242. *cis*-Bis(2-Phenylpyridine)platinum(II) (CBPPP). A Simple Molecular Platinum Compound

Preliminary Communication

by **Laurent Chassot**[1] and **Alex von Zelewsky***

Institute of Inorganic Chemistry, University of Fribourg, Pérolles, CH–1700 Fribourg

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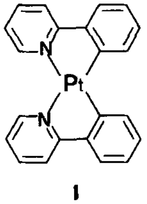
Summary

The deprotonated 2-phenylpyridine forms a 2:1 chelate with platinum(II) in *cis*-configuration, which exists as a dimer in a molecular solid.

In the present communication we report on the synthesis of a remarkably simple complex, which combines several of the interesting features of Pt(II)-compounds. Moreover, it is the basic unit of a potentially large family of related complexes, in which it will be possible to tune various properties to a considerable degree.

The structural formula of the title compound is given by **I** (= $Pt(phpy)_2$ = CBPPP). The complex can be obtained from 2′-lithiumphenyl(2-pyridine) and *trans*-$PtCl_2$ $(S(Et)_2)_2$.



I

It forms bright, red-orange, air-stable crystals which show a very strong emission at room temperature under irradiation by UV light ($\lambda_{\text{emission}} \approx 650$ nm). The compound can be sublimed at *ca.* 200 °C without decomposition. The yellow solution of CBPPP in CH_2Cl_2 shows a strong absorption ($\varepsilon = 10{,}500$) at 402 nm. This absorption obeys at room temperature the *Beer-Lambert* law, pointing to a single molecule origin of the band. No emission is observed from fluid solutions at room temperature. The absorption of the solid at 500 nm and the strong emission are thus due to intermolecular interactions in the crystal.

The electrochemical behavior was examined using CV in acetonitrile as solvent and tetraethylammoniumperchlorate as electrolyte. The CV shows a reversible reduction of the compound at −1.96 V and a completely irreversible oxidation at +0.46 V (*vs.*

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[1] Part of the planned doctoral thesis, University of Fribourg.

S.C.E). These values indicate a ligand-centered reduction, where the extra electron is in a π^*-orbital. The electrochemical oxidation is probably metal-centered, leading to a formal Pt(III)-complex which reacts rapidly to an unknown product. Semiempirical MO-calculations yield orbital energies in agreement with this behavior.

Oxidation by halogen X_2 is rapid, proceeding, most probably, by an oxidative addition mechanism to the corresponding $PtX_2(phpy)_2$-complex.

The mass spectrum yields M^{+}, with the pattern characteristic for the isotopic mass distribution around 503 atomic mass units. IR-, Raman-, ^1H-, ^{13}C-, ^{195}Pt-NMR-spectra are all in agreement with structure **I** in its pure *cis*-isomeric form, which was finally also confirmed by an X-ray analysis. The latter reveals the existence of dimeric units in which two molecules are symmetrically connected by a center of inversion located halfway between the two Pt-atoms which are 353 pm apart.

The present complex can be compared on the one hand with the complex of 2,2′-bipyridine [1] and, on the other hand with complexes of N–C-chelating ligands [2]. The 2:1 complex of the former is an ionic species, $Pt(bpy)_2^{2+}$, generally soluble only in strongly polar solvents, whereas $Pt(phpy)_2$ is neutral. This difference in charge will have a profound influence on the self-association of the complexes [3]. The dimeric units in the solid state show that self-association is possible and it should be rather easy to control this property by suitable modification of the phenylpyridine ligand.

Pt-complexes of N–C-chelates are quite numerous [4] but the present $Pt(phpy)_2$ is, to the best of our knowledge, the first homoleptic complex with a ligand in which the C- and the N-donor atoms are members of aromatic rings.

Experimental Part

General. All reactions with organometallic compounds were carried out under Ar in carefully dried solvents. $PtCl_2(S(Et)_2)_2$ was prepared according to [5].

2-(o-Bromophenyl)pyridine was obtained by a typical *Gomberg-Hey* reaction [6]. The method reported in [7] was followed for the preparation of 2-(*o*-lithiumphenyl)pyridine.

cis-*Bis(2-phenylpyridine)platinum(II)* (**I**). A solution of 960 mg (2.15 mmol) *trans*-$PtCl_2(S(Et)_2)_2$ in Et_2O (24 ml) and THF (6 ml) was added dropwise to a stirred suspension of 2-(*o*-lithiumphenyl)pyridine (890 mg, 5.55 mmol) in Et_2O (30 ml) at −40°. After 20 min the solvent was evaporated and the residue dissolved in CH_2Cl_2, washed with H_2O and dried over $MgSO_4$. From this solution 230 mg of pure **I** was obtained. The compound can be recrystallized from a CH_2Cl_2/hexane solution.

$C_{22}H_{16}N_2Pt$ Calc. C 52.48 H 3.21 N 5.57% Found C 52.43 H 3.29 N 5.35%

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