Acta Chemica Scandinavica, 1996: 50: 107–113
Printed in Belgium – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904-213X

Crystal Structures of $Bu_4N[Pt(ppy)Cl_2]$, $Et_4N[Pt(tpy)Cl_2]$ and [Pt(ppy)en]Cl (ppy = *N,C′*-Chelated 2-Phenylpyridinate, tpy = *N,C′*-Chelated 2-(2′-Thienyl)pyridinate, en = *N,N′*-Chelated 1,2-Diaminoethane)

Per-Inge Kvam,[†] Thoralf Engebretsen, Knut Maartmann-Moe and Jon Songstad

Department of Chemistry, University of Bergen, N-5007 Bergen, Norway

Kvam, P.-I., Engebretsen, T., Maartmann-Moe, K. and Songstad, J., 1996. Crystal Structures of $Bu_4N[Pt(ppy)Cl_2]$, $Et_4N[Pt(tpy)Cl_2]$ and [Pt(ppy)en]Cl (ppy = *N,C′*-Chelated 2-Phenylpyridinate, tpy = *N,C′*-Chelated 2-(2′-Thienyl)pyridinate, en = *N,N′*-Chelated 1,2-Diaminoethane). – Acta Chem. Scand. 50: 107–113 © Acta Chemica Scandinavica 1996.

The crystal structures of $Bu_4N[Pt(ppy)Cl_2]$, **I**, $Et_4N[Pt(tpy)Cl_2]$, **II**, and [Pt(ppy)en]Cl, **III**, have been determined at 93 K.

The anions in **I** and **II** are nearly planar, while the cation in **III** deviates from planarity due to the en ligand. The shortest Pt–Pt distance is 7.726(6) Å in **I**, 7.612(2) Å in **II** and 5.901(3) Å in **III**. The Pt–Cl and Pt–N bonds *trans* to the Pt–C bonds are 0.07–0.08 Å longer than the corresponding bonds *trans* to the Pt–N bonds. The relative *trans* influence of a carbon atom and a pyridine nitrogen atom is therefore retained in the cyclometalated compounds. It is concluded that the formation of only *trans*-N products in substitution reactions toward this class of species is probably due to a rapid isomerization of the initially formed *trans*-C products. A longer than expected Pt–Cl bond *trans* to the Pt–N bond in **I** is observed, 2.329(2) Å. The weakening of this bond may facilitate the isomerization reaction that take place in this class of compounds.

The length of the carbon–carbon bond linking the two aromatic rings in **II**, 1.427(9) Å, as compared with 1.47(1) and 1.46(1) Å in **I** and **III**, suggests that the conjugation between the rings is higher in compounds containing tpy than ppy. The Bu_4N^+ ion in **I** has two butyl groups with a zigzag antiperiplanar conformation and two butyl groups with a synclinal conformation.

Organometallic complexes containing *N,C′*-chelated ligands derived from various 2-aryl- and 2-(2′-thienyl)-substituted pyridines and related compounds are known for a number of transition metals; for a literature survey, see Refs. 1–9. The upsurge in interest in this class of compounds is due to their particular high absorbing and light emitting properties,[10] mostly in glassy solution at low temperatures,[5,8] but also as solids and in solution at room temperature.[3,4,11,12] The origin of the photophysical and photochemical properties of this class of compounds seems to be due to the strong ligand-field influence of the formally negatively charged carbon atom combined with the possibility of π-back-donation into the *N,C′*-chelated aromatic ligands. Since the metal-to-ligand charge transfer (MLCT) appears to be related to the covalency in the metal–ligand bonds,[5] platinum species have been in focus in recent years. Square planar d^8 Pt^{II} complexes are particularly interesting, since they are coordinatively unsaturated and as such may have interesting synthetic applications.[13]

Apart from the extensive photochemical, photophysical and electrochemical studies performed in recent years far less is known about the chemistry of this class of compounds in their ground state. Homoleptic bis-cyclometalated Pt^{II} compounds, *cis*-$[Pt{<}N\text{–}C{>}_2]$, are known to add alkyl halides with a remarkable high stereospecificity.[6,14] (Here <N–C> is a commonly used abbreviation for *N,C′*-chelated ligands like ppy, deprotonated 2-phenylpyridine, and tpy, deprotonated 2-(2′-thienyl)pyridine). It is notable that only *cis*-$[Pt{<}N\text{–}C{>}_2]$ is formed when *trans*- or *cis*-$[Pt(SEt_2)Cl_2]$ reacts with two equivalents of 2′-lithiated 2-phenylpyridine in diethyl ether.[15] The $[Pt{<}N\text{–}C{>}Cl_2]^-$ and $[Pt{<}N\text{–}C{>}en]^+$ ions react rapidly with nucleophiles, particularly in protic solvents,[9] but no kinetic studies appear to have been performed.

The strong *trans* influence of the carbon atom as compared with that of the pyridine nitrogen atom in the *N,C′*-chelated ligand would lead one to anticipate that the chloride *trans* to the carbon atom in $[Pt{<}N\text{–}C{>}Cl_2]^-$ is the

---

[†] To whom correspondence should be addressed.

most labile one. In agreement with this assumption van Eldik and co-workers[16] have recently shown that in related compounds with an aqua ligand *trans* to the carbon atom, this ligand is sufficiently labilized to act as a Brønsted acid. Nevertheless, for all substitution reactions which so far have been examined, eqn. (1),

$$[\mathrm{Pt}\!<\!\mathrm{N{-}C}\!>\!\mathrm{Cl_2}]^- + \mathrm{A} \xrightarrow[-\,\mathrm{Cl}^-]{} [\mathrm{Pt}\!<\!\mathrm{N{-}C}\!>\!\mathrm{ClA}] \tag{1}$$

only compounds with the entering ligand A being *trans* to the nitrogen atom have been isolated.[9,17,18]

In an attempt to shed some light upon these substitution reactions we wish to report the results from a structural study on some compounds which are frequently used as starting materials in synthesis, $Bu_4N[Pt(ppy)Cl_2]$, **I**, $Et_4N[Pt(tpy)Cl_2]$, **II**, and [Pt(ppy)en]Cl, **III**. From the extensive surveys of Pt–Cl[19,20] and Pt–N[21] bond lengths it was hoped to get some information on the relative *trans*-influence of a pyridine nitrogen atom and an anionic carbon atom when they are part of a *N,C′*-chelated ring. Bürgi[22] has shown that even small differences in structural parameters may dramatically affect rates of substitution reactions toward square planar Pd^{II} and Pt^{II} species.

Experimental

The preparation of $Bu_4N[Pt(ppy)Cl_2]$, **I**, and [Pt(ppy)en]Cl, **III**, has been described.[9] Crystals of **I** were grown from a dichloromethane/diethyl ether mixture, while crystals of **III** were obtained by slow evaporation from a methanolic solution. Since all attempts to make satisfactory crystals of $Bu_4N[Pt(tpy)Cl_2]$ failed, the tetraethylammonium salt, $Et_4N[Pt(tpy)Cl_2]$, **II**, m.p. 161 °C, was prepared by adding 2 mol of Et_4NCl to a slurry of the dimer, $[Pt(tpy)Cl]_2$, in dichloromethane as described for the Bu_4N^+ salt.[9] Crystals of **II** were obtained by slow evaporation from a dichloromethane solution. The crystals were cut to suitable prismatic specimens with average dimensions of approximately 0.2 mm. Measurements of cell dimensions and intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo *K*α radiation ($\lambda = 0.71073$ Å). The temperature at the crystal during data collection was 93 K. Cell parameters were determined using a least-squares fit for 25 reflections.

The intensities were corrected for Lorentz and polarization effects. Variations in three standard reflections were used for scaling the intensity data. The data were corrected for absorption by a semiempirical PSI-scan procedure.[23] The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques. Anisotropic temperature factors were applied to all non-hydrogen atoms. The hydrogen atoms were placed geometrically at a fixed C–H distance of 0.96 Å and were refined isotropically. Crystal and experimental data together with final figures of merit are listed in Table 1. All computer programs used in the calculations belong to the Enraf-Nonius Molen Package.[24] Atomic scattering factors were taken from Ref. 25. Fractional coordinates and their estimated standard deviations together with isotropic equivalent thermal parameters, $B/\text{Å}^2$, are listed in Table 2. Structure factor tables and isotropic thermal parameters are available from the authors.

Table 1. Crystal data and structural parameters.

Compound	I	II	III
Chemical formula	$Bu_4N[Pt(ppy)Cl_2]$	$Et_4N[Pt(tpy)Cl_2]$	[Pt(ppy)en]Cl
Empirical formula	$C_{27}H_{44}Cl_2N_2Pt$	$C_{17}H_{26}Cl_2N_2PtS$	$C_{13}H_{16}ClN_3Pt$
Formula weight	662.66	556.47	444.84
Temperature/K	93	93	93
Radiation/Scan-mode	Mo K_α/ω-scan	Mo K_α/ω-scan	Mo K_α/ω-scan
θ-Range/°	2–24	2–28	2–28
Scan width (x+0.34 tan θ)/°	1.10	1.3	1.3
a/Å	11.551(2)	8.996(2)	8.5675(9)
b/Å	16.759(5)	25.085(2)	15.971(2)
c/Å	14.541(9)	9.103(2)	18.875(4)
α/°	90	90	90
β/°	98.68(3)	110.60(1)	90
γ/°	90	90	90
$V/\text{Å}^3$	2782(3)	1922(1)	2582(1)
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	*Pcab* (No. 61)
Z	4	4	8
D_{calc}/g cm^3	1.582	1.922	2.288
Absorption coefficient/cm^{-1}	53.044	77.586	111.718
No. unique reflections	4362	4622	3110
No. $I > N\sigma/N$	3229/2.0	3541/2.0	2132/2.5
$R=\Sigma\lvert F_o-F_c\rvert/\Sigma F_o$	0.038	0.029	0.029
$R_w=[\Sigma w(F_o-F)^2/\Sigma(F_o)^2]^{0.5}$	0.031	0.031	0.030
$S=[\Sigma w(\Delta F)^2/N-n)]^{0.5}$	1.405	1.341	1.394

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters.

Atom	*x*	*y*	*z*	$B/Å^{2\,a}$
Compound **I**				
Pt	0.11465(3)	0.20978(2)	0.07715(2)	0.990(5)
Cl1	0.0739(2)	0.2026(1)	0.2290(1)	1.74(4)
Cl2	0.3027(2)	0.1507(1)	0.1258(1)	1.56(4)
N1	0.1391(5)	0.2212(4)	−0.0565(4)	1.5(1)
N2	0.7772(5)	0.0677(4)	0.7548(4)	1.2(1)
C1	0.2344(6)	0.1963(5)	−0.0926(5)	1.3(1)
C2	0.2466(7)	0.2116(6)	−0.1842(5)	2.0(1)
C3	0.1570(7)	0.2493(5)	−0.2421(6)	1.8(2)
C4	0.0575(7)	0.2723(5)	−0.2063(5)	1.5(2)
C5	0.0479(6)	0.2582(4)	−0.1134(5)	1.1(1)
C6	−0.0527(6)	0.2809(5)	−0.0683(5)	1.2(1)
C7	−0.1528(7)	0.3147(5)	−0.1111(6)	1.5(2)
C8	−0.2405(7)	0.3367(5)	−0.0622(5)	1.3(1)
C9	−0.2258(7)	0.3212(5)	0.0342(6)	1.4(2)
C10	−0.1253(6)	0.2824(5)	0.0767(5)	1.5(1)
C11	−0.0371(6)	0.2623(4)	0.0288(5)	0.8(1)
C12	0.8225(7)	0.1250(5)	0.6876(6)	1.6(2)
C13	0.8717(7)	0.0871(5)	0.6075(6)	1.6(2)
C14	0.9062(8)	0.1502(5)	0.5420(6)	2.3(2)
C15	0.9419(8)	0.1140(6)	0.4552(6)	2.7(2)
C16	0.6802(7)	0.0159(5)	0.7043(5)	1.2(1)
C17	0.5774(7)	0.0622(5)	0.6479(6)	1.7(2)
C18	0.4737(7)	0.0066(5)	0.6189(6)	1.7(2)
C19	0.4068(8)	−0.0134(6)	0.6982(6)	2.5(2)
C20	0.7324(7)	0.1180(5)	0.8286(6)	1.5(2)
C21	0.6722(8)	0.0730(5)	0.8967(6)	2.4(2)
C22	0.6419(8)	0.1272(6)	0.9736(7)	3.0(2)
C23	0.568(1)	0.0937(9)	1.035(1)	7.8(4)
C24	0.8734(7)	0.0119(5)	0.7965(6)	1.3(1)
C25	0.9774(7)	0.0507(5)	0.8566(6)	1.7(2)
C26	1.0759(7)	−0.0090(5)	0.8858(6)	1.7(2)
C27	1.1395(8)	−0.0353(6)	0.8075(7)	2.9(2)
Compound **II**				
Pt	0.23420(3)	0.11800(1)	0.23075(3)	1.275(4)
Cl1	0.0186(2)	0.16860(7)	0.2287(2)	2.33(4)
Cl2	0.1561(2)	0.04746(7)	0.3657(2)	2.37(4)
S1	0.5078(3)	0.20602(9)	−0.0095(3)	3.57(5)
S2	0.678(2)	0.0660(6)	0.161(2)	1.6(3)
N1	0.4273(7)	0.0790(2)	0.2192(6)	1.5(1)
N2	0.8667(6)	0.1324(2)	0.6737(6)	1.4(1)
C1	0.4793(9)	0.0302(3)	0.2755(8)	2.0(2)
C2	0.616(1)	0.0091(3)	0.2647(9)	2.8(2)
C3	0.704(1)	0.0375(4)	0.200(1)	3.5(2)
C4	0.6565(9)	0.0852(3)	0.1401(9)	2.4(2)
C5	0.5160(7)	0.1075(3)	0.1494(7)	1.6(1)
C6	0.4485(8)	0.1585(3)	0.0943(7)	1.7(1)
C7	0.344(1)	0.2465(3)	−0.0215(9)	2.8(2)
C8	0.2561(9)	0.2230(3)	0.0519(8)	2.0(2)
C9	0.3118(8)	0.1730(3)	0.1188(7)	1.3(1)
C10	0.9105(9)	0.1229(3)	0.8525(8)	2.6(2)
C11	0.924(1)	0.0645(3)	0.8960(9)	2.9(2)
C12	0.707(1)	0.1061(3)	0.5848(9)	2.8(2)
C13	0.5723(9)	0.1221(3)	0.6418(8)	2.4(2)
C14	0.856(1)	0.1933(3)	0.6549(9)	2.7(2)
C15	0.815(1)	0.2109(3)	0.4811(9)	3.1(2)
C16	0.9859(9)	0.1079(3)	0.6139(9)	2.6(2)
C17	1.1544(9)	0.1305(3)	0.6943(9)	2.8(2)
Compound **III**				
Pt	0.12971(3)	0.12295(1)	0.13293(1)	0.647(3)
Cl	0.1130(2)	0.38975(8)	0.21772(8)	1.13(3)
N1	0.2443(6)	0.0441(3)	0.0677(3)	0.70(9)
N2	−0.0078(6)	0.1952(3)	0.1979(3)	1.0(1)
N3	0.2264(6)	0.0840(3)	0.2316(3)	1.00(9)
C1	0.3498(7)	−0.0126(4)	0.0906(4)	1.0(1)
C2	0.4045(8)	−0.0757(4)	0.0462(4)	1.2(1)
C3	0.3519(7)	−0.0785(4)	−0.0227(4)	1.3(1)
C4	0.2462(8)	−0.0196(4)	−0.0463(3)	1.1(1)
C5	0.1926(7)	0.0422(4)	−0.0002(3)	0.9(1)
C6	0.0774(7)	0.1072(4)	−0.0160(4)	0.9(1)
C7	0.0122(7)	0.1186(4)	−0.0832(3)	1.1(1)
C8	−0.0921(8)	0.1826(4)	−0.0940(4)	1.2(1)
C9	−0.1313(8)	0.2355(4)	−0.0383(4)	1.3(1)
C10	−0.0684(8)	0.2236(4)	0.0285(4)	1.1(1)
C11	0.0365(7)	0.1577(4)	0.0412(4)	0.8(1)
C12	−0.0004(8)	0.1628(4)	0.2713(4)	1.1(1)
C13	0.1673(7)	0.1414(4)	0.2874(3)	1.2(1)

[a] $B=4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

During the refinement process a disorder in the crystal packing of $Et_4N[Pt(tpy)Cl_2]$, **II**, was detected. Around 10% of the molecules were observed to be flipped 180° around an axis through the platinum atom and bisecting the Cl–Pt–Cl bond angle placing the sulfur atom close to C4 in the pyridine ring. Similar types of disorder in compounds containing a thienyl group have been encountered previously.[26,27] Disorder may also exist in **I** and **III** but the geometrical similarity of the phenyl and pyridine group will obscure it.

Results and discussion

Description of the structures. Drawings of the anions in **I** and **II** and the cation in **III** are shown in Fig. 1 together with numbering of the atoms. (The cations in **I** and **II** will be discussed below.) The anion in **I** is presented with the chelated N and C atoms together with the two chloro atoms in the plane of the paper; the platinum atom being slightly above this plane, 0.022(1) Å. In the anion of **II** the platinum atom is in the plane of the four surrounding atoms within experimental error. The disordered position of the sulfur atom in **II**, denoted by S2, is indicated by a dotted circle on the C3–C4 bond. The cation in **III** is shown with Pt, N1 and C11 in the plane of the paper; N2 residing 0.213(5) Å below this plane while N3 is 0.039(5) Å above. The most important bond lengths and bond angles in the three ions are listed in Table 3.

Intra- and intermolecular non-bonding distances. In **I** and **II** all nonbonding H····Cl distances are greater than 2.60 Å. The distance from Cl2 to the hydrogen atom linked to C1, H1, is 2.61 Å in **I** and 2.70 Å in **II**. These distances suggest that the experimental down-field shift of this hy-

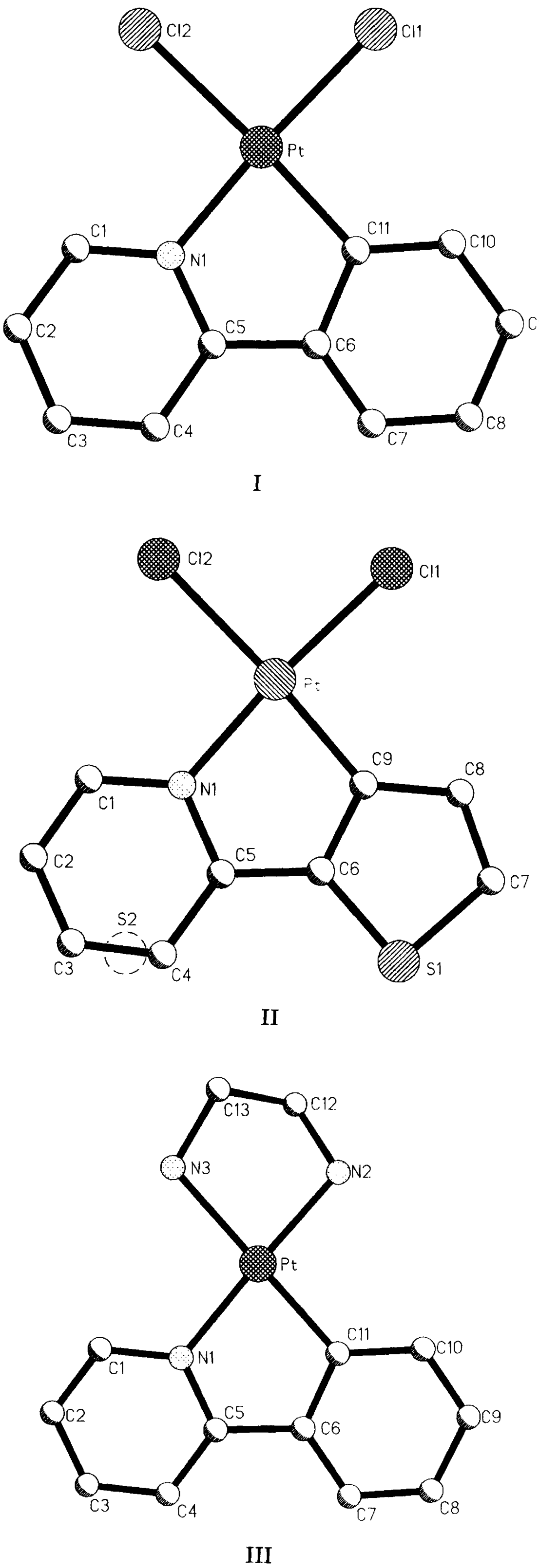

Fig. 1. Drawings of the anions in **I** and **II** and the cation in **III**. In the plane of the paper: **I**: N1, C11, Cl1 and Cl2, Pt is 0.022(1) Å above. **II**: N1, C9, Cl1, Cl2 and Pt. **III**: N1, C11 and Pt, N2 is 0.213(5) Å below, N3 is 0.039(5) Å above. For the sake of clarity the hydrogen atoms are omitted.

drogen, 9.91 ppm in **I** and 9.56 ppm in **II**,[9] can hardly be due to proximity effects excerted by the chloride atom *cis* to N1. The corresponding distances from Cl1 to H10 in **I** and from Cl1 to H8 in **II** are 2.63 and 2.93 Å. The shortest intermolecular H····Cl distances in **I** are between Cl1 and H20 and between Cl2 and H24, both 2.77 Å; H20 and H24 are hydrogen atoms linked to α-carbon atoms in the cation. The chlorine atoms *trans* to C11 in **I**, Cl2, is separated from a second α-hydrogen atom, H16, by 2.89 Å and from two aromatic hydrogen atoms in an adjacent anion, H4 by 2.81 and H7 by 2.87 Å, respectively. Evidently, if interactions between the chlorine atoms and the hydrogen atoms in **I** do exist it is the chlorine atom *trans* to C11, Cl2, that acts as the better donor atom. In **II** there is only one intermolecular H····Cl contact that may be of importance, Cl1–H15, 2.67 Å. H15 resides on a β-carbon atom in Et_4N^+.

The presence of an en ligand, a chloride ion and the absence of a large tetraalkylammonium ion in **III** give rise to several fairly short hydrogen bonds. Each chloride ion is in close contact with three amine hydrogen atoms in three different cations; the distances being 2.31, 2.36 and 2.40 Å. The distance to one additional N–H proton and to two hydrogen atoms belonging to the aromatic ligands are significantly longer, 2.78, 2.98 and 2.99 Å. Apparently, these contacts are sufficient to satisfy the coordination need of the chloride ion and to prevent **III** from being hygroscopic or to crystallize with crystal water. The en ligand itself is retained in a synclinal conformation with a N2–C12–C13–N3 torsion angle of −53.7(6)° with equal N2–C12–C13 and N3–C13–C12 bond angles, 108.0(6) and 108.8(6)°, and with fairly equal Pt–N2–C12 and Pt–N3–C13 bond angles, 109.7(5) and 107.8(4)°.

In the compounds there are no donor atoms close to an axis perpendicular to the coordination planes shown in Fig. 1, and the cations do not form stacks of the type observed in $[Pt(2,2'\text{-bpy})Cl_2]$[28] and in [Pt(tpy)(CO)Cl].[18] Furthermore, there are no obvious interactions between the aromatic ligands and between the Pt atoms, the shortest Pt–Pt distance being 7.726(6) Å in **I**, 7.612(2) Å in **II** and 5.901(3) Å in **III**. One may therefore consider the anions in **I** and **II** and the cation in **III** to be true square-planar Pt^{II} complex ions in the crystalline state. The structural parameters obtained ought to be quite reliable since variations in these parameters in square planar Pt^{II} compounds due to intermolecular forces are negligible except for very accurate structure determinations.[20]

The aromatic ligands. The ppy and tpy ligands are not perfectly planar but the torsion angles between the two aromatic rings are very small when taking the experimental error into consideration; 3.6(2.4)° in **I**, 3.8(2.4)° in **II** and 2.4(3.2)° in **III**. Most of the bond lengths and bond angles in these ligands are as expected and are presented in Table 3 as average values. The bond linking the two aromatic rings, C5–C6, are 1.47(1) Å in **I** and 1.46(1) Å in **III**. These bonds may therefore not be significantly shorter than a carbon–carbon single bond between two

Table 3. Selected bond lengths (in Å) and bond angles (in °) in the cyclometalated ions of **I**, **II** and **III** with estimated standard deviation.

Bond lengths	I	II	III
Pt–Cl1 (*trans*-N)	2.329(2)	2.312(2)	
Pt–N2 (*trans*-N)			2.055(6)
Pt–Cl2 (*trans*-C)	2.395(2)	2.395(2)	
Pt–N3 (*trans*-C)			2.131(7)
Pt–N1	2.014(6)	2.028(6)	2.016(5)
Pt–C11 (C9,II)	1.993(7)	1.982(7)	1.987(7)
N1–C1	1.356(9)	1.345(9)	1.351(8)
N1–C5	1.385(9)	1.381(9)	1.358(9)
C5–C6	1.47(1)	1.427(9)	1.462(9)
C6–C11 (C9,II)	1.43(1)	1.37(1)	
C12–C13			1.508(9)
Pt····Pt	7.726(6)	7.612(2)	5.901(3)
C–C (Ph)	1.39(1)		1.38(1)
C–C (Py)	1.38(1)	1.36(2)	1.38(1)
S1–C6		1.718(7)	
S1–C7		1.76(1)	

Bond angles	I	II	III
Cl1–Pt–Cl2	90.18(7)	90.73(7)	
N2–Pt–N3			82.3(2)
Cl1–Pt–N1	175.7(2)	174.5(2)	
N2–Pt–N1			173.8(2)
Cl1–Pt–C11 (C9,II)	93.7(2)	93.4(2)	
N2–Pt–C11			97.6(3)
Cl2–Pt–N1	94.1(2)	94.7(2)	
N3–Pt–N1			99.3(2)
Cl2–Pt–C11 (C9,II)	175.8(2)	175.8(2)	
N3–Pt–C11			179.0(2)
N1–Pt–C11 (C9,II)	82.1(3)	81.1(3)	80.7(2)
Pt–N1–C1	125.8(5)	127.4(5)	123.3(5)
Pt–N1–C5	114.5(5)	114.7(4)	115.6(4)
Pt–C11–C10	128.0(6)		127.9(5)
Pt–C9–C8		135.0(6)	
Pt–C11–C6	114.7(5)		114.4(5)
Pt–C9–C6		113.3(5)	
N1–C5–C6	115.5(7)	112.4(6)	113.4(6)
C5–C6–C11 (C9,II)	113.2(6)	118.4(6)	115.0(6)
C6–C11–C10	117.3(7)		117.6(7)
C6–C9–C8		111.7(6)	
S–C6–C5		129.6(6)	
C7–S–C6		91.1(4)	
Pt–N2–C12			109.7(5)
Pt–N3–C13			107.8(4)
N2–C12–C13			108.0(6)
N3–C13–C12			108.8(6)
Pt–N2–C12			109.7(5)
Pt–N3–C13			107.9(4)

sp^2 carbon atoms, 1.48 Å.[29] In **II**, however, the C5–C6 bond length is only 1.427(9) Å which indicates that the conjugation between the two rings is significant. Fairly short C5–C6 bond lengths in cyclometalated compounds derived from 2-(2′-thienyl)pyridine have been noted previously,[18,27,30,31] and may be the cause for the distinct difference in the photochemical behaviour of complexes with tpy and ppy as ligands.[12,32] 2-(2′-Thienyl)pyridine is known to be a weaker hydrogen base than 2-phenylpyridine[33] and complexes derived from the former ligand absorb light at significantly lower energy than the corresponding ppy compounds.[9] Presumably, owing to the increase in electron density in the C5–C6 bond in **II**, the adjacent bonds are elongated; N1–C5 being slightly longer than N1–C1 and C6–S1, 1.76(1) Å, significantly longer than C7–S1, 1.718(7) Å. The C6–S–C7 bond angle is only 91.1(4)° as compared with 93.8(4)° in the non-coordinated ligand.[34] One may further mention the N1–C5–C6 bond angle which is slightly smaller in **II** than in **I**, 112.4(2)° in **II** vs. 115.5(2)° in **I**. It has previously been suggested that a smaller N1–C5–C6 bond angle in **II** combined with a shortening of the C5–C6 bond may be one of the reasons for the significantly better yield of cyclometalated products from 2-(2′-thienyl)pyridine than from 2-phenylpyridine.[9]

The *ipso*-carbon bond angles in **I** and **III** are only 117.3(7) and 117.6(7)°, 111.7(6)° in **II**. As viewed by the downfield shift of the *ipso*-carbon atoms, 141.4, 145.6 and 146.7 ppm in **I**, **II** and **III**, respectively,[9] there is no evidence for a residual negative charge on these atoms.

Coordination around the platinum atoms. The angles between the bonds to the ligating atoms are as expected from previous studies on related compounds; for a review of references see Ref. 3. A comparison between the structures of the anions in **I** and **II** is particularly interesting owing to the difference in photochemical behaviour.[12,32] The N1–Pt–C9 bond angle in **II**, 81.1(3)°, may be slightly less than the corresponding bond angle in **I**, N1–Pt–C11, 82.1(3)°. These bond angles may furthermore be slightly larger than the N–Pt–N bond angle in the corresponding compounds derived from 2,2′-bipyridine, ca. 80°.[28] The differences, however, may not be significant when taking the uncertainties into consideration. Characteristic for all three ions is that the *trans* bond angles are not strictly 180°, and range from 173.8(2)° for the N1–Pt–N2 bond angle in **III** to the N3–Pt–C11 bond angle, 179.0(2)°, also in **III**.

Based upon the difference in the coupling constants between Pt and C10 in **I** and between Pt and C8 in **II** it was recently suggested that the Pt atom might be more strongly linked to the thienyl part of the tpy ligand than to the phenyl part of ppy.[32] The Pt–C11 bond length in **I**, 1.993(7) Å and the Pt–C9 bond length in **II**, 1.982(7) Å, however, are not sufficiently accurately determined to substantiate this conclusion. The Pt–N1 bond lengths in the three ions are likewise equal within experimental error. These bond lengths are only slightly longer than the Pt–C bonds to the carbon atoms in the cyclometalated ring; in **I** the difference between the Pt–N1 and the Pt–C11 bond lengths is hardly significant. Apparently, the difference between Pt–N and Pt–C bond lengths in cyclometalated Pt^{II} compounds is significantly smaller than in related Rh, Ru and Ir complexes.[7,15] The N2–Pt–N3 bond angle in **III**, 82.3(3)°, is similar to those observed in a number of Pt complexes containing chelated 1,2-diaminoethane.[21]

The Pt–Cl and Pt–N bond lengths. As pointed out in the introduction, the main purpose of this study was to investigate the Pt–Cl and Pt–N bond lengths in an attempt to explain the formation of only *trans*-N products in substitution reactions [eqn. (1)]. The results listed in Table 3 show clearly that the Pt–Cl and Pt–N bonds *trans* to the Pt–C bond are from 0.07 to 0.08 Å longer than the corresponding bonds *trans* to the Pt–N bond. The Pt–Cl bonds in **I** and **II** *trans* to Pt–C, are both 2.395(2) Å, similar to those observed in several *trans*-alkyl, *trans*-aryl and *trans*-carbene Pt^{II} complexes.[19,35–37] Apparently, the strong *trans*-influence of the carbanionic ligand, possibly as large as that of trialkylphosphines and second only to the hydride ligand, is retained when the carbon atom is part of a *N,C′*-chelate system. The long Pt–N bond in **III**, 2.131(7) Å, has roughly the same length as that observed in *cis*-$[Pt(ppy)_2]$[15] and indicates that the formally negatively charged carbon atom is exerting the same *trans*-influence on Pt–N(py) and Pt–N(en) bond lengths.

From the extensive surveys of Pt–Cl bond lengths one may conclude that this bond, when unaffected by other ligands, is close to 2.30 Å.[19,20] The Pt–Cl bonds *trans* to the nitrogen atom, particularly that in **I**, 2.329(2) Å, seems longer than in the uncharged compound derived from 2,2′-bipyridine, $[Pt(bpy)Cl_2]$, 2.281(4)–2.300(3) Å,[28] in *cis-N,N′*-$[Pt(Hppy)_2Cl_2]$, 2.293(6) Å,[38] and in *cis*- and *trans*-$[Pt(py)_2Cl_2]$, 2.30 Å.[39] This may suggest that the pyridine part of the cyclometalated ligand in **I**, ppy, excerts a stronger *trans* influence on the Pt–Cl bond than each of the pyridine groups in chelated 2,2′-bipyridine and in compounds derived from non-chelated pyridines. The alternative explanation based upon a *cis*-lengthening effect[40] by the carbanionic ligand is less probable, since Pt–Cl bond lengths do not seem to depend on ligands *cis* to the Pt–Cl bond.[19] Regardless the origin of the possible elongation of the Pt–Cl bond *trans* to the nitrogen atom in **I**, this bond may be sufficiently weakened to facilitate the isomerization of the kinetic *trans*-C product to the final *trans*-N product; cf. eqn. (1). It is notable that a similar elongation of the short Pt–N(en) bond in **III**, Pt–N2, is not observed.

The Bu_4N^+ *and* Et_4N^+ *ions.* Although a large number of crystal structures of salts of the two tetraalkylammonium ions have been determined, the actual structure of the cations has seldom been the subject of a discussion;[41–43] for a survey of recent references cf. Ref. 44. While the Et_4N^+ ion generally seems to prefer a structure with a zigzag antiperiplanar ('trans') conformation of the ethyl groups, as indeed was observed in the present study, the Bu_4N^+ ion, and presumably other large R_4N^+ ions, have a versatility to crystallize as the conformer best matching the packing requirements of the anion.[41] While the energy difference between the numerous possible conformers is undoubtedly very small, the various conformers will fill space in different ways, from the relatively flat cation with close to D_{2d} symmetry to the more spherical type with near S_4 symmetry. The determining factor is how the cation can arrange its aliphatic chains to avoid contact with the counter-ion.[42]

Snow and Ibers[41] showed that in $(Bu_4N)_2[Fe(edt)_2]_2$ (edt = 1,2-dithiolatoethane) all butyl groups had the antiperiplanar conformation with all N–C–C–C and C–C–C–C torsion angles close to 180°, while all C–N–C–C torsion angles were close to 60 or −60°. In $Bu_4N[PhTeCl_3I]$ three of the butyl groups attained the same conformation, while one group had a C–C–C–C torsion angle close to a synclinal one, ca. 60°.[42] In $Bu_4N[Pt(ppy)Cl_2]$, **I**, a third conformer is observed, two of the butyl groups being antiperiplanar, while two groups are synclinal with C–C–C–C torsion angles of 75.8(8) and 70.9(9)°. A similar conformation of the butyl groups has previously been observed in one of the two crystallographic independent cations in $Bu_4N[Cu(CN)_2]$.[43]

The C–C and N–C bond lengths in the two cations are as expected when taking the uncertainty into account. It is notable that two of the C–N–C bond angles are less than tetrahedral in both cations, 106.9(6) and 106.6(6)° in **I** and 104.7(5) and 106.8(6)° in **II**; the remaining four C–N–C bond angles being slightly greater than 109°. The N–C–C bond angles in the cations range from 114.9(6) to 115.9(7)° in Bu_4N^+ and from 112.8(6) to 114.6(7)° in Et_4N^+. Large N–C–C bond angles appear to be general for R_4N^+ ions, regardless the conformation of the alkyl groups,[44] and is the probable cause for the ability of the α-hydrogen atoms to make hydrogen bonds to electron-rich atoms in anions;[45] cf. the Cl····H contacts in **I**.

Conclusion

The Pt–Cl and Pt–N bonds *trans* to the Pt–C bond are from 0.07 to 0.08 Å longer than the corresponding bonds *trans* to the Pt–N bond in square planar Pt complexes containing *N,C′*-chelated metallocycles derived from 2-phenylpyridine and 2-(2′-thienyl)pyridine. The difference in the *trans* influence of a carbanionic ligand and a pyridine nitrogen ligand is therefore retained when these ligand atoms are part of a *N,C′*-chelate. The formation of only *trans*-N products in substitution reactions suggests that the rate of isomerization from the presumably initially formed *trans*-C products to the *trans*-N products is very high for this class of species. A fairly long Pt–Cl bond *trans* to the Pt–N bond in $Bu_4N[Pt(ppy)Cl_2]$ may indicate that the *trans*-influence of a pyridine nitrogen atom when part of an aromatic *N,C′*-chelate is larger than in *N,N*-chelated bipyridines and in non-chelated pyridines. This possible elongation of the Pt–Cl bond *trans* to N may prove to be the cause for the high rate of isomerization from *trans*-C to *trans*-N products.

Acknowledgement. We gratefully acknowledge the financial support given by Statoil under the VISTA program.

References

1. Constable, E. C. and Sousa, L. R. *J. Organomet. Chem. 427* (1992) 125.

2. Carlson, G. A., Djurovich, P. I. and Watts, R. J. *Inorg. Chem. 32* (1993) 4483.
3. Garces, F. O. and Watts, R. J. *Magn. Res. Chem. 31* (1993) 529.
4. Schmid, B., Garces, F. O. and Watts, R. J. *Inorg. Chem. 33* (1994) 9.
5. Yersin, H., Huber, P. and Wiedenhofer, H. *Coord. Chem. Rev. 132* (1994) 35.
6. von Zelewsky, A., Belser, P., Hayoz, P., Dux, R., Hua, X., Suckling, A. and Stoeckli-Evans, H. *Coord. Chem. Rev. 132* (1994) 75.
7. Frei, G., Zilian, A., Raselli, A., Güdel, H. and Bürgi, H.-B. *Inorg. Chem. 31* (1992) 4766.
8. Colombo, M. G., Hauser, A. and Güdel, H. U. *Inorg. Chem. 32* (1993) 3088.
9. Kvam, P.-I. and Songstad, J. *Acta Chem. Scand. 49* (1995) 313.
10. Fox, M. A. and Chanon, M., Eds., *Photoinduced Electron Transfer*, Elsevier, Amsterdam 1989.
11. Chassot, L. and von Zelewsky, A. *Inorg. Chem. 26* (1987) 2814.
12. Kvam, P.-I., Puzyk, M. V., Cotlyr, V. S., Songstad, J. and Balashev, K. P. *Acta Chem. Scand. In press.*
13. Chan, C.-W., Cheng, L.-K. and Che, C.-M. *Coord. Chem. Rev. 132* (1994) 87.
14. von Zelewsky, A., Suckling, A. P. and Stoeckli-Evans, H. *Inorg. Chem. 32* (1993) 4585.
15. Chassot, L., Müller, E. and von Zelewsky, A. *Inorg. Chem. 23* (1984) 4249.
16. Schmülling, M., Ryabov, A. D. and van Eldik, R. *J. Chem. Soc. Dalton Trans.* (1994) 1257.
17. Craig, C. A. and Watts, R. J. *Inorg. Chem. 28* (1989) 309.
18. Engebretsen, T., Kvam, P.-I., Lindeman, S.V. and Songstad, J. *Acta Chem. Scand. 49* (1995) 853.
19. Russell, D. R., Tucker, P. A. and Wilson, S. *J. Organomet. Chem. 104* (1976) 387.
20. Bengtsson, L. A. and Oskarsson, Å. *Acta Chem. Scand. 46* (1992) 707.
21. Deng, Y. and Khokhar, A. R. *Inorg. Chim. Acta 204* (1993) 35.
22. Bürgi, A. B. *Collected Abstracts, XII EMC*, Moscow, USSR, Vol. 3, p. 307.
23. North, A. C., Phillips, D. C. and Mathews, F. S. *Acta Crystallogr., Sect. A 24* (1968) 351.
24. *Molen, Structure Determination System*, Enraf Nonius, Delft 1990.
25. Cromer, D. T. and Waber, J. T. *International Tables for X-Ray Crystallography*, Vol IV, Kynoch Press, Birmingham 1974.
26. Visser, G. J., Heeres, G. J., Walters, J. and Vos, A. *Acta Crystallogr. Sect. B 24* (1968) 467.
27. Giordano, T. J. and Rasmussen, P. G. *Inorg. Chem. 14* (1975) 1628.
28. Herber, R. H., Croft, M., Coyer, J. M., Bilash, B. and Sakiner, A. *Inorg. Chem. 33* (1994) 2422.
29. Bastiansen, O. and Trætteberg, M. *Tetrahedron 17* (1962) 147.
30. Neve, F., Ghedini, N. and Crispini, A. *J. Organomet. Chem. 466* (1994) 259.
31. Maeder, U., von Zelewsky, A. and Stoeckli-Evans, H. *Helv. Chim. Acta 75* (1992) 1320.
32. Kvam, P.-I., Puzyk, M. V., Cotlyr, V. S., Balashev, K. P. and Songstad, J. *Acta Chem. Scand. 49* (1995) 645.
33. Bouwhuis, E. and Janssen, M. J. *Tetrahedron Lett. 3* (1972) 233.
34. Constable, E. C., Henney, R. P. G. and Tocher, D. A. *J. Chem. Soc., Dalton Trans.* (1991) 2335.
35. Reveco, P., Schmehl, R. H., Cherry, W. R., Fronczek, F. R. and Selbin, J. *Inorg. Chem. 24* (1985) 4078.
36. Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. and Taylor, R. *J. Chem. Soc., Dalton Trans.* (1989) S1.
37. Pregosin, P. S., Wombacher, F., Albinati, A. and Lianza, F. *J. Organomet. Chem. 418* (1991) 249.
38. Kvam, P.-I., Engebretsen, T., Maartmann-Moe, K. and Songstad, J. *Acta Chem. Scand. To be published.*
39. Colamarino, P. and Orioli, P. L. *J. Chem. Soc., Dalton Trans.* (1975) 1656.
40. Bugarcic, Z., Norén, B., Oskarsson, Å, Stålhandske, C. and Elding, L. I. *Acta Chem. Scand. 45* (1991) 361.
41. Snow, M. R. and Ibers, J. A. *Inorg. Chem. 12* (1973) 249.
42. Alcock, N. W. and Harrison, W. D. *J. Chem. Soc., Dalton Trans.* (1983) 2015.
43. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand., Ser. A 37* (1983) 165.
44. Langkjær, M., Larsen, E. and Larsen, S. *Acta Chem. Scand., Ser. A 39* (1985) 187.
45. Reetz, M. F., Hütte, S., Goddard, R. and Minet, U. *J. Chem. Soc., Chem. Commun.* (1995) 275.

Received April 27, 1995.