200. Highly Stereoselective Photochemical Oxidative Addition Reactions

Preliminary Communication

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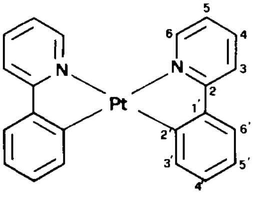
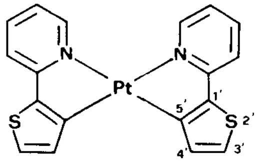
Cyclometallated complexes of the type *cis*-bis(2-phenylpyridine)platinum(II) ($C_{22}H_{16}N_2Pt$) and *cis*-bis(2-(2'-thienyl)pyridine)platinum(II) ($C_{18}H_{12}N_2S_2Pt$) undergo thermal or photochemical oxidative addition (TOA or POA) reactions with a number of substrates. TOA (with CH_3I, CH_3CH_2I *etc.*) yield mixtures of several isomers which rearrange slowly (within *ca.* one week at room temperature) to one of the possible *cis*-isomers. CH_2Cl_2, $CHCl_3$, or (*E*)-ClCH=CHCl, *e.g.*, do not react thermally. POA yield directly complexes of Pt(IV) with the halide and a σ-bonded C-atom in *cis*-position. The configuration, as assigned by extensive use of ^{1}H-NMR data, can be characterized for the two chelating ligands C···N and C'···N' by C,C'-*cis*; N,N'-*cis* and C(chelate), Cl-*trans*.

Oxidative addition is a fundamental step in many catalytic processes. Until recently [1], only thermal oxidative addition reactions (TOA) were described.

In our investigations of the photochemical and photophysical properties of a new type of cyclometallated complexes of several transition metals [2], we have found that these compounds are photochemically reactive towards most organic substrates (generally present as the solvent). The reactions between the Pt(II) compounds **I** and **II** and alkyl halides can be classified as thermal oxidative (TOA) or photochemical oxidative (POA) additions.



Pt(Phpy)$_2$
I

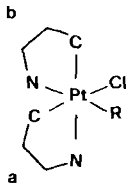


Pt(Thpy)$_2$
II

The addition in the dark (TOA) of Br_2 or I_2 to Pt(Phpy)$_2$ or Pt(Thpy)$_2$, respectively, gives palely colored precipitates. In the same way, the addition of CH_3I, CH_3CH_2I, CH_3Br, CH_3COCl to **II** yields pale yellow microcristalline products. Elemental analyses indicate a TOA of the organic substrate. ^{1}H-NMR spectra of Pt(Thpy)$_2$I$_2$ and Pt(Thpy)$_2$(CH$_3$)I show 2 or 3 isomers *(vide infra)*, which, in the case of the latter complex, rearrange slowly to only one product.

The Pt(II) complexes **I** and **II** are thermally stable in CH_2Cl_2, $CHCl_3$, or in (*E*)-ClCH=CHCl, even under reflux for extended periods of time. However, exposure of the deaerated or atmosphere-equilibrated solutions to visible light (sunlight or a 250-W halogen lamp) results in the formation of Pt(IV) compounds. UV/VIS spectra recorded during irradiation show fairly clean isosbestic points indicating a single reaction channel. The elemental analyses and ^{1}H-NMR spectra indicate a *cis*-insertion into a Cl–C bond and the formation of only one Pt(IV)isomer.

M(AB)$_2$CD complexes have a total of 11 stereoisomers [3]. Three of them have the ligands C and D in *trans*-position, the other 8 (4 pairs of enantiomers) in *cis*-position. The type of isomers formed in the POA reactions can be determined by ^{1}H-NMR spectroscopy in the following way: *i*) The non-equivalence of the protons in the two chelate ligands rule out the three *trans*-isomers. *ii*) Two protons in β-position with respect to Pt-atom, show upfield shifts [4]. One of those is in the phenyl or thienyl ring, the other one in the pyridine ring, indicating *cis*-positions for N–Pt–N and C–Pt–C for the chelate ligands. *iii*) The values of the coupling constants ^2J(Pt, H) are strongly affected by the *trans*-influence [5] and unambiguously differentiate the two remaining *cis*-structures. The configuration of the Λ-enantiomeric form of the product is given by structure **III**.



III

The TOA give mixtures of *trans*- and *cis*-stereoisomers which rearrange slowly (within about one week) to the *cis*-isomer **III** (probably the thermodynamically most stable form).

All Pt(IV) complexes obtained by POA have the structure **III**. ^{1}H-NMR spectra taken during irradiation of a solution of Pt(Thpy)$_2$ in CDCl$_3$ clearly show the formation of only this product.

Thorough photochemical and photophysical investigations with a special emphasis on mechanistic details are under way. Preliminary results indicate that it is not the emitting excited state of the Pt(II) complex which reacts with RX [6]. Furthermore, there is no direct analogy to the mechanism of oxidative addition reactions initiated by a photochemical step [1].

Experimental. – *General.* The syntheses of the Pt(II) complexes are analogue to a procedure in [2]. Photochemical reactions (at r.t.) were carried out using a 250-W halogen projector lamp. The products are purified by prep. TLC (silica gel, eluent CH$_2$Cl$_2$).

Characterization of the Compounds. Pt(Phpy)$_2$Br$_2$. Anal. calc.: C 39.83, H 2.65, N 4.22; found: C 39.74, H 2.59, N 4.15.

Pt(Thpy)$_2$I$_2$. Anal. calc.: C 28.1, H 1.57, N 3.64; found: C 28.03, H 1.55, N 3.66.

Pt(Thpy)$_2$(CH$_3$)I. Anal. calc.: C 34.71, H 2.3, N 4.26; found: C 34.66, H 2.41, N 4.28.

Pt(Thpy)$_2$(CH$_3$)(Br). Anal. calc.: C 37.40, H 2.48, N 4.59; found: C 37.43, H 2.54, N 4.66.

Pt(Phpy)$_2$(CHCl$_2$)(Cl)(CH$_2$Cl$_2$)$_{0.33}$. ^{1}H-NMR (360 MHz, (D$_7$)DMF): 9.66 (*ddd*, H–C(6a)); 7.82 (*ddd*, J(Pt) = 16.7, H–C(3'b)); 7.58–7.53 (*m*, H–C(6b), H–(4'b)); 6.73 (*s*, J(Pt) = 52.4, CHCl$_2$); 6.41 (*ddd*, J(Pt) = 45.6, H–C(3'a)). Anal. calc.: C 43.09, H 2.74, N 4.31; found: C 43.08, H 2.79, N 4.28.

$Pt(Phpy)_2(CH_2Cl)(Cl)(CH_2Cl_2)_{0.25}$. ^{1}H-NMR (360 MHz, (D$_7$)DMF): 9.72 (*ddd*, H–C(6a)); 7.61 (*ddd*, H–C(6b)); 7.52–7.45 (*m*, H–C(3'b), H–C(4'b)); 6.45 (*dd*, *J*(Pt) = 49.6, H–C(3'a)); 4.65 (*d*, *J*(Pt) = 90, 1 H, CH_2Cl); 4.16 (*d*, *J*(Pt) = 30.6, 1 H, CH_2Cl). Anal. calc.: C 45.8, H 3.06, N 4.54; found: C 45.88, H 3.10, N 4.54.

$Pt(Thpy)_2(CHCl_2)(Cl)(CHCl_3)_{0.33}$. ^{1}H-NMR (360 MHz, $CDCl_3$): 9.53 (*ddd*, H–C(6a)); 7.65–7.62 (*m*, H–C(4'b), H–C(3a), H–C(4b)); 7.30 (*ddd*, H–C(6b)); 6.89 (*s*, *J*(Pt) = 55.8, $CHCl_2$); 6.17 (*d*, *J*(Pt) = 17.5, H–C(4'a)). Anal. calc.: C 34.44, H 2.00, N 4.15; found: C 34.52, H 2.11, N 4.09.

$Pt(Thpy)_2(CH_2Cl)Cl$. ^{1}H-NMR (360 MHz, $CDCl_3$): 9.57 (*ddd*, H–C(6a)); 7.65–7.59 (*m*, H–C(3a), H–C(4b), H–C(4'b)); 7.44 (*ddd*, H–C(6b)); 6.15, (*d*, *J*(Pt) = 19.4, H–C(4')); 4.75 (*d*, *J*(Pt) = 87.2, 1 H, CH_2Cl_2); 4.4 (*d*, *J*(Pt) = 34.8, 1 H, CH_2Cl_2). Anal. calc.: C 38.00, H 2.35, N 4.67; found: C 37.87, H 2.40, N 4.72.

$Pt(Thpy)_2(CH{=}CHCl)Cl$. ^{1}H-NMR (360 MHz, (D$_7$)DMF): 9.43 (*ddd*, H–C(6a)); 7.98–7.92 (*m*, H–C(4'b), H–C(3a), H–C(4b)); 7.83 (*ddd*, H–C(6b)); 6.85 (*d*, *J*(Pt) = 36, 1 H, CH=CHCl); 6.1 (*d*, *J*(Pt) = 18.8, H–C(4'a)); 5.33 (*d*, *J*(Pt) = 39.1, 1 H, CH=CHCl).

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