47. Cyclometalated Compounds of Platinum(II) with Two Different C,N-Aromatic Ligands

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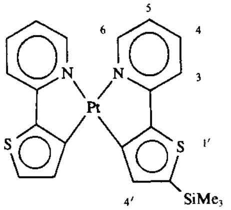
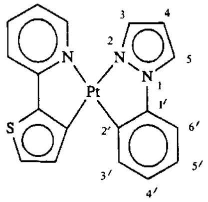
A synthetic route leading to bis-heteroleptic cyclometalated complexes Pt($\widehat{CN}$)($\widehat{CN'}$) is described. The complexes [2-(2′-thienyl)pyridinato-*N*,$C^{3'}$]{2-[3′-(trimethylsilyl)2′-thienyl]pyridinato-*N*,$C^{3'}$}platinum(II) ([Pt(thpy)(TMS-thpy)]; **I**) and (1-phenylpyrazolato-N^2,$C^{2'}$)[2-(2′-thienyl)pyridinato-*N*,$C^{3'}$]platinum ([Pt(Phpz)(thpy)]; **II**) are characterized by UV/VIS, NMR, and mass spectroscopy. Thermal and photochemical oxidative addition reactions yield two out of the 10 possible pairs of enantiomers of octahedral Pt(IV) compounds.

Introduction. – A series of cyclometalated, bis-homoleptic Pt(II) complexes with aromatic ligands containing N as the donor atom, was recently prepared [1–5]. Such species show light emission, in some cases even at room temperature [6–9]. Of special interest are the photochemical properties [10]. Light-induced stereospecific oxidative addition reactions yield Pt(IV) compounds with three C ligands [11]. Further investigations of this novel type of reaction requires the use of starting complexes of varied structures. In the present paper, a synthetic route is described for the preparation of Pt(II) complexes with two different chelated *C,N* ligands: *cis*-[2-(2′-thienyl)pyridinato-*N*,$C^{3'}$]-{2-[5′-(trimethylsilyl)-2′-thienyl]pyridinato-*N*,$C^{3'}$}platinum(II) ([Pt(thpy)(TMS-thpy)]; **I**) and *cis*-(1-phenylpyrazolato-N^2,$C^{2'}$)[2-(2′-thienyl)pyridinato-*N*,$C^{3'}$]platinum(II) ([Pt-(Phpz)(thpy)]; **II**).



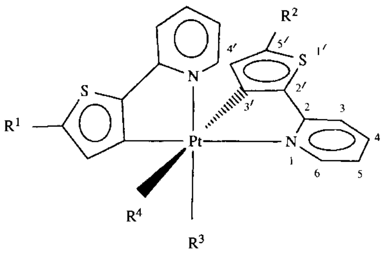
I [Pt(thpy)(TMS-thpy)]



II [Pt(Phpz)(thpy)]

TMS = Me_3Si

Thermal and photochemical oxidative addition reactions of such complexes with CH_3I or $CHCl_3$ yield Pt(IV) complexes **III** to **VI**.



III $R^1 = H$, $R^2 = TMS$, $R^3 = CH_3$, $R^4 = I$
IV $R^1 = TMS$, $R^2 = H$, $R^3 = CH_3$, $R^4 = I$
V $R^1 = H$, $R^2 = TMS$, $R^3 = CHCl_2$, $R^4 = Cl$
VI $R^1 = TMS$, $R^2 = H$, $R^3 = CHCl_2$, $R^4 = Cl$

(TMS = Me_3Si)

Experimental. – *Materials.* 2-(2'-Thienyl)pyridine was purchased from *Aldrich*, 2-[3'-(trimethylsilyl)-2'-thienyl]pyridine [12], 1-(2'-bromophenyl)pyrazole [13], [$PtCl_2(Et_2S)_2$] [14], [pt(thpy)$_2$] [2], [PtI(thpy)(HThpy)] [15] were prepared according to published procedures. Solvents were dried prior to use by standard techniques. Reactions involving Li reagents were carried out under a N_2 atmosphere using *Schlenk*-tube techniques.

Measurements. Electronic spectra: *Perkin-Elmer 555* spectrometer. ^{1}H- and ^{13}C-NMR: *Bruker AM-360* spectrometer (internal standard TMS). MS: *7070E VG Instrument* spectrometer.

*[2-(2'-Thienyl)pyridinato-*N,C$^{3'}$*]{2-[5'-(trimethylsilyl)-2'-thienyl]pyridinato-*N,C$^{3'}$*}platinum(II)* ([Pt(thpy)-(TMS-thpy)]; **I**). *Direct Method.* BuLi (3.8 ml, 1.6N in hexane) was added dropwise to a stirred soln. containing 2-(2'-thienyl)pyridine (480 mg, 3 mmol) and 2-[3'-(trimethylsilyl)-2'-thienyl]pyridine (700 mg, 3 mmol) in Et_2O (50 ml) at 0°. The soln. was stirred during 30 min at 0°, then cooled to −78°. *trans*-[$PtCl_2(Et_2S)_2$] (600 mg, 1.34 mmol) in Et_2O/THF 4:1 (30 ml) was added dropwise to the stirred suspension. After stirring during 45 min at −78°, the mixture was chromatographed (flash, SiO_2, Et_2O). The resulting soln. was concentrated to an oil which was again purified by chromatography (flash, SiO_2, CH_2Cl_2/hexane 3:2). Three fractions were separated: 90 mg [Pt(thpy)(TMS-thpy)], 50 mg [Pt(TMS-thpy)$_2$], and an insignificant amount of [Pt(thpy)$_2$]. The products were recrystallized from CH_2Cl_2/hexane to give red crystals. MS: 587 (M^+). Anal. calc. for $C_{21}H_{20}N_2S_2SiPt$: C 42.92, H 3.43, N 4.76; found: C 42.69, H 3.51, N 4.70.

Chloro(diethyl sulfide)[2-(2'-thienyl)pyridinato-N,C$^{3'}$]platinum(II) [PtCl(Et_2S)(thpy)]. HCl (6.84 ml, 0.46M) was added to a soln. of [Pt(thpy)$_2$] (820 mg, 1.5 mmol) in acetone (60 ml) and EtOH (140 ml). After stirring during 20 h at r.t. in the dark, the soln. was concentrated to *ca.* 20 ml. Upon addition of i-PrOH (5 ml) and cooling, a yellow powder precipitated. After filtration and washing with cold i-PrOH and Et_2O, 830 mg of [Pt(μ-Cl)(thpy)]$_2$ were isolated. The binuclear complex was solved in CH_2Cl_2 (60 ml) and acetone (10 ml), and mixed with an excess of Et_2S (50 mg 1:5). After stirring the soln. in the dark during 48 h at r.t., the solvents were evaporated. The orange residue was chromatographed (flash, SiO_2, CH_2Cl_2). Recrystallization (CH_2Cl_2/hexane) gave 500 mg of [PtCl-(SEt_2)(thpy)] as orange needles showing a correct ^{1}H-NMR spectrum. Anal. calc. for $C_{13}H_{16}ClNSPt \cdot 1.3\ CH_2Cl_2$: C 32.55, H 3.52, N 2.66; found: C 32.59, H 3.61, N 3.00.

*(Diethyl sulfide)iodo[2-(2'-thienyl)pyridinato-*N,C$^{3'}$*]platinum(II)* [Pt(Et_2S)I(thpy)]. Et_2S (500 mg) was added to a soln. of [PtI(thpy)(Hthpy)] (1.22 g) in DMF (150 ml). The soln. was stirred in the dark during 48 h at r.t. Et_2S and DMF were evaporated. The orange residue was chromatographed (flash, SiO_2, CH_2Cl_2). Recrystallization (CH_2Cl_2/hexane) gave 340 mg of [Pt(Et_2S)I(thpy)] as orange needles showing a correct ^{1}H-NMR spectrum. Anal. calc. for $C_{13}H_{16}INSPt$: C 28.89, H 2.98, N 2.59; found: C 28.60, H 2.84, N 2.53.

Preparation of [Pt(Phpz)(thpy)] from [PtCl(Et_2S)(thpy)]. A soln. of Li-Phpz (1 mmol) in Et_2O (15 ml) was added dropwise during 15 min to a stirred suspension of [PtCl(Et_2S)(thpy)] (480 mg, 1 mmol) in Et_2O/THF 4:1 (50 ml) at −78°. After stirring the mixture during 75 min at −78°, the suspension was hydrolyzed at 0° with 10 ml of H_2O. The org. layer was separated, extracted with CH_2Cl_2, dried ($MgSO_4$), and reduced in the volume. Upon cooling, [Pt(Phpz)(thpy)] crystallized. After recrystallization, 140 mg of pure product was obtained. MS: 498 (M^+). Anal. calc. for $C_{18}H_{13}N_3SPt$: C 43.37, H 2.60, N 8.43; found: C 43.35, H 2.66, N 8.46.

Thermal Oxidative Addition of [Pt(thpy)(TMS-thpy)] with CH_3I yielding [PtI(CH_3)(thpy)(TMS-thpy)]. [Pt(thpy)(TMS-thpy)] (40 mg) was dissolved in CH_3I (10 ml) in the dark. After 15 min, CH_3I was evaporated and the residue purified by prep. TLC (SiO_2, CH_2Cl_2): 5 mg of [PtI(CH_3)(thpy)(TMS-thpy)] (**III**) and 15 mg of its isomer **IV** were isolated as pale yellow microcrystalline powders. Anal. calc. for $C_{22}H_{23}IN_2S_2SiPt$: C 36.21, H 3.17, N 3.84; found: C 36.42, H 3.19, N 3.90.

Photochemical Oxidative Addition of [Pt(thpy)(TMS-thpy)] with $CHCl_3$ yielding [PtCl($CHCl_2$)(thpy)(TMS-thpy)]. [Pt(thpy)(TMS-thpy)] (60 mg) was dissolved in $CHCl_3$ (5 ml). After 10 min of irradiation (with a 250-W halogen projector lamp), the solvent was evaporated and the residue purified by prep. TLC (SiO_2, CH_2Cl_2): 10 mg of [PtCl($CHCl_2$)(thpy)(TMS-thpy)] (**V**) and 7 mg of its isomer **VI** were isolated as white microcrystalline powders. The ^{1}H-NMR spectra are in agreement with that reported for the similar compound [PtCl($CHCl_2$)$(thpy)_2$] [11]. Anal. calc. for $C_{22}H_{20}Cl_3N_2S_2SiPt \cdot 0.4\ CH_2Cl_2$: C 36.19, H 2.80, N 3.78; found: C 36.40, H 3.01, N 3.77.

Discussion. – *Synthesis.* Although some heteroleptic Pd compounds with *C,N*-chelate ligands have been described [16] [17], no general method to prepare heteroleptic Pt(II) complexes with aromatic *C,N*-chelate ligands seem to be established[1]. *Pfeffer* and coworkers [17] have prepared a series of bis-heteroleptic Pd complexes by mixing binuclear Pd complexes, like *e.g.* chloro[(dimethylamino)benzenato-*N,C*]palladium dissolved in THF with lithiated *C,N*-ligands. This method is not applicable for our Pt complexes, because the analogous binuclear (benzo[h]quinolinato-*N,C*)chloroplatinum [19] is soluble neither in THF nor in CH_2Cl_2. We propose here a novel route to prepare heteroleptic Pt(II) complexes. A direct method, in which a mixture of two different lithiated ligands is applied in a one-step synthesis, yields in principle also the mixed ligand complexes. It was successfully used for the synthesis of [Pt(thpy)(TMS-thpy)] (I). In general, however, a mixture of heteroleptic and homoleptic complexes is obtained, and the isolation of the pure mixed complexes, in reasonable yields, is thus not possible. The separation can be achieved only by chromatography procedures and not by recrystallization. The indirect four-steps method (*Scheme*) is, therefore, preferable in most cases. The first step is the well-established preparation of the bis-homoleptic compound. The second step, formation of the dimer by HCl, is similar to the reaction reported by *Uson et al.* [20]. The Cl bridge can, then, be broken with Et_2S. The mixed complex is finally obtained by adding slowly a solution of 1 equiv. of $\mathrm{Li{-}}\widehat{\mathrm{CN}}'$ to a strongly diluted solution of the monochelated Pt complex. (If $[\mathrm{PtCl}(\widehat{\mathrm{CN}})(\mathrm{Et_2S})]$ is added to a solution of $\mathrm{Li{-}}\widehat{\mathrm{CN}}'$ the major product is $[\mathrm{Pt}(\widehat{\mathrm{CN}}')_2]$[2].)

Scheme

$$[\mathrm{PtCl_2(Et_2S)_2}] + 2(\mathrm{Li}-\widehat{\mathrm{CN}}) \xrightarrow[-2\,\mathrm{LiCl}]{-2\,\mathrm{Et_2S}} [\mathrm{Pt}(\widehat{\mathrm{CN}})_2] \xrightarrow[-(\mathrm{H}-\widehat{\mathrm{CN}})]{\mathrm{HCl}}$$

$$1/2\,[\mathrm{Pt}(\mu\text{-}\mathrm{Cl})(\widehat{\mathrm{CN}})]_2 \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{Et_2S}} [\mathrm{PtCl(Et_2S)}(\widehat{\mathrm{CN}})] \xrightarrow[\substack{-\mathrm{Et_2S}\\ -\mathrm{LiCl}}]{(\mathrm{Li}-\widehat{\mathrm{CN}}')} (\widehat{\mathrm{CN}})\mathrm{Pt}(\widehat{\mathrm{CN}}')$$

[Pt(thpy)(TMS-thpy)] (I) and [Pt(Phpz)(thpy)] (II) are red and orange, air-stable crystalline compounds, respectively. Mass spectroscopy yields the direct evidence for the formation of mixed chelated Pt complexes in comparison with a mixture of 1:1 homoleptic Pt compounds.

^{1}H-NMR Spectroscopy. The chemical shifts of protons in *ortho*-position to the donor atoms of the same ligand have different values (*Table 1*), if this ligand belongs either to

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[1] Except the preparation of the mixed complex [(dimethylamino)benzylato-*N,C*][8-(dimethylamino)-naphthylato-*N,C*]platinum(II) [18].

[2] Instead of $[\mathrm{Pt(thpy)_2}]$, also [PtI(thpy)(Hthpy)] [15] can be used as starting material. The N-bonded Hthpy ligand is easily substitued by Et_2S, but the reaction of $[\mathrm{Pt(Et_2S)I(thpy)}]$ with Li-Phpz gives the mixed complex [Pt(Phpz)(thpy)] in very poor yields.

Table 1. *^{1}H-NMR Chemical Shifts* [ppm] *of Some Pt(II) and Pt(IV) Complexes* (in $CDCl_3$). J(Pt, H) in parentheses.

	H–C(4′)	H–C(6)	H–C(3′)	H–C(3)
[Pt(thpy)$_2$][a]	7.69	8.61		
[Pt(Phpz)$_2$][a]			8.12	7.90
[Pt(TMS-thpy)$_2$][a]	7.85	8.63		
[Pt(thpy)(TMS-thpy)]	7.80*s*	8.63		
	7.70*d*			
[Pt(Phpz)(thpy)]	7.70	8.77	8.26	7.93
	(17.2)	(13)	(55)	
[PtCl(Et$_2$S)(thpy)]	7.17	9.40		
	(19.9)	(38.5)		

	H–C(5′a)	H–C(4′a)	H–C(6a)	H–C(5′b)	H–C(4′b)	H–C(6b)	CH_3	$CHCl_2$
[PtCl(CHCl$_2$)(thpy)(TMS-thpy)] (**VI**)	7.17	6.12	9.53		7.62	7.28	1.58	
	(9.96)	(7.63)	(10.85)			(11)	(69.63)	
[PtCl(CHCl$_2$)(thpy)(TMS-thpy)] (**V**)		6.22	9.54	7.56	7.66–7.62	7.28	1.56	
		(16.24)		(10)			(69.7)	
[PtI(CH$_3$)(thpy)(TMS-thpy)] (**IV**)	7.13	5.96	9.98		7.43	7.28		6.91
	(11.02)	(20.1)			(15.56)			(55.31)
[PtI(CH$_3$)(thpy)(TMS-thpy)] (**III**)		6.07	9.97	7.62	7.34	7.26		6.86
		(18.55)	(11)	(10.5)	(16.8)			(54.53)

[a] From [2].

the bis-homoleptic compound or to the mixed chelated complex. The assignment was achieved following the argument in [2]. As expected, the difference of the chemical shift of the same protons in the homoleptic and the heteroleptic compound is bigger for [Pt(Phpz)(thpy)] than for [Pt(thpy)(TMS-thpy)]. Thus, NMR spectroscopy is a useful tool to determine the purity of mixed chelated complexes. The presence of the corresponding bis-homoleptic compounds can be detected with a sensitivity of *ca.* 2% with a 360-MHz NMR spectrometer.

Electronic Spectra. The electronic spectra of mixed chelated Pt complexes do not differ basically from the homoleptic compounds (*Table 2*). The *Figure* shows the absorption spectra of the [Pt(Phpz)(thpy)] in comparison with the homoleptic parent compounds.

Table 2. *Absorption Maxima of Some Pt(II) Complexes* [nm] (ε)

[Pt(thpy)$_2$][a][b]	[Pt(TMS-thpy)$_2$][a][c]	[Pt(Phpz)$_2$][a][c]	[Pt(thpy)(TMS-thpy)][b] (**I**)	[Pt(Phpz)(thpy)][b] (**II**)	[PtCl(Et$_2$S)(thpy)][b]
460(sh)	464(sh)	342	464	420	420(sh)
(1900)	(3200)	(14000)	(2975)	(3180)	(4140)
420	424	308	422	380	408
(10700)	(11700)	(10000)	(9720)	(8640)	(4410)
392	400(sh)	294(sh)	356	342(sh)	330
(4970)	(3040)	(13350)	(15240)	(10600)	(14110)
350	359	264	328	305	272
(14140)	(18000)	(17950)	(22080)	(17430)	(16180)
322(sh)	329	252	310	288	
(22550)	(25650)	(27530)	(27860)	(19750)	
304	310			265	
(31530)	(35100)			(21450)	

[a] In CH_2Cl_2. [b] In $CHCl_3$. [c] From [2].

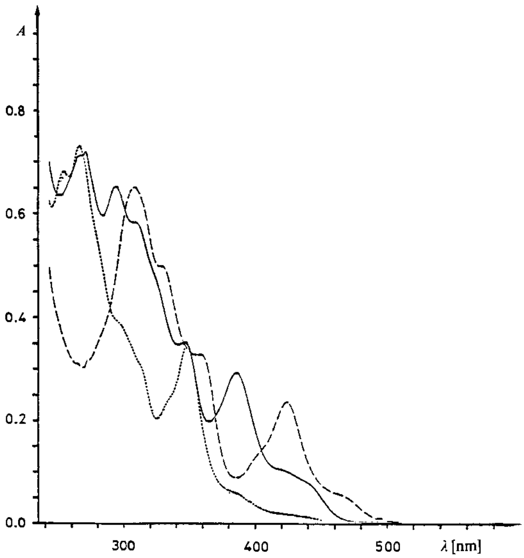

Fig. *UV/VIS spectra of [Pt(Phpz)(thpy)]* (——; $c = 3.5 \cdot 10^{-5}$ M), *[Pt(thpy)$_2$]* (– – –; $c = 2.2 \cdot 10^{-5}$ M), *and [Pt(Phpz)$_2$]* (· · ·; $c = 2.4 \cdot 10^{-5}$ M) *in CH$_2$Cl$_2$*

All the mixed complexes absorb in the VIS region. By analogy with [Pt(thpy)$_2$] [7a], these long-wavelength transitions can be attributed to metal-to-ligand charge transfers (MLCT) bands.

As expected, the UV/VIS spectrum of [Pt(thpy)(TMS-thpy)] is very similar to the spectra of [Pt(thpy)$_2$] and [Pt(TMS-thpy)$_2$] [2]. The spectrum of [Pt(Phpz)(thpy)] is a superposition of the shifted spectrum of [Pt(Phpz)$_2$] and the hypsochromically shifted spectrum of [Pt(thpy)$_2$]. The absorption band at 380 nm and the shoulder at 420 nm can be attributed to a MLCT from Pt to Phpz$^-$ and thpy$^-$, respectively [21].

Emission Spectra. As the complex [Pt(thpy)$_2$] itself, also the mixed complexes containing the ligand thpy emit at room temperature in CH$_2$Cl$_2$ *(Table 3)*. Detailed investigations of the photophysical properties have already been published [21]. The emission at 570 nm for the [Pt(Phpy)(thpy)] is attributed to a MLCT involving the thpy$^-$ ligand [21].

Table 3. *Emission* [nm] *of Some Pt(II) Complexes in CH$_2$Cl$_2$ at r.t.*

Complexes		$\lambda_{\text{excitation}}$	$\lambda_{\text{emission}}$
[Pt(thpy)(TMS-thpy)]	(I)	420	590, 640 (sh)
[Pt(Phpz)(thpy)]	(**II**)	385	570, 611 (sh)
[Pt(thpy)$_2$] [4]		420	580, 627 (sh)
[Pt(Phpz)$_2$] [4]		no emission observed	

Reactivity. Like the bis-homoleptic cyclometalated Pt complexes [11], the mixed compounds also undergo thermal and photochemical oxidative addition with alkyl halides.

The reaction of CH$_3$I with [Pt(thpy)(TMS-thpy)] in the dark gives two *cis*-adducts **III** and **IV** in the ratio of 1:3. The photochemical reaction of [Pt(thpy)(TMS-thpy)] in CHCl$_3$

results in two *cis*-products **V** and **VI** in the ratio of 1:1. These mixtures can be separated by TLC *(cf. Experimental)*. The structures of all the products can be determined unambiguously by ^{1}H-NMR spectroscopy in comparison with the known structure of thermal and photochemical oxidative addition products of $[Pt(Thpy)_2]$ [2] [10] [11]: the *cis*-addition of the solvent molecule is established by the inequivalence of all protons and the large values of $J(CHCl_2, {}^{195}Pt)$ and $J(CH_3, {}^{195}Pt)$ indicating *trans* position of $CHCl_2$ or CH_3 to a N donor [3].

This reaction is highly stereospecific as also observed in the photochemical oxidative addition of the homoleptic complexes [10] [11]. In the present case, 2 out of 10 possible pairs of enantiomers are formed. These two pairs correspond in their configuration to the one pair obtained from the homoleptic compound, *i.e.* C, C, C facial; C,X *trans*.

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