15. Complexes with a Pincers. 2,6-Diphenylpyridine as Twofold-Deprotonated (C ∧ N ∧ C) Terdentate Ligand in C,C-*trans*-, and as Mono-deprotonated (C ∧ N) Chelate Ligand in Chiral C,C-*cis*-Complexes of Platinum(II) and Palladium(II)

Preliminary Communication

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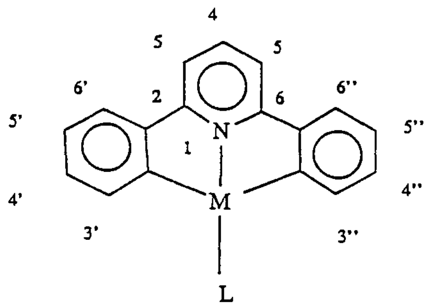
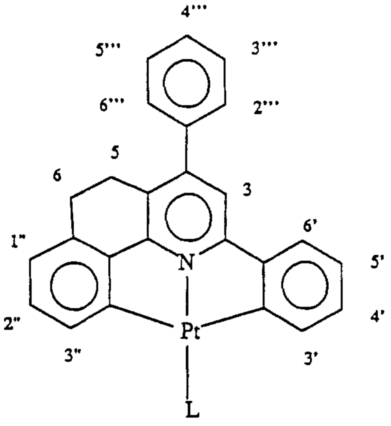
2,6-Diphenylpyridine forms, as twofold-deprotonated, terdentate ligand, complexes with Pt(II) and Pd(II), having two adjacent five-membered metallocycles. As mono-deprotonated, bidentate ligand, it forms *cis*-bis-complexes having a chirality axis. Pt(II) complexes undergo thermal and photochemical oxidative addition reactions, yielding stable Pt(IV) compounds. Pd(II) complexes yield substitued 2,6-diphenylpyridine in photochemical reactions.

Recently, several compounds of a series of neutral, homoleptic members of Pt(II) and Pd(II) [1][2], containing two aromatic (C ∧ N) ligands (*e.g.* phenylpyridine anion) in a *cis*-arrangement, have been prepared. This series was extended then to isomeric complexes of Pt(II) and Pd(II) [3], containing two different aromatic ligands (C ∧ C) and (N ∧ N) (2,2'-biphenyldiyl dianion and 2,2'-bipyridine). These compounds show interesting thermal and photochemical [5–8] reactivities. In this communication, we report the synthesis and some properties of several compounds, which have either C,C-*trans*- (**I**) or C,C-*cis*-configurations. The latter comprises a chirality axis. The new complexes **I–IV** are members of two classes of cyclometalated compounds. 2,6-Diphenylpyridine (H_2diphpy) acts as terdentate (C ∧ N ∧ C) ligand in compound **I** and as bidentate (C ∧ N) ligand in **III**. The analogous complexes with 5,6-dihydro-2,4-diphenylbenzo[*h*]quinoline (H_2diphquin) are **II** and **IV**.

Few complexes of platinum or palladium contain multidentate ligands in a C,C- or N,N-*trans*-arrangement [9–11]. There have been attempts [12] to prepare a cyclometalated Pd(II) complex where diphpy acts as a terdentate (C ∧ N ∧ C) ligand. Recently, *Canty et al.* [13] reported the synthesis of Pd compounds containing a terdentate (C ∧ N ∧ C) aromatic ligand, where the two benzyl moieties and the pyridine form six-membered chelate rings with the metal. Two adjacent five-membered metallocycles analogous to 2,2':6',2''-terpyridine are more difficult to prepare, particularly for Pd(II).

The compounds are prepared by transmetalation of the dilithiated (C ∧ N ∧ C) ligand with $M(SEt_2)_2Cl_2$ (M = Pt, Pd), and subsequent exchange of thioether by pyridine. The reaction always gives the two products, *trans*-M(C ∧ N ∧ C)L (**I**) and *cis*-$M(C \wedge N)_2$ (**III**). The latter can also be prepared from the monolithiated ligands.

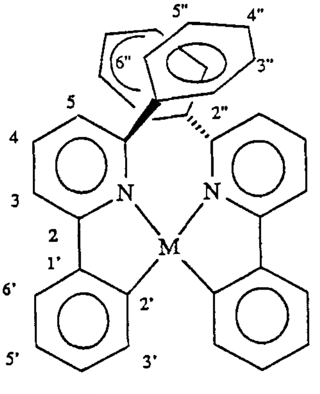




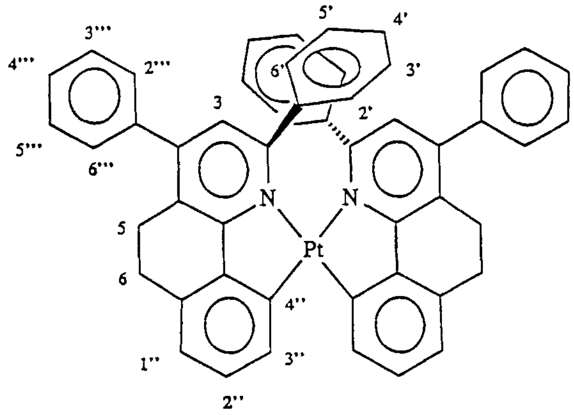
L = SEt_2, pyridine
M = Pt(II), Pd(II)

I M(diphpy)L

II Pt(diphquin)L



M = Pt(II), Pd(II)



III $M(Hdiphpy)_2$

IV $Pt(Hdiphquin)_2$

Products **I** and **III** were characterized by elemental analysis, ^{1}H-NMR, ^{13}C-NMR, ^{195}Pt-NMR, UV/VIS, and IR spectroscopies. Preliminary results from X-ray diffraction analysis show clearly *cis*-configuration for $Pt(Hdiphpy)_2$.

MLCT (Metal-to-Ligand Charge Transfer) transitions are observed for all the new compounds (M(diphpy) (py): λ_{max} = 347 nm (14580) for M = Pt; λ_{max} = 384 nm (6380) for M = Pd; $M(Hdiphpy)_2$: λ_{max} = 404 nm (2580) for M = Pt; λ_{max} = 362 nm (4000) for M = Pd).

As the *cis*-bis(phenylpyridinato,N,C$^{2'}$)platinum(II) [7] and the (biphenylato,C^2,C$^{2'}$)-(bipyridine,N,N')platinum(II) [3], the presently studied Pt(II) complexes dissolved in CH_2Cl_2 undergo thermal oxidative addition reactions with an excess of CH_3I, yielding stable Pt(IV) compounds. After prolonged time in contact with CH_3I, the thermodynamically stable *cis*-adducts were isolated. Pd(diphpy)(py) does not react thermally with CH_3I. The photochemical behavior of all Pt(II) and Pd(II) complexes is remarkable, as already observed for *cis*-Pt(II) compounds [3] [7] [8] [14]. UV/VIS spectroscopy shows one or more isosbestic points during irradiation in halogenated solvents. The disappearance of the first MLCT band in the VIS part of the spectrum indicates a photochemical oxidative addition, leading to Pt(IV) complexes. Sterically hindered *cis*-Pt(II) compounds **II** and **IV** do not react in a clean manner. As observed with other Pd complexes [3] [14], Pd(diphpy)(py) yields RX_{n-1}-substituted diphpy from RX_n halogenated solvents as photodecomposition product. These reactions are promising for the catalytic formation of C–C bonds and for introducing functional groups on aromatic rings.

Experimental. – $Pt(SEt_2)Cl_2$ [15], $Pd(SEt_2)Cl_2$ [15] [16], and 5,6-dihydro-2,4-diphenylbenzo[*h*]quinoline [17] were prepared according to published procedures, 2,6-diphenylpyridine was purchased from *Aldrich*. All solvents were dried and distilled under N_2 prior to use. Reactions involving Li reagents were carried out under N_2 using *Schlenk* tube techniques.

General Procedure. BuLi (6.8 ml in 1.6N hexane) was added to the ligand (5.8 mmol) in Et_2O (50 ml) at –5°. The reddish soln. was stirred at –5° for 2 h, and then (only for the diphpy) kept for 12 h at 8°. A soln. of dilithiated ligand (1.08 mmol) in Et_2O (50 ml) was added slowly to a suspension of $PtCl_2(SEt_2)_2$ (0.95 mmol) in Et_2O (20 ml) at –10°. After stirring 45 min at –10°, the mixture was hydrolyzed and extracted with CH_2Cl_2. The org. phases were dried and concentrated to an oil, which was then purified by flash chromatography (SiO_2, acetone/hexane/CH_2Cl_2 1:6:3). Products **I** (R = SEt_2; yield 10%) and **III** were recrystallized in CH_2Cl_2/hexane (Pt(diphpy) (SEt_2) as orange plates, Pt(diphquin) (SEt_2) as orange-red needles, and $Pt(Hdiphpy)_2$ and $Pt(Hdiphquin)_2$ as yellow needles). Pt(C ∧ N ∧ C) (SEt_2) dissolved in CH_2Cl_2 reacted with pyridine to give Pt(C ∧ N ∧ C) (py) as orange needles.

A soln. of Li_2diphpy (5.8 mmol) in Et_2O (80 ml) was added extremely slowly to a suspension of $Pd(SEt_2)_2Cl_2$ in Et_2O (50 ml) at –78°. After stirring 1 h, pyridine (4 ml) was added slowly and the temp. raised to –65°. The tan heterogeneous mixture was stirred 30 min at –78°, before removal of the refrigerant bath. Once the soln. had reached 0°, it was hydrolyzed. After extractions with CH_2Cl_2, the org. phase was dried, reduced in volume, and purified by flash chromatography several times (SiO_2, Et_2O/hexane 1:6, then acetone/hexane/CH_2Cl_2 6:6:3) giving **I** (yield 1.4%) and **III**.

Characterization of the Compounds. (2,6-Diphenylpyridinato,N,$C^{2'}$*,*$C^{2''}$*)(pyridine)platinum(II)* (**I**; L = py, M = Pt(II)). ^{1}H-NMR (360 MHz, $CDCl_3$): 6.92 (*ddd, J*(Pt, H) = 24, H–C(3'), H–C(3")); 9.07 (*ddd, J*(Pt, H) = 44, H–C(2) of py, H–C(6) of py). Anal. calc.: C52.42, H 3.18, N 5.57; found: C 52.48, H 3.20, N 5.56.

cis-*Bis(2,6-diphenylpyridinato,N,*$C^{2'}$*)platinum(II)* (**III**; M = Pt(II)). ^{1}H-NMR (360 MHz CD_2Cl_2): 8.25 (*d, J*(Pt, H) ≈ 50, H–C(3')); 8.37 (br., H–C(2")). Anal. calc.: C 62.40, H 3.72, N 4.28; found: C 62.28, H 3.69, N 4.27.

(2,6-Diphenylpyridinato,N,$C^{2'}$*,*$C^{2''}$*)(pyridine)palladium(II)·0.5* CH_2Cl_2 (**I**; L = py, M = Pd(II)). ^{1}H-NMR (360 MHz, CD_2Cl_2): 7.03 (*dd,* H–C(3'), H–C(3")); 8.84 (*dd,* H–C(2) of py, H–C(6) of py). Anal. calc.: C 59.09, H 3.80, N 6.13; found: C 59.10, H 3.75, N 6.21.

cis-*Bis(2,6-diphenylpyridinato,N,*$C^{2'}$*)palladium(II)·2* CH_2Cl_2 (**III**; M = Pd(II)). ^{1}H-NMR (360 MHz, CD_2Cl_2): 8.25 (*d,* H–C(3')); 8.84 (*d,* H–C(2")). Anal. calc. C 57.42, H 3.92, N 3.88; found: C 58.68, H 3.82, N 3.80.

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