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cis-Bis(2-phenylpyridine)platinum(II) (CBPPP): A Simple Molecular Platinum Compound

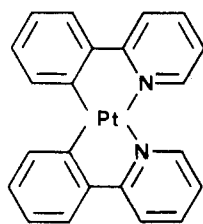
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Synthesis, crystal and molecular structure, electronic spectra in solution and in the solid state, electrochemical properties, the mass spectrum, and ^1H , ^{13}C , and ^{195}Pt NMR spectra as well as some results on the reactivity of *cis*-Pt^{II}(Phpy)₂ (I), C₂₂H₁₆N₂Pt, are reported (Phpy⁻ = deprotonated 2-phenylpyridine). The complex is prepared from *trans*-PtCl₂(SEt₂)₂ and 2-(2'-lithiophenyl)pyridine. The molecular structure reveals a pure *cis* form with bowllike distortions of the Phpy⁻ ligands. In the crystal (space group monoclinic *P*2₁/*n*, *a* = 12.339 (2)  , *b* = 11.790 (2)  , *c* = 11.788 (3)  , β = 106.02 (2)  , *Z* = 4, *d* = 2.029 g cm⁻³; diffractometer measurements, full-matrix least-square refinements, final *R* = 0.02, *R*_w = 0.023) distances are Pt-N = 2.13   and Pt-C = 1.99  . The molecules are associated to dimeric units with essentially parallel planes at a distance of 3.37  . The Pt-Pt distance in the dimer is 3.53  . A thermal motion analysis is reported. Electronic spectra feature a strong absorption band around 400 nm ($\epsilon \approx 10000$), whose position depends on the solvent. No indication of molecular association is found in solution. The solid emits strongly in the range 500-600 nm at room temperature. *cis*-Pt(Phpy)₂ reacts with Br₂ in an oxidative-addition reaction to PtBr₂(Phpy)₂.

Introduction

In the present paper¹ we report on a remarkably simple platinum(II) complex that forms the basic unit of a potentially large group of compounds: *cis*-bis(2-phenylpyridine)platinum(II), CBPPP.



This complex contains deprotonated 2-phenylpyridine (Phpy) as an anionic ligand, which is isoelectronic with 2,2'-bipyridine (bpy). Complexes of Phpy⁻ carry one positive charge less per ligand compared to those with bpy.

Besides the difference in total charge, there is also a considerable variation in the donor/acceptor properties of Phpy⁻ compared to bpy. Phpy⁻ is a much stronger base, but not necessarily a stronger π acceptor than bpy.² Metal compounds with the C,N-coordinated Phpy⁻ have been described before,³ but Pt(Phpy)₂ is the first example of a homoleptic complex with this ligand.

Experimental Section

Materials. 2-(*o*-Bromophenyl)pyridine was prepared by a typical Gomberg-Hey reaction.⁴ Lithium was introduced by a reported method.⁵ PtCl₂(S(C₂H₅)₂)₂ was prepared according to Kaufmann et al.⁶ Solvents were dried prior to use by standard techniques. Reactions involving lithium reagents were carried out under an argon atmosphere.

Measurements. Molecular weights were determined by vapor pressure osmometry.⁷ Electronic spectra were recorded with a Perkin-Elmer 555 spectrophotometer. ^1H and ^{13}C NMR spectra were

collected with a Varian XL-300 spectrometer.⁸ Electrochemical measurements were carried out with a Metrohm Polarecord 506 coupled with a VA scanner E612.

Preparation of *cis*-Bis(2-phenylpyridine)platinum(II). A solution of *trans*-PtCl₂(SEt₂)₂ (0.96 g, 2.15 mmol) in diethyl ether (24 mL) and THF (6 mL) was added dropwise to a stirred suspension of 2-(*o*-phenylpyridine)lithium (0.86 g, 5.55 mmol) in diethyl ether (30 mL) at 233 K. After the suspension was stirred for 20 min, the solvent was evaporated. The residue was dissolved in CH₂Cl₂, washed with water, and dried over MgSO₄. Upon reduction of volume, a red-orange solid precipitated, and after filtration and washing with cold CH₂Cl₂, 0.23 g of pure Pt(Phpy)₂ was obtained. Further concentration of the mother liquors yielded a second crop (0.1 g) of the red-orange complex. The product can be recrystallized from dichloromethane/hexane. Anal. Calcd for PtC₂₂H₁₆N₂: C, 52.48; H, 3.21; N, 5.57. Found: C, 52.43; H, 3.29; N, 5.35.

Reaction of *cis*-Pt(Phpy)₂ with Bromine. A diluted solution of bromine in dichloromethane was added dropwise to a solution of *cis*-Pt(Phpy)₂ (35 mg) in 20 mL of dichloromethane. Decoloration of the yellow solution occurred. The addition of the bromine solution was terminated, when the color of Br₂ persisted. After evaporation of the solvent, a cream-colored powder was obtained. Anal. Calcd for PtC₂₂H₁₆N₂Br₂: C, 39.83; H, 2.65; N, 4.22. Found: C, 39.74; H, 2.59; N, 4.15.

X-ray Crystallography. Data Collection. Preliminary investigations with precession photographs, taken on a relatively large crystal, revealed the space group as well as the approximate cell dimensions. A small specimen was chosen for data collection. The crystal was mounted in a 0.3-mm Lindemann glass capillary with a little epoxy cement. Precise geometric and intensity data were collected at room temperature on an automated four-circle diffractometer (Enraf-Nonius CAD 4), equipped with a molybdenum X-ray tube and a graphite monochromator. The unit cell parameters as well as the orientation of the crystal with respect to the goniometer reference frame were determined by a least-squares fit to the angular positions of 14 reflections in the range 10   < θ < 15  . Integrated intensity data were collected in equatorial setting for 4371 reflections in the range of 0   < θ < 27  , using an ω -scan motion (required $\sigma(I)/I < 0.03$ or a time limit of 90 s for 0   < θ < 20   and 180 s for 20   < θ < 27  ). The first and the last sixth of the total scan were used to determine the background radiation corrections. Periodic intensity and orientation controls during the data collection showed the crystal to be perfectly stable within the 135 h of X-ray exposure. The usual Lorentz and polarization corrections were applied to the raw data, and a numerical absorption correction was performed, using a matrix of 8   8   8 grid points throughout the crystal.

Structure Solution and Refinement. The positions of the platinum atoms were located from a Patterson map. Two cycles of least-squares

- (1) A preliminary paper was reported in: Chassot, L.; von Zelewsky, A. *Helv. Chim. Acta* 1983, 66, 2443.
- (2) MO calculations in the EHT-SCCC frame give a slightly higher π - σ^* energy difference in Pt(Phpy)₂ as compared to Pt(bpy)₂²⁺, which is, however, entirely due to a stronger σ interaction ($\pi = d_{zz}, d_{yz}; \sigma^* = d_{x^2-y^2}$).
- (3) Gutierrez, M. A.; Newkome, G. R.; Selbin, J. J. *Organomet. Chem.* 1980, 202, 341.
- (4) Abramovitch, R. A.; Saha, J. G. *J. Chem. Soc.* 1964, 2175.
- (5) Madeja, K.; H  sing, E.; Ahrens, N. *Z. Chem.* 1967, 7, 22.
- (6) Kaufmann, G. B.; Cowan, D. O. *Inorg. Synth.* 1960, 6, 211.
- (7) We thank B. Magyar of the Swiss Federal Institute of Technology, Z  rich, for carrying out the measurements.

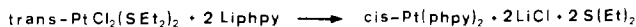
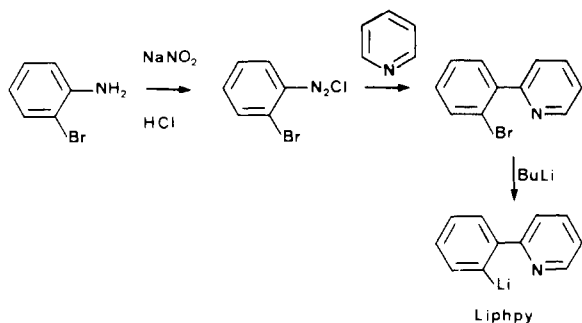
- (8) We thank the Varian NMR Application Laboratory, Zug, Switzerland, for the opportunity to carry out the measurements.

Table I. Crystal Measurement and Refinement Parameters

formula	PtC ₂₂ H ₁₆ N ₂
space group	monoclinic <i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	12.339 (2)
<i>b</i> , Å	11.790 (2)
<i>c</i> , Å	11.788 (3)
β , deg	106.02 (2)
<i>V</i> , Å ³	1648.3
<i>d</i> _{calcd} , g/cm ³	2.029
<i>Z</i>	4
cryst size, mm	0.19 × 0.14 × 0.12
limiting faces of the cryst	(110), (101̄), (110̄), (110), (101), (110)
μ (Mo K α), cm ⁻¹	86.1
range of θ , deg	0–27
no. of reflns, $F_o > 3\sigma(F_o)$	3012
no. of variables	227
<i>R</i> ^a	0.0196
<i>R</i> _w ^b	0.0232

^a $R = (\sum |F_o - F_c|) / (\sum F_o)$. ^b $R_w = ((\sum w(F_o - F_c)^2) / (\sum w F_o^2))^{1/2}$, where $w = ((\sigma(F_o))^2 + (0.01 F_o)^2)^{-1/2}$. $\sigma(F_o)$ was derived from counting statistics.

Scheme I



refinements and subsequent Fourier synthesis revealed all the remaining non-hydrogen atoms. After further refinement cycles, hydrogen atoms were added in calculated positions but not refined. Weighted refinements (weights, $w = ((\sigma(F_o))^2 + (0.01 F_o)^2)^{-1/2}$) converged to a final agreement of $R = 0.020$ ($R_w = 0.023$) with three positional and six thermal parameters refined for each of the non-hydrogen atoms. The isotropic extinction coefficient, which was included in the refinement procedure,⁹ converged to 3.68×10^{-7} . The program system used was the Enraf-Nonius structure determination package.¹⁰ A survey of crystal measurement and refinement parameters is given in Table I.

Results and Discussion

Synthesis. The preparation of CBPPP follows the route given in Scheme I.¹¹ The complex is soluble in dichloromethane, acetonitrile, toluene, mesitylene, and probably most other organic solvents. It decomposes to unknown products under irradiation with UV or daylight.

It is noteworthy that the formation of the complex is completely stereospecific. There is no indication that appreciable quantities of the trans isomer are formed. The formation of the pure cis isomer from the *trans*-PtCl₂(SEt₂)₂ complex can be understood if the first step is a substitution of a thioether ligand by the N-donor atom, assuming the generally accepted sequence $C \approx S > Cl > N$ in trans labilization.¹² Scheme

Scheme II

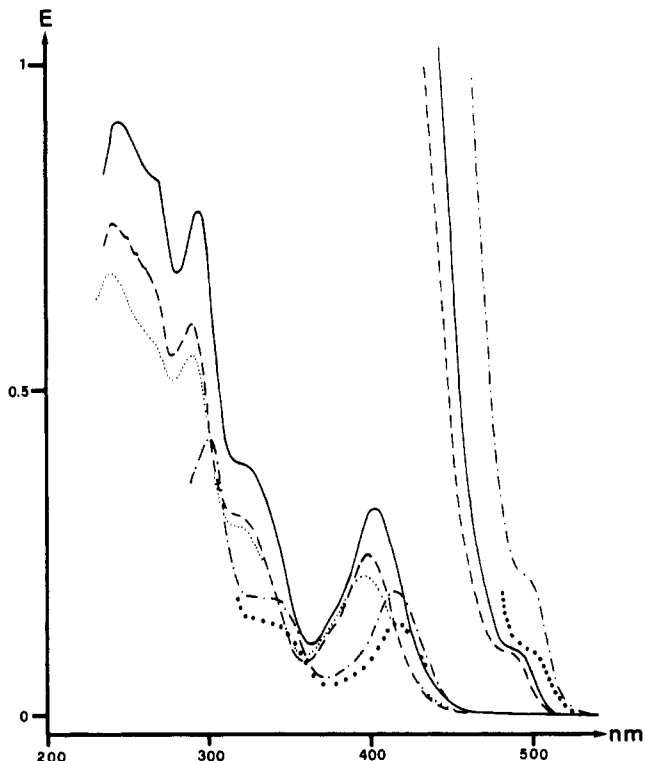
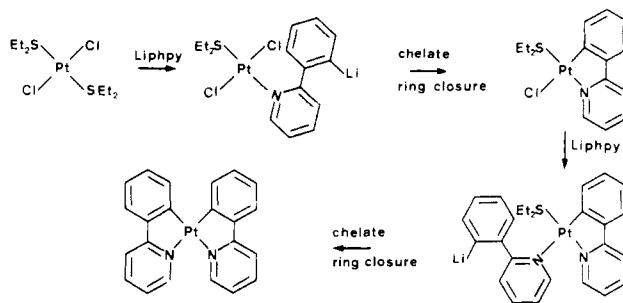


Figure 1. UV/vis spectra of Pt(Phpy)₂ in various solvents at two different concentrations each, except for EtOH: (—) in CH₂Cl₂, c 10⁻³ M, 3.1 × 10⁻⁵ M; (---) in CH₃CN, c 10⁻³ M, 2.3 × 10⁻⁵ M; (---) in EtOH, c 3.5 × 10⁻⁵ M; (·-·) in toluene, c 2 × 10⁻³ M, 1.8 × 10⁻⁵ M; (•) in mesitylen, c 10⁻³ M, 1.4 × 10⁻⁵ M.

II rationalizes the reaction sequence.

The mass spectrum of the compound yields, upon heating of the source to 120 °C, first a pattern characteristic for a Pt compound with mol wt 560.¹³ The corresponding peaks disappear at higher temperatures, and at 190 °C only the spectrum with M⁺ at 503, which corresponds to Pt(Phpy)₂⁺, is present. The most likely explanation for the species at a mass of 560 is the presence of a small amount of a butylated product, insignificant at the level of the accuracy of the elemental analysis, which is more volatile than the parent complex.

Addition of Br₂ to Pt(Phpy)₂ yields by an oxidative-addition reaction a product of stoichiometry PtBr₂(Phpy)₂.

Properties in Solution

Electronic Spectra. From the position that deprotonated phenylpyridine presumably occupies in the spectrochemical series, it is to be expected that no d-d transitions will lie in the visible region of the spectrum. Figure 1 gives the ab-

(9) $F_o = F_c / ((1 + g)I_c)$, where g is the extinction coefficient.
 (10) Frenz, B. A. "Structure Determination Package", SDP Users Guide, Version of Jan 6, 1983 Scattering factors are those from: "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.
 (11) It is quite obvious that the Phpy ligand can, in principle, be easily varied because both components, 2-bromoaniline and pyridine, are accessible in substituted forms or they can be changed to other aromatic substrates.

(12) Basolo, F.; Pearson, R. G. *Prog. Inorg. Chem.* **1962**, *4*, 381.
 (13) We thank Prof. U. P. Schlunegger, Institute of Organic Chemistry, University of Berne, for the mass spectra.

Table II. Positions and Extinction Coefficients of Absorption Bands in Various Solvents

solvent	λ_{\max} , nm (ϵ)				
	<i>b</i>				
ethanol	<i>b</i>	396 (8910)	316 (12 200) ^a	289 (23 334)	238 (30 083)
acetonitrile	481 (100) ^a	398 (10 630)	316 (11 359) ^a	290 (25 178)	240 (32 400)
dichloromethane	484 (90) ^a	402 (10 450)	322 (12 516) ^a	293 (25 129)	244 (29 581)
toluene	494 (100) ^a	414 (10 270)	334 (9729) ^a	300 (22 865)	
mesitylene	499 (100) ^a	416 (10 160)	336 (10 140) ^a		

^a Shoulder. ^b Not observable due to insufficient solubility.

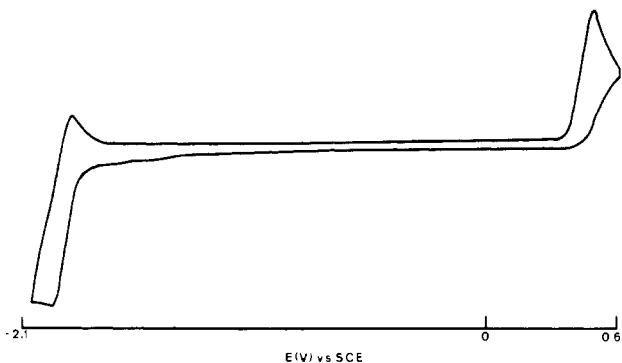


Figure 2. Cyclic voltammogram of Pt(Phpy)₂ in acetonitrile (scan rate 0.1 V s⁻¹; T = 298 K; glassy-carbon working electrode; tetraethylammonium perchlorate, 0.1 M).

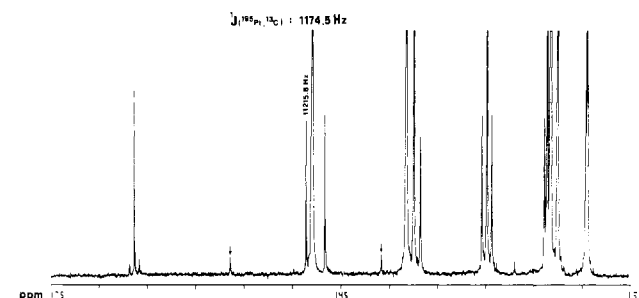


Figure 3. 75-MHz ¹³C NMR spectrum of Pt(Phpy)₂ in CD₂Cl₂ at 295 K.

sorption spectrum of the complex, which shows a weak shoulder ($\epsilon \approx 100$) and a strong band ($\epsilon \approx 10\,000$) in the visible region. The position of this band, as well as of some bands in the UV are solvent dependent (Table II). The strong long-wavelength absorption in the range from 396 to 416 nm (depending on the solvent) is most probably a MLCT transition. It occurs also in the solid but disappears completely in the product of the oxidative addition, PtBr₂(Phpy)₂. Such a transition can also explain the photochemical lability of the complex, because the excited state is formally a Pt(III) species, which is expected to be very reactive. In the solid state, there is an additional absorption at ca. 500 nm and a very strong emission in the range 600–700 nm.¹⁴ The solution spectra obey the Beer–Lambert law up to the saturation concentration (ca. 5 · 10⁻² M). These spectral features of the solid must be due to the dimeric structure of the complex in the solid state (vide infra).

Electrochemistry. In a cyclic voltammogram in acetonitrile as solvent, a one-electron reduction and a one electron oxidation are observed (Figure 2). The reduction at -1.94 V (vs. SCE) is nearly reversible ($\Delta E_p = 0.07$ V), corresponding most likely to the reduction of one of the coordinated Phpy ligands to the corresponding radical anion. The oxidation is irreversible in the sense that the reduction wave is completely absent. This must be due to an EC process, where Pt^{III}.

Table III. Bond Distances (Å) and Angles (deg)^a

	ligand 1		ligand 2		mean value ^c
	dist	value	cor value ^b	value	
Pt--Pt					3.528 (1)
Pt-N	2.125 (3)	2.129	2.128 (3)	2.133	2.127 (4)
Pt-Cl	1.984 (4)	1.989	2.002 (3)	2.006	1.988 (25)
C1-C2	1.398 (5)	1.401	1.398 (5)	1.401	1.398 (0)
C2-C3	1.395 (6)	1.399	1.373 (5)	1.375	1.384 (31)
C3-C4	1.359 (7)	1.362	1.391 (6)	1.394	1.375 (45)
C4-C5	1.390 (7)	1.394	1.391 (6)	1.393	1.391 (1)
C5-C6	1.391 (5)	1.394	1.400 (5)	1.402	1.396 (13)
C6-C1	1.429 (5)	1.431	1.411 (5)	1.414	1.420 (25)
C6-C7	1.460 (5)	1.464	1.462 (5)	1.466	1.461 (3)
C7-C8	1.382 (5)	1.385	1.404 (5)	1.407	1.393 (31)
C8-C9	1.385 (7)	1.388	1.386 (6)	1.389	1.386 (1)
C9-C10	1.369 (7)	1.373	1.375 (6)	1.378	1.372 (8)
C10-C11	1.373 (6)	1.376	1.372 (6)	1.375	1.373 (1)
C11-N	1.336 (5)	1.339	1.337 (5)	1.341	1.337 (1)
N-C7	1.356 (5)	1.359	1.359	1.352	1.353 (10)

normal distance between the two planes of the dimer: 3.37 Å

angle	ligand 1		ligand 2		mean value ^c
	value	cor value ^b	value	cor value ^b	
N-Pt-N				101.9	101.9 (1)
Cl-Pt-Cl				99.3	99.3 (2)
N-Pt-Cl(trans)	176.4 (1)	176.4	176.8 (1)	176.4	176.6 (6)
N-Pt-Cl(cis)	79.3 (1)	79.3	79.3 (1)	79.3	79.3 (0)
Pt-N-C7	112.8 (2)	112.8	113.3 (3)	113.3	113.1 (7)
Pt-Cl-C6	113.5 (3)	113.5	114.1 (3)	114.0	113.8 (8)
N-C7-C6	113.6 (3)	113.6	114.3 (3)	114.2	114.0 (10)
C7-C6-C1	115.8 (3)	115.8	116.1 (3)	116.1	116.0 (4)
Pt-N-C11	128.6 (3)	128.6	128.6 (3)	128.6	128.6 (0)
Pt-Cl-C2	131.2 (3)	131.2	130.4 (3)	130.4	130.8 (11)
C7-N-C11	118.4 (3)	118.5	118.1 (3)	118.1	118.3 (4)
N-C11-C10	123.5 (4)	123.5	124.0 (4)	123.9	123.8 (7)
C11-C10-C9	117.8 (4)	117.8	118.1 (4)	118.1	118.0 (4)
C10-C9-C8	120.1 (4)	120.1	119.7 (4)	119.6	119.9 (6)
C9-C8-C7	119.0 (4)	119.1	118.6 (4)	118.6	118.8 (6)
C8-C7-N	121.0 (4)	121.0	121.2 (4)	121.1	121.1 (3)
C8-C7-C6	125.1 (4)	125.1	124.4 (4)	124.4	124.8 (10)
C6-C1-C2	115.3 (4)	115.3	115.6 (3)	115.6	115.5 (4)
C1-C2-C3	122.3 (4)	122.3	122.9 (4)	122.9	122.6 (8)
C2-C3-C4	120.5 (5)	120.9	120.6 (4)	120.6	120.6 (1)
C3-C4-C5	120.2 (5)	120.2	118.9 (4)	119.0	119.6 (18)
C4-C5-C6	119.5 (4)	119.6	119.6 (4)	119.7	119.6 (1)
C5-C6-C1	121.9 (4)	121.9	122.2 (4)	122.2	122.1 (4)
C5-C6-C7	121.9 (4)	121.9	121.3 (4)	121.3	121.6 (8)

torsional angle	value		
	ligand 1	ligand 2	mean value ^c
N-C7-C6-C1	1.1	0.6	0.9 (7)
C8-C7-C6-C5	1.8	3.2	2.5 (20)

sum of the four "in plane" angles around Pt: 359.8
 sum of the five angles in chelate ring 1: 535.0
 sum of the five angles in chelate ring 2: 537.1 } 536.1 (29) (mean)

^a Numbers in parentheses correspond to estimated standard deviations in terms of the least significant digits. ^b Corrected values for thermal motion effects. ^c With population esd's of the mean in parentheses; esd = 2^{1/2} abs(a - b).

(14) We thank Dr. B. Klein, Institute of Inorganic Chemistry, University of Lausanne, for the reflectance spectra of the solid.

(Phpy)₂⁺ reacts in a fast, irreversible step, most probably with the solvent.

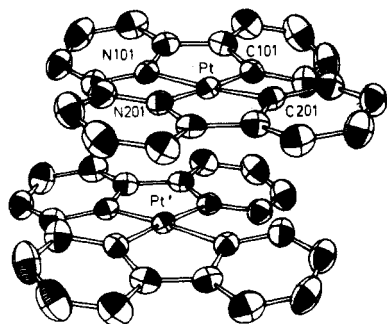


Figure 4. ORTEP plot of the $\text{Pt}(\text{Phpy})_2$ dimer.

NMR Spectra. Molecular Weight in Solution. The ^{13}C NMR spectrum is given in Figure 3. The assignment is straightforward through the use of DEPT pulse sequence and 2-D spectroscopy. Coupling between ^{195}Pt ($I = 1/2$, 33% natural abundance) and ^{13}C is observed for most ^{13}C nuclei. The coupling constant with the directly bound C atom is particularly large ($^1J_{^{195}\text{Pt}-^{13}\text{C}} = 1174.5$ Hz). From ^1H and ^{13}C NMR spectra it is not possible to deduce the configuration of the complex, because cis (C_{2v} symmetry) and trans (C_{2h} symmetry) isomers are indistinguishable from the point of view of NMR spectroscopy. The number of lines indicates, however, that only one isomer is present. This is confirmed by the ^{195}Pt NMR, which was measured with a signal to noise ratio of ca. 60. Only one single resonance could be detected (at -122.91 ppm relative to $\text{trans-PtCl}_2(\text{SEt}_2)_2$ in CH_2Cl_2), indicating an isomeric purity of $>98\%$. ^{195}Pt is known to show extremely large chemical shifts,¹⁵ and it is very improbable that the two isomers would give unresolved lines at this frequency.

The molecular weight determination in dichloromethane solution yields the correct value for a monomeric species.

Crystal and Molecular Structure

Structural Results. In the solid state, the compound $\text{Pt}(\text{Phpy})_2$ forms dimeric units, the two molecules of a dimer being related to each other by a center of inversion of the space group (Figure 4). The Pt...Pt distance of 3.53 Å (Table III) implies some weak interaction between the two molecules. (Compare with the Pt...Pt distance of 3.15 Å in the dimers of bis((phenylazo)acetaldoximato)platinum(II)¹⁶ and with the Pt...Pt distances in the stacked $\text{Pt}(\text{CN})_4^{2-}$ compounds, which range from 3.75 to 2.80 Å.¹⁷) The somewhat shorter distance of 3.37 Å between the aromatic planes shows that the platinum-platinum vector is not perpendicular to the plane of the ligands (the inclination angle is about 73°).

The complex has clearly the cis configuration. The two longer Pt-ligand distances (2.13 Å) correspond to the Pt-N bonds. The nitrogen atoms can be unambiguously assigned by their shorter bond distances to their neighboring carbon atoms in the aromatic rings: N-C11 = 1.34 Å, N-C7 = 1.35 Å vs. C1-C2 = 1.40 Å, C1-C6 = 1.42 Å (Figure 5). These Pt-N bonds are long, compared with the bonds of 2.02 Å in $\text{Pt}(\text{bpy})_2^{2+}$ and $\text{Pt}(\text{phen})_2^{2+}$,¹⁸⁻²⁰ showing clearly a strong trans influence of the carbon ligands. The Pt-C distances (1.99 Å) are relatively short, if compared to other Pt(II)-carbon com-

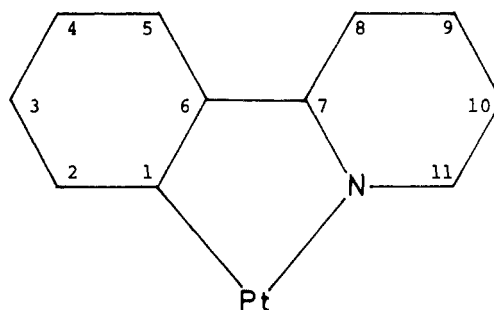
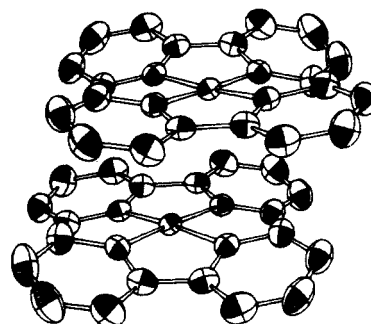


Figure 5. Atom-numbering scheme of the phenylpyridine ligands. Ligand 1 has the numbers 101, 102, etc., and ligand 2 has the numbers 201, 202, etc.

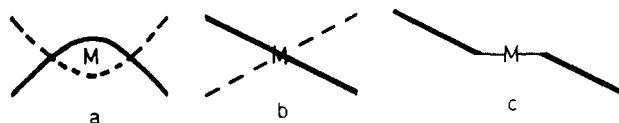


Figure 6. Conformations of complexes with two "coplanar" bipyridine or phenanthroline ligands: (a) bow; (b) anti-twist; (c) syn-twist. The direction used in the projection in (c) is perpendicular to that used in (a) and (b).

pounds, which tend to have Pt-C bond distances in the order of 2.05^{21,22}-2.18 Å.²³ Short Pt-C distances have been, however, observed in a complex with a platinum-chlorine bond trans to the carbon ligand: Pt-C = 1.94 Å.²⁴

The mutual steric influence of the hydrogen atoms on C102/C202 and C111/C211, respectively, causes the ligands to be bowl-like distorted (Figure 6), as the ligands are in the $\text{Pt}(\text{bpy})_2^{2+}$ complex.^{18,19} An anti-twist distortion (Figure 6) occurs in the complexes $\text{Pt}(\text{phen})_2^{2+}$,²⁰ $\text{Pd}(\text{phen})_2^{2+}$,²⁵ and $\text{Pd}(\text{bpy})_2^{2+}$,^{26,27} and a syn-twist distortion (Figure 6) in the complex $\text{trans-Ru}(\text{phen})_2(\text{py})_2^{2+}$.²⁸

The ligand bond distances C6-C7 (1.46 Å) (Figure 5) lie between a C-C single bond (1.54 Å) and an aromatic bond (1.39 Å), indicating a significant amount of conjugation between the two aromatic rings of the ligand. The same is observed in coordinated bpy.^{18,19} This finding is confirmed by the magnitudes of the torsional angles C1-C6-C7-N, which are zero within the standard deviations.

- (15) von Zelewsky, A. *Helv. Chim. Acta* **1968**, *51*, 803.
 (16) Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.* **1983**, *22*, 1315.
 (17) Yersin, H. Habilitation Thesis, University of Regensburg, GFR, 1980.
 (18) Dong, V.; Endres, H.; Keller, H. J.; Moroni, W.; Nöthe, D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 2428.
 (19) Endres, H.; Keller, H. J.; Moroni, W.; Nöthe, D.; Dong, V. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 1823.
 (20) Hazell, A.; Mukhopadhyay, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1647.

- (21) Bardi, R.; Del Pra, A.; Piazzesi, A. M.; Trozzi, M. *Cryst. Struct. Commun.* **1981**, *10*, 301.
 (22) Debaerdemaeker, T.; Klein, H.-P.; Wiege, M.; Brune, H. A. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 958.
 (23) Van Koten, G.; Timmer, K.; Noltes, J. G.; Spek, J. G. *J. Chem. Soc., Chem. Commun.* **1978**, 250.
 (24) Elder, R. C.; Cruickshank, R. D. P.; Morrison, R. F. *Inorg. Chem.* **1976**, *15*, 1623.
 (25) Rund, J. V.; Hazell, A. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 3103.
 (26) Hinamoto, M.; Ooi, S.; Kuroya, H. *J. Chem. Soc., Chem. Commun.* **1972**, 356.
 (27) Chieh, P. C. *J. Chem. Soc., Dalton Trans.* **1972**, 1643.
 (28) Bonneson, P.; Walsh, J. L.; Pennington, W. T.; Cordes, A. W.; Durham, B. *Inorg. Chem.* **1983**, *22*, 1761.

Table IV. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B ^a
Pt1	0.07450 (1)	0.09972 (1)	0.10415 (1)	2.374 (2)
N101	0.0247 (3)	0.2048 (3)	-0.0479 (3)	2.72 (6)
C101	-0.0488 (3)	0.1881 (4)	0.1402 (3)	2.78 (8)
C102	-0.1111 (4)	0.1688 (4)	0.2210 (4)	3.8 (1)
C103	-0.1862 (4)	0.2489 (5)	0.2429 (4)	5.1 (1)
C104	-0.2024 (5)	0.3494 (5)	0.1841 (5)	5.5 (1)
C105	-0.1488 (4)	0.3708 (4)	0.0968 (4)	4.5 (1)
C106	-0.0755 (3)	0.2903 (4)	0.0732 (4)	3.28 (8)
C107	-0.0328 (3)	0.2982 (4)	-0.0304 (4)	3.12 (8)
C108	-0.0568 (4)	0.3849 (4)	-0.1125 (4)	4.4 (1)
C109	-0.0243 (5)	0.3738 (4)	-0.2154 (4)	5.0 (1)
C110	0.0279 (4)	0.2766 (4)	-0.2363 (4)	4.2 (1)
C111	0.0501 (3)	0.1943 (4)	-0.1505 (3)	3.37 (9)
N201	0.2131 (3)	0.0095 (3)	0.0734 (3)	2.80 (7)
C201	0.1249 (3)	0.0094 (3)	0.2533 (3)	2.74 (8)
C202	0.0981 (4)	0.0210 (4)	0.3605 (4)	3.35 (9)
C203	0.1339 (4)	-0.0542 (4)	0.4521 (4)	3.9 (1)
C204	0.2018 (5)	-0.1459 (4)	0.4426 (4)	4.4 (1)
C205	0.2367 (4)	-0.1575 (4)	0.3407 (4)	3.9 (1)
C206	0.1996 (3)	-0.0799 (3)	0.2483 (4)	2.90 (8)
C207	0.2472 (3)	-0.0787 (3)	0.1476 (4)	2.90 (8)
C208	0.3280 (4)	-0.1561 (4)	0.1312 (4)	3.9 (1)
C209	0.3789 (4)	-0.1357 (4)	0.0421 (4)	4.5 (1)
C210	0.3497 (4)	-0.0409 (4)	-0.0276 (4)	4.3 (1)
C211	0.2666 (4)	0.0281 (4)	-0.0093 (4)	3.41 (9)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

The four atoms C101, N101, C201, and N201, which are coordinated to the platinum atom, lie in a plane within 0.01 Å. The Pt atom itself is slightly displaced by 0.05 Å out of this plane toward the second platinum atom of the dimer. The vibrational ellipsoids of the individual atoms indicate a merely rigid-body behavior of the complex. A thermal motion analysis according to Schomaker and Trueblood²⁹ fitted the observed vibrational parameters to a rigid-body model with an *R* value of 0.093 (unit weights) and a root-mean-square deviation between observed and calculated U_{ij} 's of 0.0033 Å². The Hirshfeld test for rigid bonds³⁰ was applied separately to (i) all bonded atom pairs, (ii) all atom pairs within the six-membered rings, (iii) all atom pairs between the two six-membered rings of the same ligand, and (iv) all atom pairs

between the two ligands. The mean values obtained ($\langle \Delta U \rangle = 0.0032$ (25), 0.0029 (25), 0.0036 (25), and 0.0046 (38) Å², respectively) are comparable with the experimental errors of the individual U 's ($\langle \sigma(U) \rangle = 0.0023$ (6)) and support therefore a rigid-body model. There is, however, an indication of some flexibility between the two phenylpyridine moieties. In a nonintersecting axes description of the rigid-body motion, the directions of the three libration axes correspond approximately to the inertial frame of the molecule; their displacements from its origin (Pt atom) are all smaller than 0.51 Å and the effective screw translations along them smaller than 0.02 Å. The Pt atom is thus in a good approximation the pivot of the motion, which can be expressed in terms of a translational part with eigenvalues $T_x = 0.033$ Å², $T_y = 0.035$ Å², and $T_z = 0.018$ Å² and a librational part with eigenvalues $L_x = 10.9$ deg², $L_y = 6.6$ deg², and $L_z = 4.0$ deg², where *z* is the axis normal to the molecular plane, *x* lies in the molecular plane bisecting the phenylpyridine ligands, and *y* lies in the molecular plane separating the two ligands. The observed molecular parameters were corrected for effects of thermal motion. The corrected values for bond distances and angles are also contained in Table III together with the uncorrected ones. Positional parameters for non-hydrogen atoms and the equivalent isotropic temperature factors *B* are given in Table IV.

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Registry No. 1, 88821-71-0; Pt(Phpy)₂Br₂, 92787-95-6; trans-PtCl₂(SEt₂)₂, 15337-84-5; LiPhpy, 13764-19-7.

Supplementary Material Available: Listings of calculated positional parameters of all hydrogen atoms (Table IVa), anisotropic vibrational parameters for non-hydrogen atoms (Table V), root-mean-square amplitudes of thermal vibration for non-hydrogen atoms (Table VI), rigid-body motion parameters in a Cartesian crystal frame and corresponding transformation matrices (Table VII), least-squares planes for a plane defined by the Pt atom and its coordination sphere with normal deviations from the plane for the remaining non-hydrogen atoms (Table VIII), and observed and calculated structure factors (Table IX) and mass spectra of cis-Pt(Phpy)₂ at source temperatures of 120 and 190 °C (Figure 7a,b), solid-state reflection spectrum of cis-Pt(Phpy)₂ at room temperature (Figure 8), ¹H NMR spectrum of cis-Pt(Phpy)₂ at 300 MHz (Figure 9), and stereoview of the unit cell content of cis-Pt(Phpy)₂ (Figure 10) (25 pages). Ordering information is given on any current masthead page.

(29) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1968, B24, 63. Program THMB6 (1982).

(30) Hirshfeld, F. L. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* 1976, A32, 239.