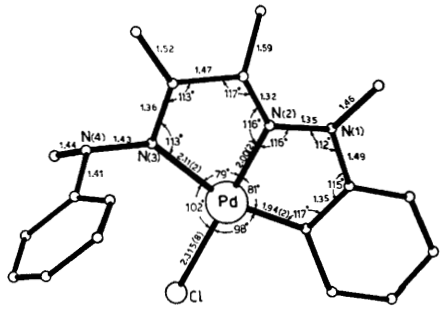

FIGURE

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[1] L. Caglioti, L. Cattalini, M. Ghedini, F. Gasparrini, and P. A. Vigato, submitted to *J. Chem. Soc.*
[2] A. C. Cope and R. M. Sickman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272.
[3] J. P. Kleimann and M. Dubeck, *J. Amer. Chem. Soc.*, 1963, **85**, 1544.