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Preliminary communication

ORGANOMETALLIC COMPLEXES CONTAINING THE BRIDGING GROUP *N,N'-o*-PHENYLENEBIS(SALICYLIDENEIMINE); CRYSTAL AND MOLECULAR STRUCTURE OF *μ-N,N'-o*-PHENYLENEBIS(SALICYLIDENE IMINATO)BIS(2-*C,N*-ACETOPHENONEOXIMEPALLADIUM(II))

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The existence of a binuclear complex of the ligand *N,N'-o*-phenylenebis-(salicylideneimine) (Salophen), viz. $[(CH_3)_2Au]_2$Salophen, was recently reporte [1] and attention drawn to previous suggestions [2] that conjugation in this ligand prevented sufficient distortion for it to bridge two metal ions.

The dimethylgold complex proved unsuitable for X-ray crystallographic study and attention has been directed to the related complexes *μ-N,N'-o*-phenylenebis(salicylideneiminato)bis(*N,N*-dimethylbenzylamine-2-*C,N*)palladium(II), $(DmbaPd)_2$Salophen, and *μ-N,N'-o*-phenylenebis(salicylideneiminato)bis(acetophenoneoxime-2-*C,N*)palladium(II), $(ApoPd)_2$Salophen. The analogous compounds $(DmbaPd)_2$Salen and $(DmbaPt)_2$Salen have been described [3]. Both salophen compounds are readily prepared by the action of Tl_2Salophen on the appropriate bridged halide, e.g. $[ApoPdCl]_2$ in dichloromethane.

A single crystal X-ray study has been carried out on the acetophenone-oxime complex.

Crystal data: $C_{36}N_4O_4H_{30}Pd_2$, M = 797.5; monoclinic, $P2_1/c$, a = 7.109(4)[*] b = 25.321(13), c = 17.979(8) Å, β = 107.8(4)°, Z = 4, D_c = 1.72 g/cm³, D_m = 1.72(1) g/cm³. Cu-K_α, λ = 1.5418, μ = 101.5 cm^{-1}.

A crystal 0.07 × 0.07 × 0.09 mm was mounted on an automated diffractometer and intensity data were collected by ω scans for $2\theta \leqslant 90°$ and $\theta - 2\theta$ scans for $90° < 2\theta < 120°$ with Cu-K_α radiation[**]. Of the 4562 *hkl* reflections measur 3122 were found to be statistically above background and these were used to solve the structure by Patterson and Fourier techniques [5]. Refinement by least squares methods [6] has led to a current conventional R of 0.069, with isotropic thermal parameters. Hydrogen atoms have not been found.

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[*] Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations of the least significant digits;

[**] For data reduction techniques and data reduction programs see ref. 4.

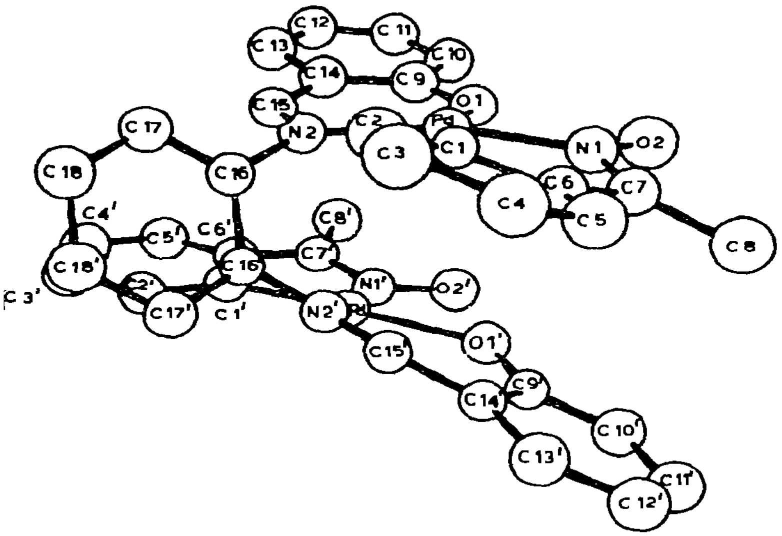

Fig. 1. The structure of (ApoPd)$_2$Salophen. The primed labels refer to the chemically, but not crystallographically, related half of the molecule.

Each palladium atom in the molecule possesses approximate square planar geometry (Fig. 1) being coordinated by N and C of the Apo ligand and N and O of a Schiff base moiety. Bridging by the salophen ligand is achieved by twisting the salicylidene—Pd—Apo moieties out of the plane of the phenylene bridge, about the C(16)—N(2) bonds; the angles formed by the plane of the bridge and the planes of the two salophen units are 48.3 and 50.1°, respectively.

This bridging arrangement gives an intramolecular Pd—Pd distance of 3.696(4) Å, which is considerably greater than twice the covalent radius of Pd^{II}, 1.31 Å, thus excluding any metal—metal bonding interaction.

The (DmbaPd)$_2$Salophen complex has a large unit cell (a = 32.2, b = 10.2, c = 42.1 Å, β = 92.8°) and a structural study was therefore not proceeded. However, evidence for the distortion of the salophen system from a planar arrangement is found in the ^{1}H NMR spectrum of the complex. The methylene protons of the Dmba unit appear as an AB system (chemical shift difference = 0.46 ppm, J = 14.0 Hz) and the N-methyl protons show 2 singlets (chemical shifts difference = 0.36 ppm), whereas in analogous complexes containing bidentate salicylideneimine ligands [3], DmbaPdSal=NR, these sets of protons both appear as singlets, presumably due to rapid inversion in solution of both the 5-membered "organometallic" chelate and the Schiff-base chelate rings leading to an average planar configuration for the molecules.

In the Dmba—salophen complex the molecule cannot achieve a single planar configuration for all its parts because rotation about the phenylene—N bonds is restricted by the other half of the molecule.

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