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Preparation and Characterization of Some Cyclometalated Pt(II) Complexes from 2-Phenylpyridine and 2-(2′-Thienyl)pyridine

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The preparation of cyclometalated Pt(II) compounds from 2-phenylpyridine, Hppy, and 2-(2′-thienyl)pyridine, Htpy, is considered. Salts of the monomeric $[<N-C>PtCl_2]^-$ anions are difficult to obtain in a pure state, but by addition of methanol to the reaction mixtures the dimers, $[<N-C>PtCl]_2$, are precipitated in satisfactory yield. The dimers can then be transformed into pure $Bu_4N[<N-C>PtCl_2]$ in close to quantitative yield by means of Bu_4NCl in dichloromethane. The preparation of several derivatives of the general type $[<N-C>PtX_2]^Z$, Z being + 1, 0 and − 1, and X_2 representing two monodentate or one bidentate ligand is described. The compounds have been characterized by IR and NMR and the ^1H and ^{13}C resonances have been completely assigned.

The chlorides of the complex ions from 1,2-diaminoethane, $[<N-C>Pten]Cl$, are readily prepared both from the dimers, $[<N-C>PtCl]_2$, and the monomers, $[<N-C>PtCl_2]^-$. These salts function as valuable precursors for $[<N-C>PtX_2]^Z$ for reactions which have to be performed in aqueous solution.

The reactions between $[<N-C>PtCl_2]^-$ and one equivalent of a monodentate ligand, L, lead to complexes in which L is *trans* to the nitrogen atom in the chelate ring.

Initiated by the remarkable photochemistry of the $[Ru(bpy)_3]^{2+}$ complex ion,[1] a large number of transition metal complexes containing <N–N>-type ligands, <N–N> representing 2,2′-bipyridine, bpy and related ligands, have been synthesized and characterized. The elements of choice have been various d^6 and d^8 metal ions such as Ru(II), Ir(III), Pd(II) and Pt(II).[2]

The d^6 metal ion complexes suffer from being coordinatively saturated, and their interactions and photochemical reactions with substrates will usually be restricted to the outer-sphere type. Square planar Pd(II) and Pt(II) complexes, however, may be covalently attached to substrates and undergo inner-sphere interactions and atom transfer reactions. Recent studies have shown that emission from Pt(II) complexes originates from triplet metal-to-ligand charge transfer (MLCT) excited states or from triplet ligand-centered (LC) excited states.[3–8] Apparently, a metal complex will only be emissive, particularly in fluid solution at room temperature, when a sufficiently high energy gap between the lowest emitting excited states and upper-lying metal-centered (MC) excited states is present. Since the larger Pt(II) ion will interact more strongly with rigid aromatic ligands than the Pd(II) ion,[7] Pt(II) complexes may be more promising candidates for the design of strongly luminescent species.[9–11]

Several metal complexes have been synthesized with ligands of stronger σ-donor character than that of the nitrogen atoms in, for example, 2,2′-bipyridine. Of particular interest has been the structurally related cyclometalated <N–C> complexes derived from 2-phenylpyridine and related species. The strong ligand field influence of the formally negatively charged carbon atom in this class of complexes combined with the possibility of π-back donation into the metallocycle leads generally to high-lying MC states. The <N–C> complexes are therefore significantly better photoreducing agents in their excited states than are the <N–N> complexes.[12,13]

When taking into account that an aromatic C–H bond is broken during the cyclometalation reaction, many <N–C> complexes are formed surprisingly rapidly, even from fairly dilute solutions of the reagents at room temperature.[12,14] K_2PtCl_4 in water/acetonitrile mixtures or various onium salts of $PtCl_4^{2-}$ in organic solvents can often be applied as the source of Pt(II). Less reactive but potential N,C-chelating agents, H<N–C>, can react with more labile Pt(II) complexes such as $(Et_2S)_2PtCl_2$ [15] or complexes with coordinated solvent molecules such as $(MeCN)_2PtCl_2$ and $[(MeCN)_4Pt](ClO_4)_2$.[16] However, the

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yield of cyclometalated products that act as precursors for further reactions remains as an obstacle. From 2-phenylpyridine, Hppy and $PtCl_4^{2-}$ the yield of $[<N-C>PtCl_2]^-$ rarely exceeds 15–20% [eqn. (1)],

$$PtCl_4^{2-} \xrightarrow[-2Cl^-,\ -H^+]{H<N-C>} [<N-C>PtCl_2]^- \quad (1)$$

the main product being *cis-N,N*-$[(Hppy)_2PtCl_2]$ from Hppy acting solely as a nitrogen donor [eqn. (2)].

$$PtCl_4^{2-} \xrightarrow[-2Cl^-]{H<N-C>} \textit{cis-N,N}\text{-}[(H<N-C>)_2PtCl_2] \quad (2)$$

A large excess of H<N–C> offers no advantage, since the first-formed cyclometalated product, eqn. (1), is converted into the undesired *trans-N,N*-[<N–C>Pt(Cl)(Hppy)], eqn. (3), where Hppy reacts as a nitrogen nucleophile.[4]

$$[<N-C>PtCl_2]^- \xrightarrow[-Cl^-]{Hppy} \textit{trans-N,N}\text{-}[<N-C>Pt(Cl)(Hppy)] \quad (3)$$

The salts of the $[<N-C>PtCl_2]^-$ anions are not readily isolated in pure form owing to the well known dimerization reaction [eqn. (4)].[17,18]

$$2[<N-C>PtCl_2]^- \longrightarrow [<N-C>PtCl]_2 + 2Cl^- \quad (4)$$

The dimerized species may undergo substitution reactions as described for the monomer by eqn. (3) and thus further initiate a reduction of the yield of $[<N-C>PtCl_2]^-$.[19] It was therefore of interest to examine to what extent the reaction depicted by eqn. (4) can be prevented, and if not, how the yield of the dimers can be increased and how these compounds can act as precursors for further reactions instead of salts of $[<N-C>PtCl_2]^-$.

Salts of the $[<N-C>PtCl_2]^-$ ions are not emissive in solution and have to be transformed into other complexes.[4] The bis(cyclometalated)Pt(II) complexes, *cis*-$[(<N-C>)_2Pt]$, have been shown to be interesting compounds.[20] These compounds, however, suffer from the disadvantage that they are uncharged and are virtually insoluble in protic solvents which seriously limits their applications. It was therefore of interest to convert salts of $[<N-C>PtCl_2]^-$, or the dimers, $[<N-C>PtCl]_2$, by suitable nucleophiles into cationic or anionic complex ions which, together with hydrophilic counterions, might allow photochemical studies in several types of solvents.

Although some determinations of crystal structures of cyclometalated Pt(II) complexes have been performed (for a survey cf. Ref. 21), the poor crystal quality of many compounds has forced one to depend upon ^1H NMR and, in some cases, upon ^{13}C NMR [4,20] for characterization. The use of NMR, however, has mostly been based upon 1D spectra. Assignments have often been based upon assumptions and by referring to literature data of related compounds. In this work we have tried to make a systematic study on the synthesis of some cyclometalated Pt(II) complexes derived from 2-phenylpyridine and 2-(2′-thienyl)pyridine. The photochemical, photophysical and electrochemical properties of these compounds will be published elsewhere.

Experimental

Materials. K_2PtCl_4 was crystallized from water, washed with methanol and diethyl ether and dried in vacuum prior to use. $PtCl_2$, Alpha Products, was used as received. 2-Phenylpyridine, Hppy, Fluka, was distilled prior to use. 2-(2′-Thienyl)pyridine, Htpy, Fluka, was used without further purification. The disodium salt of *cis*-1,2-dicyano-1,2-dithiolatoethene, $Na_2[S-C(CN)=C(CN)-S]$, Na_2mnt, was made and purified as described by Davidson.[22] 1,2-Bis(phenylthio)ethane, $(PhSCH_2-)_2$, edt, was made according to Ref. 23. Tris(morpholino)phosphine, $(O(-CH_2-CH_2)_2N)_3P$, mor_3P, was made as previously described [24] and was carefully crystallized from toluene and finally from acetonitrile. All manipulations with this compound were performed in an argon atmosphere. 1,10-Phenanthroline, phen, Baker Analyst, and 2,2′-bipyridine, bpy, Fluka, were crystallized from hexane. 1,2-Bis(diphenylphosphino)ethane, edp, Fluka, was crystallized before use from benzene/hexane. 1,2-Diaminoethane, en, Fluka, was distilled and kept frozen until used. Tetrabutylammonium chloride, Bu_4NCl, Fluka, was crystallized from ethylacetate/pentane, carefully dried in vacuum and kept protected from atmospheric moisture. Carbon monoxide, CO, Messer Griesheim, was 99.97 % pure. Dichloromethane was distilled from CaH_2 and stored in darkness. All other solvents, including the deuterated solvents, were used as received.

Instrumentation. The infrared spectra were recorded on a Perkin-Elmer 683 infrared spectrophotometer. The KBr technique was used throughout. The NMR experiments were carried out at 400.13 MHz (^1H), 161.98 MHz (^{31}P) and at 100.61 MHz (^{13}C) on a Bruker AM-400 WB spectrometer and at 200.13 MHz (^1H) and at 50.32 MHz (^{13}C) on a Bruker AC-200 F spectrometer. The chemical shifts throughout this work are presented on the δ-scale with reference to the solvent. Recent literature values [25] for the solvent shifts are summarized in Table 1.

Table 1. Chemical shift of the solvent peaks.[25]

	δ(ppm relative to TMS)	
	^1H	^{13}C
Dichloromethane-d_2	5.32	53.8
Acetone-d_6	2.05	29.8 and 206.0
Methanol-d_4	3.31	49.0
Acetonitrile-d_3	1.95	1.3 and 118.2
Dimethyl sulfoxide-d_6	2.50	39.5

Synthetic procedures

Bis(2-phenylpyridinato-C^2,N')-di-μ-chlorodiplatinum(II), [Pt(ppy)Cl]$_2$. To 2.62 g $PtCl_2$, 9.8 mmol, and 1.84 g 2-phenylpyridine, Hppy, 11.9 mmol, was added a small amount of Bu_4NCl, 0.26 g, 0.95 mmol, dissolved in 10 ml dichloromethane. The mixture was stirred and gently heated, allowing the solvent to evaporate slowly. Small amounts of dichloromethane were added to compensate for the solvent loss and to keep the reactants mixed. After approximately 1 h the colour of the reaction mixture had changed to yellow–green. After a further 3 h all $PtCl_2$ had reacted and the residue was treated with methanol. The insoluble part was carefully washed with dichloromethane which removed all possible by-products according to eqns. (1)–(3) together with unreacted 2-phenylpyridine and its hydrochloride, except traces of elemental Pt. Yield 30%, m.p. 275 °C (dec.). An additional yield of 7% was obtained from the mother liquor and the combined washings after treatment with concentrated hydrochloric acid, water and finally dichloromethane. The compound is virtually insoluble in dichloromethane and in the usual organic solvents when the reactants, the various by-products and particularly Bu_4NCl are absent.

Bis(2-(2'-thienyl)pyridinato-C^3,N')-di-μ-chlorodiplatinum(II), [Pt(tpy)Cl]$_2$. 2.62 g K_2PtCl_4, 6.31 mmol, were dissolved in water and transferred into $(Bu_4N)_2PtCl_4$ in dichloromethane as described by Craig *et al.*[4] Traces of water and excess Bu_4NCl were carefully removed from the dichloromethane solution, ca. 50 ml. After addition of 30 ml methanol the mixture was treated with small portions of a solution of 1.84 g 2-(2'-thienyl)pyridine, Htpy, 11.9 mmol, in ca.10 ml dichloromethane during 6 h. The reaction mixture was stirred and kept at reflux temperature, ca. 40 °C, and was finally slowly evaporated to dryness. After washings with hydrochloric acid and water the residue was redissolved in dichloromethane and repeatedly treated with methanol and the solvents removed. In this way the Bu_4N^+ salt of $[Pt(tpy)Cl_2]^-$ was converted into the dimeric compound which, contrary to all other compounds in the reaction mixture, is nearly insoluble in dichloromethane. Yield 43%, m.p. 246 °C (dec.). An additional amount of ca. 30% could be obtained after numerous treatments of the mother liquor with methanol followed by evaporation and redissolution in dichloromethane. Alternatively, the mother liquor could be treated with an excess of 1,2-diaminoethane which rapidly transformed all $Bu_4N[Pt(tpy)Cl_2]$ and $[Pt(ppy)Cl]_2$ being present into [Pt(tpy)en]Cl (see below). This salt, unlike all other solid compounds in the reaction mixture, is soluble in water and is readily extracted and purified. All attempts to obtain pure $Bu_4N[Pt(tpy)Cl_2]$ directly from the reaction mixture proved unsuccessful.

Tetrabutylammonium [dichloro(2-phenylpyridinato-C^2,N')-platinate(II)], $Bu_4N[Pt(ppy)Cl_2]$, and tetrabutylammonium [dichloro(2-(2'-thienyl)pyridinato-C^3,N')platinate(II)], Bu_4N-[Pt(tpy)Cl$_2$]. The dimeric compounds were treated with dry Bu_4NCl, 2 mol of chloride per mol dimer, dissolved in a minimum amount of dichloromethane. The dimer from 2-phenylpyridine dissolved immediately while the dimer from 2-(2'-thienyl)-pyridine dissolved during 1 h at room temperature. After filtration to remove traces of undissolved dimers and elemental Pt the salts were precipitated in close to quantitative yield by addition of diethyl ether, m.p. 188 and 158 °C, respectively. Bu_4NCl will not precipitate under these conditions. All attempts to prepare pure $Bu_4N[Pt(ppy)Cl_2]$ directly from $(Bu_4N)_2[PtCl_4]$ and excess 2-phenylpyridine in a dichloromethane–methanol mixture as described by Craig *et al.*[4] failed. The yellow–green crystals reported in Ref. 4 are actually *cis-N,N*-$[Pt(Hppy)_2Cl_2]$, eqn. (2), as shown by a structural study.[26] The mother liquor from the reaction described in Ref. 4, however, contains some $Bu_4N[Pt(ppy)Cl_2]$. After evaporation of the solvent the residue was dissolved in dichloromethane. Upon selective precipitation it was possible to obtain $Bu_4N[Pt(ppy)Cl_2]$ in ca. 20% yield. This product, however, was not pure.

The dimer, [Pt(ppy)Cl]$_2$, from $Bu_4N[Pt(ppy)Cl_2]$. 0.812 g $Bu_4N[Pt(ppy)Cl_2]$, 1.2 mmol, was dissolved in a minimum amount of dichloromethane, ca. 2 ml. 100 ml methanol were slowly added with stirring at room temperature, causing the dimer to precipitate. The dimer was filtered from the reaction mixture, washed with methanol, dichloromethane and diethyl ether and isolated in 97% yield. The corresponding dimer from $Bu_4N[Pt(tpy)Cl_2]$, $[Pt(tpy)Cl]_2$, was made in a similar way but only in 87% yield, presumably owing to its slight solubility in methanol.

[(1,2-Diaminoethane-N,N')(2-phenylpyridinato-C^2,N')platinum(II)] chloride, [Pt(ppy)en]Cl. 1.196 g $Bu_4N[Pt(ppy)Cl_2]$, 1.80 mmol, were dissolved in 50 ml dry dichloromethane. 0.444 g 1,2-Diaminoethane, en, 7.38 mmol, in 10 ml dichloromethane, was added dropwise to the stirred solution at room temperature. The yellow colour of the solution disappeared rapidly and a faintly yellowish compound precipitated within minutes. After 45 min stirring the product was collected and washed with dichloromethane and diethyl ether. The compound was dissolved in 100 ml methanol and the solution was filtered. After removal of some of the methanol the compound was precipitated with dichloromethane in 86% yield, m.p. 266 °C (dec.).

[Pt(ppy)en]Cl from [Pt(ppy)Cl]$_2$ and 1,2-diaminoethane. To a stirred slurry of the dimer in dichloromethane at room temperature was added a small excess en. During 30–40 s the yellow dimer dissolved, while the more voluminous and faintly yellow en complex precipitated in close to quantitative yield.

[Pt(ppy)en]ClO_4. This compound was precipitated from a methanolic solution of the chloride with a solution of

$LiClO_4$ in methanol. Yield 90%, m.p. 287 °C (dec.). *[Pt(tpy)en]Cl*, m.p. 263 °C (dec.) and *[Pt(tpy)en]ClO_4*, m.p. 278 °C (dec.) were made as the corresponding $[Pt(ppy)en]^+$ salts.

Tetrabutylammonium [dicyano(2-phenylpyridinato-C^2,N')-platinate(II)], (Bu_4N)[Pt(ppy)$(CN)_2$]. To an aqueous solution of 0.194 g [Pt(ppy)en]Cl, 0.44 mmol, was added 0.058 g KCN, 0.90 mmol, dissolved in ca. 10 ml water. A faintly yellow precipitate was formed within minutes which was transformed into the Bu_4N^+ salt by means of Bu_4NCl in dichloromethane.[4] The organic phase was washed with water, filtered and dried. The desired Bu_4N^+ salt was then precipitated in 80% yield by addition of diethyl ether to a filtered dichloromethane solution; m.p. 169 °C. IR (KBr-disc) showed ν_{CN} at 2135 and 2120 cm^{-1}. The corresponding salt from [Pt(tpy)en]Cl, (Bu_4N)[Pt(tpy)$(CN)_2$], m.p. 114 °C, was made in a similar way in ca. 80% yield, but had to be fractionally crystallized from acetone/diethyl ether to be obtained pure. IR showed ν_{CN} at 2120 and 2115 cm^{-1} (KBr). The first minor fraction was a by-product which was not further examined.

[(1,2-Bis(phenylthio)ethane)(2-phenylpyridinato-C^2,N')platinum(II)] perchlorate, [Pt(ppy)edt]ClO_4. 0.315 g Bu_4N[Pt(ppy)Cl_2], 0.46 mmol, and 0.224 g 1,2-bis(phenylthio)ethane, edt, 0.91 mmol, each dissolved in ca. 10 ml dichloromethane, were mixed. No immediate reaction seemed to take place. Upon slow addition of methanol the yellow colour of the mixture slowly disappeared. The solvents were removed in vacuum leaving a faintly yellow residue. No attempt was made to isolate the product, [Pt(ppy)edt]Cl, but it was transformed into the perchlorate by means of $LiClO_4$ in methanol. Yield, 80%, from acetonitrile/diethyl ether, m.p. 250 °C (dec.). [Pt(tpy)edt]ClO_4, m.p. 238 °C (dec.) was made in a similar way in 89% yield.

Carbonylchloro(2-phenylpyridinato-C^2,N')platinum(II), [Pt(ppy)(CO)Cl]. 1.694 g (Bu_4N)[Pt(ppy)Cl_2], 2.56 mmol, was dissolved in a mixture of 150 ml dichloromethane and 100 ml methanol. Carbon monoxide was bubbled through the solution under constant stirring for 48 h and a precipitate was slowly formed. The reaction mixture was finally cooled to −20 °C. The solid was filtered from the reaction mixture and washed with cold dichloromethane and finally with diethyl ether. Yield 86%, m.p. 247 °C (dec.), ν_{CO} at 2100 cm^{-1} (KBr). The corresponding compound from 2-(2'-thienyl)pyridine, [Pt(tpy)(CO)Cl], was obtained in a similar way in 70% yield, m.p. 227 °C (dec.), ν_{CO} at 2105 cm^{-1} (KBr). These two compounds are nearly insoluble in all the usual solvents at room temperature. Only in acetone was it possible to obtain poor quality NMR spectra.

[(1,2-Bis(diphenylphosphino)ethane)(2-phenylpyridinato-C^2,N')platinum(II)] chloride, [Pt(ppy)(edp)]Cl. To 0.224 g Bu_4N[Pt(ppy)Cl_2], 0.34 mmol, in ca. 10 ml deoxygenated dichloromethane was added dropwise 0.167 g 1,2-bis(diphenylphosphino)ethane, edp, 0.42 mmol, also dissolved in deoxygenated dichloromethane. After 1 h the solvent was removed and the solid was washed with water. Traces of water were removed azeotropically. The solid was dissolved in dichloromethane, and some benzene was added. When the dichloromethane was slowly removed a faintly yellow solid precipitated. The solid was filtered off and washed with diethyl ether. Yield 80%, m.p. 283 °C. Various attempts were made to prepare the corresponding compound from Htpy, [Pt(tpy)(edp)]Cl. This compound and the perchlorate, [Pt(tpy)(edp)]ClO_4, however, were never obtained pure as viewed by, particularly, the ^{31}P-NMR spectrum.

Tetrabutylammonium [(1,2-dicyano-1,2-dithiolatoethene)(2-phenylpyridinato-C^2,N')platinate(II)], Bu_4N[Pt(ppy)mnt]. 0.193 g [Pt(ppy)en]Cl, 0.43 mmol, dissolved in 25 ml methanol, was treated dropwise with a methanolic solution, 25 ml, of 0.082 g Na_2mnt, 0.44 mmol, at room temperature. After 12 h the solvent was removed and the residue was dissolved in acetone. The solution was filtered and the solvent once more removed in vacuum. To an aqueous extract of the residue was added Bu_4NCl in slight excess which precipitated the desired salt. The product was extracted with dichloromethane, the extract carefully washed with water and finally dried. The product was then crystallized from acetone/diethyl ether in 75% yield, m.p. 196 °C. The corresponding salt from Htpy, Bu_4N[Pt(tpy)mnt], m.p. 162 °C, was made in a similar way in 61% yield but was preferably crystallized from dichloromethane/diethyl ether. IR (KBr disc) showed ν_{CN} at 2205 cm^{-1} for Bu_4N[Pt(ppy)mnt] and at 2215 cm^{-1} for Bu_4N[Pt(tpy)mnt].

[(1,10-Phenanthroline)(2-phenylpyridinato-C^2,N')platinum(II)] chloride, perchlorate and acetate, [Pt(ppy)phen]X, (X = Cl^-, ClO_4^- and CH_3COO^-). 0.115 g $[Pt(ppy)Cl]_2$, 0.20 mmol, was added in small portions to a stirred melt of 1,10-phenanthroline. The reaction mixture turned immediately red but was stirred at melting temperature for 1 h. The cooled residue was treated with methanol leaving a yellow solution. After filtration the product was precipitated in 90% yield by addition of diethyl ether, m.p. 296 °C. The corresponding perchlorate was made in 85% yield using $LiClO_4$ in methanol, m.p. 308 °C (dec.). The acetate was formed from the chloride by means of a slight excess of silver acetate in warm methanol, m.p. 279 °C (dec.). The $[Pt(ppy)phen]^+$ salts are nearly insoluble in dichloromethane. The chloride and the acetate are slightly soluble in water and in methanol while the perchlorate is slightly soluble in acetonitrile.

[(2,2'-Bipyridyl)(2-phenylpyridinato-C^2,N')platinum(II)] chloride, [Pt(ppy)bpy]Cl. This salt, m.p. 285 °C, and the perchlorate, m.p. 293 °C (dec.), were made as the corresponding salts from 1,10-phenanthroline in 85% yield.

Chloro-(2-phenylpyridinato-C^2,N')(tris(morpholino)phosphine)-platinum(II), [Pt(ppy)(mor_3P)Cl]. 0.0922 g mor_3P, 0.32 mmol, dissolved in benzene, was added drop by drop to a slurry of 0.100 g [Pt(ppy)(CO)Cl], 0.24 mmol, in warm benzene. The solid complex dissolved gradually during the addition of the aminophosphine. After 40 min the solvent was removed and the residue was washed several times with diethyl ether to remove traces of mor_3P. The solid was finally dissolved in acetonitrile, the solution filtered and cooled to ca. 20 °C. Beautiful yellow crystals were slowly obtained in 70% yield, m.p. 261 °C (dec.). This compound dissolves slowly in dichloromethane but has a limited solubility in acetonitrile and methanol. The compound can also be prepared from mor_3P and $Bu_4N[Pt(ppy)Cl_2]$ as described below for [Pt(tpy)(mor_3P)Cl].

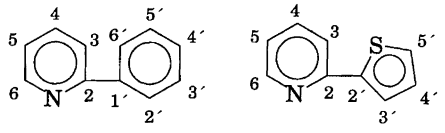
Chloro-(2-(2'-thienyl)pyridinato-C^3,N')(tris(morpholino)phosphine)platinum(II), [Pt(tpy)(mor_3P)Cl]. 0.133 g mor_3P, 0.45 mmol, dissolved in benzene, was added drop by drop to a solution of 0.257 g $Bu_4N[Pt(tpy)Cl_2]$, 0.39 mmol, in warm benzene. After 3 h the solution was filtered, the solvent was removed in vacuum and the residue was washed several times to remove Bu_4NCl. The compound was further purified as [Pt(ppy)(mor_3P)Cl] giving orange crystals in 50% yield, m.p. 243 °C (dec.). The solubility of this compound in dichloromethane, acetonitrile and methanol is as observed for [Pt(ppy)(mor_3P)Cl].

Results and discussion

Synthetic considerations. The main purpose of this work was to establish improved synthetic procedures for the preparation of salts of $[<N-C>PtCl_2]^-$, <N–C> representing cyclometalated 2-phenylpyridine, ppy, and 2-(2'-thienyl)pyridine, tpy; cf. eqn. (1). These salts function as precursors for other cyclometalated complexes. The parent reagents, Hppy and Htpy, with numbering of the atoms, is shown in Scheme 1. With regard to Htpy, a solid compound at room temperature, it is known that the *cis* configuration, or configurations close to *cis*, are the most stable ones.[27] Recent calculations have shown that the barrier of rotation is only some 10 kJ mol^{-1}, with the *cis* configuration being only 4.3 kJ mol^{-1} more stable than the *trans*.[28] Since the *trans* configuration is the reacting one in the cyclometalation reaction, this configuration has been chosen to represent Htpy in Scheme 1.

It is apparent from the present study that the cyclometalated products from Htpy are obtained in considerably larger yield, ca. 73 %, than are the corresponding compounds from Hppy, ca. 37%. 2-Phenylpyridine is known to react in two ways with electrophilic metal cations; as a nitrogen nucleophile forming a *cis*-(N'-Hppy)$_2$ complex [eqn. (2)], or as a cyclometalating <N–C> ligand by which the hydrogen atom at C2', H2', is removed. 2-(2'-Thienyl)pyridine may additionally react as a sulfur ligand. Since thiophene and substituted thiophenes are very weak sulfur nucleophiles,[29] few bidentate N- and S-linked complexes are known; for a literature survey, see Ref. 30. Generally, 2-(2'-thienyl)pyridine undergoes cyclometalation involving the C3' carbon atom owing to the low reactivity of the sulfur atom combined with the low barrier of rotation around the C2–C2' bond. This kind of complex is often obtained in high yield from 2-(2'-thienyl)pyridine and related species.[31] The negligible yield of products from 2-(2'-thienyl)pyridine acting only as a monodentate nitrogen donor, in contrast to what is observed for 2-phenylpyridine,[4] is probably due to a combination of several factors. Since the steric demands of the two 2-substituents, phenyl and thienyl, are fairly equal, one may expect the more basic 2-phenylpyridine to be the more nucleophilic one. The difference in the pK_a-values, however, amounts to only 0.82 units.[32] Apparently, the governing factor is a higher rate of cyclometalation of the first formed $[N'-(Htpy)PtCl_3]^-$ complex than of $[N'-(Hppy)PtCl_3]^-$. This may be due to the ability of the readily formed *trans* form of the former to adjust more easily to a suitable bite angle for the platinum atom to be inserted into the C3'–H3' bond to initiate the cyclometalation process. A comparison between bond angles and bond lengths in the –Pt–NCCC– ring system from published crystal structures of cyclometalated compounds derived from Hppy and Htpy is difficult owing to the greatly varying *trans* and *cis* ligands present in the studied complexes.[15,19] It may appear, however, that the N–C2–C2' bond angle is somewhat smaller in the tpy compounds than the N–C2–C1' angle in the ppy complexes allowing the C3'–H3' bond to get closer to the platinum metal. The negligible yield of both *cis-N,N*-[$(Htpy)_2PtCl_2$], eqn. (2), and of *trans-N,N*-[Pt(tpy)(Htpy)Cl], eqn (3), as compared to what is observed for Hppy, is probably due to the lower nitrogen nucleophilicity of Htpy as outlined above.

Since one equivalent of H^+ is formed for each cyclometalated product, cf. eqn. (1), various experiments were performed in the presence of proton bases such as sterically hindered amines or sodium acetate. No improvements in yield were accomplished by these additives indicating that base assistance to the breaking of the C–H bond in the cyclometalating process may not be of kinetic importance.[14] The best solution to this problem, particularly when 2-phenylpyridine was the reagent, was to use



Scheme 1.

dichloromethane as solvent at ca. 40 °C and continuously allow the solvent to evaporate. It is known that dichloromethane will slowly remove hydrochloric acid from a reaction mixture when evaporating.[33] It should be emphasized that K_2PtCl_4 in protic solvents and $(Bu_4N)_2PtCl_4$ in aprotic solvents were repeatedly found to give cyclometalated products in low yield from 2-phenylpyridine. A heterogenous reaction from $PtCl_2$ and a small amount of Bu_4NCl, ca. 10%, gave the desired product in significantly better yield; cf. Experimental. Presumably, the presence of some Bu_4NCl leads to a sufficiently low concentration of $(Bu_4N)_2PtCl_4$ to allow the cyclometalation reaction to take place, but will prevent further reactions as depicted by eqns. (2) and (3). The readily purified dimer can then be transformed into the desired salt in close to quantitative yield by means of Bu_4NCl in dichloromethane, eqn. (5).

$$[Pt(ppy)Cl]_2 + 2\ Bu_4NCl \xrightarrow{CH_2Cl_2} 2\ Bu_4N\,[Pt(ppy)Cl_2] \qquad (5)$$

This reaction is quantitatively reversed when $Bu_4N[Pt(ppy)Cl_2]$ is dissolved in methanol in which the dimer is insoluble; cf. eqn. (4) and Experimental.

The corresponding salt from 2-(2′-thienyl)pyridine, $Bu_4N[Pt(tpy)Cl_2]$, was likewise impossible to obtain pure directly from $(Bu_4N)_2PtCl_4$ in dichloromethane. This salt was prepared in good yield from the corresponding dimer as outlined by eqn. (5). This dimer could be prepared as described for $[Pt(ppy)Cl]_2$ but was more readily obtained in a total yield of 75% from $(Bu_4N)_2PtCl_4$ in a dichloromethane/methanol mixture. The rate of dimerization of $Bu_4N[Pt(tpy)Cl_2]$, however, appeared slower than that of $Bu_4N[Pt(ppy)Cl_2]$. Since the precipitation of the pure dimer from the methanolic solution was not quantitative, the dimer and traces of $Bu_4N[Pt(tpy)Cl_2]$ in the mother liquor could be transformed into [Pt(tpy)en]Cl by means of 1,2-diaminoethane. [Pt(tpy)en]Cl and [Pt(ppy)en]Cl were found to be valuable precursors for further compounds, particularly for reactions that had to be performed in water or methanol; cf. the reactions with KCN and Na_2mnt. Apparently, en complexes are readily formed in aprotic solvents but the en ligand is readily displaced in protic solvents.

When a tervalent phosphorus compound is to be introduced as a ligand in this class of complex, triphenylphosphine, Ph_3P, or trialkylphosphines with small alkyl groups are generally used as reagents. These compounds form quite often poor crystals and the presence of Ph_3P will additionally lead to very complex ^{1}H-NMR spectra in the aromatic region. The readily available tris(morpholino)phosphine, mor_3P,[24] was therefore attempted. This compound was found to react in the expected way and formed nice crystals. The crystal structure of the mor_3P derivatives will be published separately.[34] It is notable that $[Pt(ppy)(mor_3P)Cl]$ and $[Pt(tpy)(mor_3P)Cl]$ are formed easily from both [<N–C>Pt(CO)Cl] and $Bu_4N[<N–C>PtCl_2]$ by displacement of CO and Cl^-, respectively.

The CO compounds, [Pt(ppy)(CO)Cl] and [Pt(tpy)(CO)Cl], could not be obtained from $Bu_4N[<N–C>PtCl_2]$ in pure dichloromethane or from a slurry of dimers

Table 2. ^{1}H chemical shifts, δ(ppm relative to TMS), of Hppy, Htpy and of the ppy and tpy parts of the complexes. For numbering of atoms see Scheme 1.

	H-3	H-4	H-5	H-6[f]	H-2′	H-3′[f]	H-4′	H-5′	H-6′
Hppy[a]	7.78	7.76	7.25	8.70	8.06	7.50	7.45	7.50	8.06
$[Pt(ppy)Cl_2]^-$[a]	7.59	7.78	7.10	9.91 (54)		7.97 (52)	7.06	7.03	7.37
$[Pt(ppy)(CN)_2]^-$[a]	7.75	7.87	7.15	9.40 (31)		8.06 (49)	7.12	7.08	7.55
$[Pt(ppy)en]^+$[b]	7.87	8.00	7.23	8.50 (37)		7.24 (–)	7.10	7.10	7.59
$[Pt(ppy)edt]^+$[c]	8.04	8.11	7.25	8.66 (40)		7.43 (–)	7.08	7.25	7.74
$[Pt(ppy)mnt]^-$[a]	7.77	7.84	7.55	9.20 (34)		7.75 (–)	7.08	7.05	7.57
Pt(ppy)CO)Cl[d]	8.20	8.26	7.65	9.43 (–)		7.54 (–)	7.22	7.30	7.87
$Pt(ppy)(mor_3P)Cl$[a]	7.80	7.89	7.35	9.68 (29)		7.93 (57)	7.17	7.15	7.56
$[Pt(ppy)edp]^+$[b]	8.13	8.02	6.96	8.31 (34)		7.05 (–)	6.76	7.10	7.83
$[Pt(ppy)bpy]^+$[e]	8.13	8.15	7.51	9.49 (35)		8.22 (–)	7.14	9.19	7.79
$[Pt(ppy)phen]^+$[e]	7.94	8.07	7.35	9.66 (–)		7.36 (–)	7.18	7.12	7.57
					H-3′	H-4′[f]	H-5′		
Htpy[a]	7.67	7.70	7.15	8.54	7.41	7.13	7.60		
$[Pt(tpy)Cl_2]^-$[a]	7.22	7.67	6.87	9.56 (47)		7.29 (–)	7.37		
$[Pt(tpy)(CN)_2]^-$[b]	7.47	7.91	7.12	9.01 (34)		7.30 (20)	7.45		
$[Pt(tpy)en]^+$[b]	7.55	7.99	7.15	8.48 (37)		7.11 (–)	7.62		
$[Pt(tpy)edt]^+$[c]	7.66	7.98	7.11	8.51 (41)		6.79 (–)	8.20		
$[Pt(tpy)mnt]^-$[b]	7.48	7.83	7.00	8.83 (35)		7.14 (16)	7.48		
Pt(tpy)(CO)Cl[d]	7.72	8.16	7.49	9.21 (34)		7.14 (28)	7.74		
$Pt(tpy)(mor_3P)Cl$[a]	7.42	7.78	7.20	9.36 (29)		7.30 (–)	7.39		

[a] In CD_2Cl_2. [b] In CD_3OD. [c] In CD_3CN. [d] In $(CD_3)_2CO$. [e] In $(CD_3)_2SO$. [f] J_{Pt-C}/Hz. (–) Indicates that J_{Pt-C} was not detectable due to lack of resolution or insufficient concentration.

in this solvent. An untractable mixture of products was obtained which, based upon the NMR spectra, suggested that the solvent had reacted. Apparently, some methanol had to be present to make the chloride ion a sufficiently good leaving group for a clean substitution reaction. A similar effect of methanol was observed in the reaction between $Bu_4N[Pt(ppy)Cl_2]$ and 1,2-bis(phenylthio)-ethane. Complexes with edp, bpy and phen were only prepared with cyclometalated 2-phenylpyridine functioning as the <N–C> ligand.

Characterization of the compounds. The most convenient method for rapid identification of the precursors and products during the synthetic work and to check their purity was NMR. Proof of cyclometalation of the two ligands was obtained by integration of the proton spectra and by the number of methine and non-methine carbon atoms from ^{13}C spin-echo experiments.[25] The assignment of the resonances was aided by ^{13}C–^{1}H XHCORR and, in some cases, by ^{1}H COSY. When possible, assignments were further aided by data from the literature on relevant compounds[4,20] and from spectra of compounds of known structure.[26,34] The ^{1}H and ^{13}C chemical shifts of the <N–C> parts of the compounds are listed in Tables 2 and 3. It should be emphasized that owing to difficulties with solubility several solvents had to be used, invalidating a discussion based on minor differences in the observed shifts. However, in all cases the shifts of the parent pyridines, Hppy and Htpy, and their cyclometalated complexes were determined in the same solvent, which gave rise to the coordination induced shifts, CIS; cf. Tables 4 and 5. For the anionic complexes the chemical shifts of the counterion, Bu_4N^+, were in agreement with literature data.[35] Since the various resonances of the starting compounds had been carefully assigned, several of the proton signals in the derived complexes could be identified from the shape of the resonances; cf. Fig. 1 for a representative ^{1}H spectrum.

Since most of the ^{13}C resonances are well separated it was often possible to determine the ^{195}Pt coupling constants for the methine carbons. Further assignments were aided by spin-echo experiments by which the non-methine carbon resonances are distinguished from the rest. From a comparison with literature data[15] the resonance at the highest frequency could be assigned to the C2 carbon atom. The ^{195}Pt satellites for most C1′ and C2′ (ppy) and C2′ and C3′ (tpy) could not be detected; cf. Table 6, and the resonances of these atoms were more difficult to assign. No obvious pattern could be deduced from the listed coupling constants. However, from the few observable J_{Pt-C}, the chemical shifts of the C2′(ppy) and C3′(tpy) atoms appeared to be more downfield than of C1′(ppy) and C2′(tpy) in the complexes with equal ligands *trans* to the N and C atom in the chelate. The assignment of C4 and C5′ (ppy) and C4 (tpy) were aided by their small coupling constants to the platinum atom, $^{4}J_{Pt-C} = 4\text{-}9$ Hz. The final assignments were made using ^{13}C–^{1}H XHCORR.

$Bu_4N[Pt(ppy)Cl_2]$ and $Bu_4N[Pt(tpy)Cl_2]$. These two compounds were the precursors for most complexes and a closer scrutiny on their NMR spectra seemed appropriate. Proper assignment of the resonances due to $Bu_4N[Pt(ppy)Cl_2]$ was only possible by applying both ^{13}C–^{1}H XHCORR and ^{1}H COSY. The resonances due to $Bu_4N[Pt(tpy)Cl_2]$ were easier to assign owing to the

Table 3. ^{13}C chemical shifts, δ(ppm relative to TMS), of Hppy, Htpy and of the ppy and tpy parts of the complexes. For numbering of atoms see Scheme 1.

	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
Hppy[a]	157.5	120.6	137.0	122.5	150.0	127.1	139.8	129.0	129.3	129.0	127.1
$[Pt(ppy)Cl_2]^-$[a]	167.8	118.0	137.1	121.9	149.8	144.7	141.4	133.3	129.4	122.4	122.6
$[Pt(ppy)(CN)_2]^-$[a]	168.2	118.7	138.8	123.4	153.2	147.1	158.2	138.7	130.4	123.8	123.0
$[Pt(ppy)en]^+$[b]	169.0	120.3	140.7	124.1	151.7	144;4	146.7	134.0	131.0	125.0	124.9
$[Pt(ppy)edt]^+$[c]	166.9	121.6	142.8	126.0	153.1	146.9	146.2	136.1	132.4	127.4	125.9
$[Pt(ppy)mnt]^-$[a]	167.2	119.5	138.0	123.2	150.2	144.6	154.5	134.4	130.9	123.1	124.2
Pt(ppy)(CO)Cl[d]	[f]	120.2	143.1	125.4	148.5	[f]	[f]	136.8	132.5	126.3	123.5
$Pt(ppy)(mor_3P)Cl$[a]	165.5	118.7	140.0	122.4	148.0	145.4	141.0	138.1	130.6	124.3	123.9
$[Pt(ppy)edp]^+$[b]	169.3	121.7	142.8	125.4	153.9	148.9	161.1	140.3	132.0	127.3	125.8
$[Pt(ppy)bpy]^+$[e]	165.1	119.5	141.6	122.8	149.3	140.2	144.5	133.5	130.0	124.9	124.3
$[Pt(ppy)phen]^+$[e]	165.9	119.8	140.7	123.8	152.9	139.5	145.4	132.8	129.7	125.0	124.1
						C-2′	C-3′	C-4′	C-5′		
Htpy[a]	152.8	118.9	136.9	122.3	149.8	145.4	127.8	128.4	124.8		
$[Pt(tpy)Cl_2]^-$[a]	163.4	116.6	138.1	119.1	150.2	137.3	145.6	133.3	126.7		
$[Pt(tpy)(CN)_2]^-$[b]	164.2	118.9	141.7	122.4	153.5	145.9	163.2	137.1	129.2		
$[Pt(tpy)en]^+$[b]	164.5	118.6	141.4	121.6	151.9	142.1	148.8	133.1	129.7		
$[Pt(tpy)edt]^+$[c]	162.1	120.2	143.4	124.0	153.2	149.2	153.1	132.9	134.9		
$[Pt(tpy)mnt]^-$[b]	163.7	119.1	140.1	121.8	150.8	140.9	159.4	133.5	130.0		
Pt(tpy)(CO)Cl[d]	[f]	119.5	149.5	121.9	144.6	[f]	[f]	133.8	132.1		
$Pt(tpy)(mor_3P)Cl$[a]	160.7	117.4	140.4	120.1	147.6	142.8	141.6	135.8	127.8		

[a] In CD_2Cl_2. [b] In CD_3OD. [c] In CD_3CN. [d] In $(CD_3)_2CO$. [e] In $(CD_3)_2SO$. [f] Signal too weak.

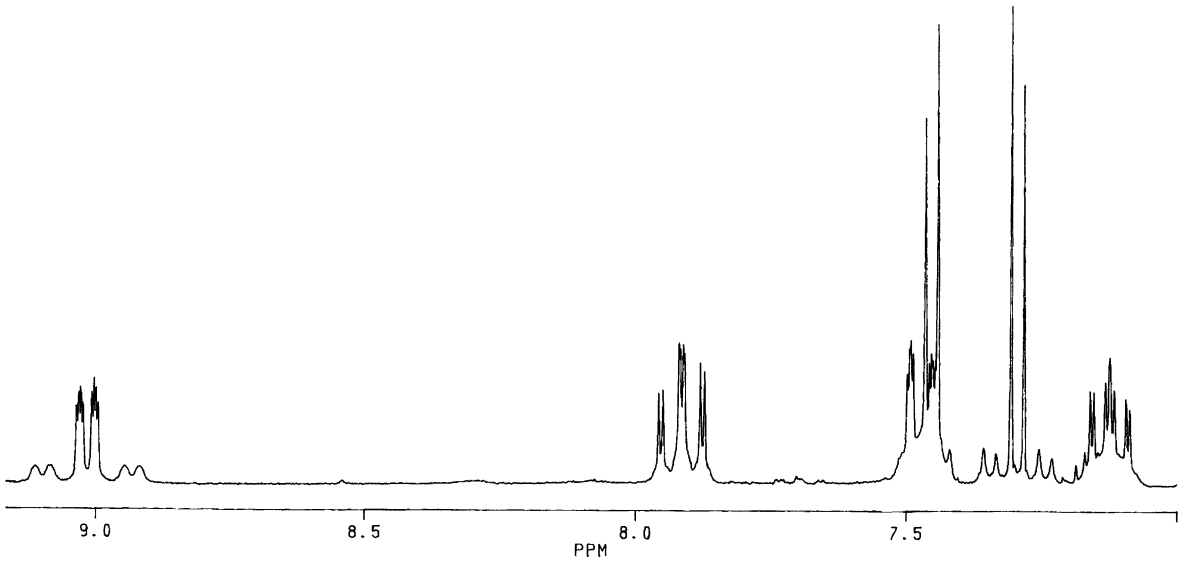


Fig. 1. ^{1}H NMR spectrum in CD_2Cl_2 of the aromatic region of $Bu_4N[Pt(tpy)(CN)_2]$.

two easily recognizable doublets of H4′ and H5′ in the thienyl ring. A further distinction between these two protons was based upon the different Pt–C coupling constants, $^2J_{Pt-C4'} = 96$ Hz and $^3J_{Pt-C5'} = 66$ Hz. The ^{1}H NMR spectrum showed unequivocally the Bu_4N^+ ion to be present in a 1:1 ratio with the anion.

The ^{1}H CIS data (Table 4), seem to indicate that the H3 proton in the tpy compound is more shielded than is the corresponding proton in the ppy compound, −0.45 and −0.19 ppm, respectively. This comparison, however, may not be valid, since the configuration of Htpy is altered from *cis* to *trans* upon coordination. H3′ and H4′ in $[Pt(ppy)Cl_2]^-$ are far more downfield and upfield, respectively, than H4′ and H5′ in $[Pt(tpy)Cl_2]^-$ relative to the free ligands. The ^{13}C CIS data (Table 5), do not indicate, however, that the corresponding carbon atoms are influenced differently when Hppy and Htpy are cyclometalated. The strong upfield shift of C2′, −8.1 ppm, upon complexing of Htpy, as compared with a downfield shift of 1.6 ppm in the ppy case, is notable and may indicate a difference in the C2–C1′ and C2–C2′ bonds or in the bond angles in the N–C2–C1′–C2′ and N–C2–C2′–C3′ parts of the two complex anions.

$Bu_4N[Pt(ppy)(CN)_2]$ and $Bu_4N[Pt(tpy)(CN)_2]$. The NMR spectra of these two salts are in principle quite similar to

Table 4. ^{1}H-NMR coordination-induced shifts (CIS).

	CIS = $\delta_{complex} - \delta_{free\ ligand}$ in the same solvent							
	H-3	H-4	H-5	H-6	H-3′	H-4′	H-5′	H-6′
$[Pt(ppy)Cl_2]^-$ [a]	−0.19	0.02	−0.15	1.21	0.47	−0.39	−0.47	−0.69
$[Pt(ppy)(CN)_2]^-$ [a]	−0.03	0.11	−0.10	0.70	0.56	−0.33	−0.42	−0.51
$[Pt(ppy)en]^+$ [b]	0.09	0.16	−0.08	−0.08	−0.21	−0.31	−0.35	−0.30
$[Pt(ppy)edt]^+$ [c]	0.20	0.28	−0.04	−0.01	−0.07	−0.38	−0.25	−0.34
$[Pt(ppy)mnt]^-$ [a]	−0.01	0.08	0.30	0.50	0.25	−0.37	−0.45	−0.49
Pt(ppy)(CO)Cl [d]	0.31	0.43	0.36	0.76	0.07	−0.19	−0.17	−0.25
$Pt(ppy)(mor_3P)Cl$ [a]	0.02	0.13	0.10	0.98	0.43	−0.28	−0.35	−0.50
$[Pt(ppy)edp]^+$ [b]	0.35	0.18	−0.35	−0.27	−0.40	−0.65	−0.35	−0.06
$[Pt(ppy)bpy]^+$ [e]	0.20	0.30	0.18	0.82	0.74	−0.28	−0.29	−0.29
$[Pt(ppy)phen]^+$ [e]	0.01	0.22	0.02	0.99	−0.12	−0.24	−0.36	−0.51
					H-4′	H-5′		
$[Pt(tpy)Cl_2]^-$ [a]	−0.45	−0.03	−0.28	1.02	0.16	−0.23		
$[Pt(tpy)(CN)_2]^-$ [b]	−0.25	0.19	−0.06	0.59	0.21	−0.17		
$[Pt(tpy)en]^+$ [b]	−0.17	0.27	−0.03	0.06	0.02	0		
$[Pt(tpy)edt]^+$ [c]	−0.10	0.30	−0.10	0	−0.34	0.55		
$[Pt(tpy)mnt]^-$ [b]	−0.24	0.11	−0.18	0.41	0.05	−0.14		
Pt(tpy)(CO)Cl [d]	−0.10	0.37	0.26	0.69	0	0.01		
$Pt(tpy)(mor_3P)Cl$ [a]	−0.25	0.08	0.05	0.82	0.17	−0.21		

[a] In CD_2Cl_2. [b] In CD_3OD. [c] In CD_3CN. [d] In $(CD_3)_2CO$. [e] In $(CD_3)_2SO$.

Table 5. ^{13}C-NMR coordination-induced shifts (CIS).

	CIS = $\delta_{complex} - \delta_{free\ ligand}$ in the same solvent										
	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
[Pt(ppy)Cl$_2$]$^-$ [a]	10.3	−2.6	0.1	−0.6	−0.2	1.6	17.6	4.3	0.1	−6.6	−4.5
[Pt(ppy)(CN)$_2$]$^-$ [a]	10.7	−1.9	1.8	0.9	3.2	7.3	31.1	9.7	1.1	−5.2	−4.1
[Pt(ppy)en]$^+$ [b]	10.1	−2.2	1.9	0.4	1.5	4.0	18.6	4.2	0.8	−4.8	−3.2
[Pt(ppy)edt]$^+$ [c]	9.2	0.4	4.9	2.7	2.5	6.7	18.6	6.4	2.5	−2.3	−1.7
[Pt(ppy)mnt]$^-$ [a]	9.7	−1.1	1.0	0.7	0.2	4.8	27.4	5.4	1.6	−5.9	−2.9
Pt(ppy)(CO)Cl [d]	[f]	−0.6	5.5	2.3	−1.9	[f]	[f]	7.4	2.8	−3.1	−4.0
Pt(ppy)(mor$_3$P)Cl [a]	8.0	−1.9	3.0	−0.1	−2.0	5.6	13.9	9.1	1.3	−4.7	−3.2
[Pt(ppy)edp]$^+$ [b]	10.4	−0.8	4.0	1.7	3.7	8.5	33.0	10.5	1.8	−2.5	−2.3
[Pt(ppy)bpy]$^+$ [e]	9.1	−0.7	4.4	0.3	−0.2	1.5	18.0	4.8	1.0	−3.8	−2.2
[Pt(ppy)phen]$^+$ [e]	9.9	−0.4	3.5	1.3	3.4	0.8	18.9	4.1	0.7	−3.7	−2.4
						C-2′	C-3′	C-4′	C-5′		
[Pt(tpy)Cl$_2$]$^-$ [a]	10.6	−2.3	1.2	−3.2	0.4	−8.1	17.8	4.9	1.9		
[Pt(tpy)(CN)$_2$]$^-$ [b]	10.4	−1.5	3.2	−0.9	3.4	0.7	34.5	8.0	2.9		
[Pt(tpy)en]$^+$ [b]	10.7	−1.8	2.9	−1.7	1.8	−3.1	20.1	4.0	3.4		
[Pt(tpy)edt]$^+$ [c]	8.8	0.6	5.5	0.9	2.9	3.3	24.4	3.7	9.2		
[Pt(tpy)mnt]$^-$ [b]	9.9	−1.3	1.6	−1.5	0.7	−4.3	30.7	4.4	3.7		
Pt(tpy)(CO)Cl [d]	[f]	0.2	11.4	−1.0	−5.6	[f]	[f]	5.0	6.6		
Pt(tpy)(mor$_3$P)Cl [a]	7.9	−1.5	3.5	−2.2	−2.2	−2.6	13.8	7.4	3.0		

[a] In CD_2Cl_2. [b] In CD_3OD. [c] In CD_3CN. [d] In $(CD_3)_2CO$. [e] In $(CD_3)_2SO$. [f] Signal too weak.

those of the dichloro complexes. It is notable that the two cyano groups cause a distinct upfield shift of ca. 0.5 ppm of the H6 atoms while the coupling constants to H6 are significantly smaller than in the dichloro complexes. The corresponding parameters in the phenyl and thienyl parts of the complexes are less altered. Apparently, the substitution of chloride by cyanide causes a larger change in the electronic distribution in the pyridine part of the *N,C*-chelate than in the phenyl and thienyl parts.

Of particular interest are the ^{13}C resonances due to the two cyano groups. These peaks, at 116.9 and 145.4 ppm in the ppy complex and at 115.7 and 145.5 ppm in the tpy complex, both determined in CD_2Cl_2, may be compared with 123.2 ppm for $[Pt(CN)_4]^{2-}$ in acetone-d_6[40] and 166.9 ppm in benzene-d_6 and 158.0 ppm in acetonitrile-d_3 for ionic cyanide.[41] The ^{13}C shifts clearly indicate that the two cyano groups are distinctly different. It is notable that the magnitude of this difference cannot be detected by IR; cf. 2135 and 2120 cm^{-1} in the ppy complex and 2120 and 2115 cm^{-1} in the tpy complex. These frequencies are as observed in [Ptphen(CN)$_2$], 2120 and 2105 cm^{-1}, and in [Pt(4,4′(Me)$_2$bpy)$_2$(CN)$_2$], 2130 and 2110 cm^{-1}.[42] In view of the strong σ-donor character and the strong *trans* effect of the carbon atom of the ppy and tpy ligands as compared with that of the pyridine nitrogen atom, one may conclude that the cyano group *trans* to the

Table 6. ^{195}Pt–^{13}C coupling constants, *J*/Hz, of the ppy and tpy parts of the complexes.

	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
[Pt(ppy)Cl$_2$]$^-$	104	52		40	27	62	1097	54	57		44
[Pt(ppy)(CN)$_2$]$^-$	72	30	4	29	34	23	804	102	56	4	28
[Pt(ppy)en]$^+$		40	7	33	19			61	51	5	38
[Pt(ppy)edt]$^+$		42	8	35	20	22		66	51	6	35
[Pt(ppy)mnt]$^-$		36	9	29	18			65	51	6	34
Pt(ppy)(CO)Cl											
Pt(ppy)(mor$_3$P)Cl		27		20	26		1081	98	73	6	41
[Pt(ppy)edp]$^+$	66	29		20	27	16	913	87	51		30
[Pt(ppy)bpy]$^+$		37	6	30	25			53	53		43
[Pt(ppy)phen]$^+$											
						C-2′	C-3′	C-4′	C-5′		
[Pt(tpy)Cl$_2$]$^-$	77	42	5	38	21		1117	96	66		
[Pt(tpy)(CN)$_2$]$^-$		26		26	31			126	62		
[Pt(tpy)en]$^+$		35	6	31	16			111	62		
[Pt(tpy)edt]$^+$		36	6	31	17	12		105	56		
[Pt(tpy)mnt]$^-$	54	30	7	25	16			102	66		
Pt(tpy)(CO)Cl		30						137	78		
Pt(tpy)(mor$_3$P)Cl		22		17	23			135	86		

carbon atom is the one most similar to ionic cyanide; i.e. the one resonating at 145.4 and 145.5 ppm. In *trans*-$[Pt(CH_3)(CN)(P(CH_3)_2Ph)_2]$, in which the cyano group is *trans* to a methyl group, the cyano carbon atom is also shifted downfield, 138.5 ppm in CD_2Cl_2.[43]

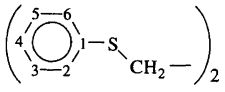
[Pt(ppy)edt]ClO_4 and [Pt(tpy)edt]ClO_4. Although the resonances due to the phenyl groups in the edt ligand interfere considerably with some of the signals arising from the cyclometalated ppy and tpy ligands, the various proton and carbon resonances could be assigned by means of ^{13}C spin-echo and ^{13}C–^1H XHCORR experiments. The assignment of the aromatic signals due to the edt ligand was further aided by the Pt–C coupling constants. The observed shifts for the free and complexed edt ligand in the two salts are listed in Table 7. It is apparent from the data that the lack of symmetry in the two cations gives rise to differences in the shift values of each of the two aromatic groups in the edt ligand.

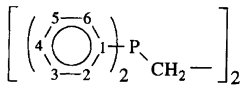
[Pt(ppy)edp]Cl. Similar arguments and experimental procedures were applied when assigning the resonances due to the $(Ph_2P–CH_2–)_2$ part of the $[Pt(ppy)edp]^+$ cation. Additionally, the ^{31}P resonances and the couplings between ^{31}P and ^{195}Pt served as an aid in the interpretation of the spectra. The observed shifts for the free and complexed edp ligand together with coupling constants are also listed in Table 7. As in the edt complexes, the $[Pt(ppy)edp]^+$ cation is unsymmetrical with regard to the edp ligand giving rise to two ^{31}P resonances with distinctly different coupling constants; 3775 and 1853 Hz. According to Crociani *et al.*[44] the one with the largest coupling constant, at 43.4 ppm, is due to the phosphorus atom *trans* to the nitrogen atom.

[Pt(ppy)bpy]Cl and [Pt(ppy)phen]Cl. Owing to the large number of atoms resonating in approximately the same region, the NMR spectra of these two salts were the most difficult to assign. In addition to ^{13}C–^1H XHCORR and ^{13}C spin-echo experiments, ^1H COSY had to be used to determine the sequence of the protons on each ring. Literature data for $[Pt(bpy)en]^{2+}$,[45] $[PtMe_2phen]$ [46] and the uncomplexed ligands served as further aid in the interpretation.

[Pt(ppy)en]Cl and [Pt(tpy)en]Cl. The aromatic resonances were readily assigned as described above. The H and C atoms in the en ligand in the two complexes resonate approximately at the same frequencies: N–H: 5.88 ppm, $J_{Pt-H} = 52$ Hz and 5.05 ppm, $J_{Pt-H} = 29$ Hz, C–H: 2.84 ppm, $J_{Pt-H} = 30$ Hz, ^{13}C: 45.0 ppm (ppy); N–H: 5.94 ppm, $J_{Pt-H} = 51$ Hz, C–H: 2.81 ppm, $J_{Pt-H} = 28$ Hz, ^{13}C: 44.9 ppm (tpy). Free en resonates at 2.68 ppm (^1H) and at 45.1 ppm (^{13}C). In both complexes the N–H reso-

Table 7. Chemical shifts, δ(ppm), of the free and coordinated edt and edp ligands (with coupling constants, *J*/Hz, in parenthesis).





		edt[a]	[Pt(ppy)edt]$^+$[a]	[Pt(tpy)edt]$^+$[a]
CH_2	^1H	3.14	2.95, 3.40	2.95, 3.40
	^{13}C	34.0	39.0(30),[d] 45.6(16)	39.0(32), 47.0(17)
1	^{13}C	136.5	129.3, 129.1	129.3, 128.9
2,6	^1H	7.33	8.06	8.04
	^{13}C	130.2	135.2(17), 135.0(19),	135.0(19), 134.9(56)
3,5	^1H	7.36	7.53	7.55
	^{13}C	130.6	131.1, 130.9(7)	131.2, 131.0(7)
4	^1H	7.25	7.60	7.59
	^{13}C	127.5	132.8, 132.5	132.9, 132.6
		edp[b]	[Pt(ppy)edp]$^+$[c]	
CH_2	^1H	2.10	2.55(m)	
	^{13}C	24.0	29.3(54)((37)),[e] 32.8(45)((44))	
P	^{31}P		43.4[f][3775],[g] 57.9[1853]	
1	^{13}C	138.6((7))	128.5(11)((46)), 127.2(26)((62))	
2,6	^1H	7.32(m)	8.03, 8.03, 8.05, 7.59, 7.97, 7.58, 7.89, 7.57	
	^{13}C	132.8((9))	135.4[h] 135.3 135.2 135.1	
3,5	^1H	7.32(m)	7.60, 7.95, 7.60, 7.90, 7.56, 8.04, 7.56, 7.91	
	^{13}C	128.6((3))	131.2 131.0 130.7 130.4	
4	^1H	7.32(m)	7.63 7.65	
	^{13}C	128.8	133.8 133.9	

[a] In acetonitrile-d_3. [b] In acetone-d_6. [c] In methanol-d_4. [d] J_{Pt-C}. [e] J_{C-P}. [f] Relative to 85% H_3PO_4 in water. [g] $[J_{Pt-P}]$. [h] The ^1H resonances listed above are due to the proton attached to these carbons.

nances are broad due to solvent exchange in CD_3OD. Only one N–H resonance for [Pt(tpy)en]Cl could be observed, presumably owing to the reduced intensity of one of the resonances caused by exchange with the solvent, or due to overlap with the broad OH peak. The assignments are in agreement with what is reported for $[Pt(bpy)en]^{2+}$ (Ref. 45) and $[Pt(en)_2]^{2+}$ (Ref. 47).

(Bu_4N)[Pt(ppy)mnt] and (Bu_4N)[Pt(tpy)mnt]. The aromatic region of the ^{13}C spin-echo spectra showed four non-methine carbon atoms which could not be assigned to the ppy and tpy ligands. These carbon atoms resonate at 119.8, 120.9, 122.9 and 124.0 ppm (ppy) and at 120.0, 121.2, 122.3 and 125.9 ppm (tpy). The free ligand shows only two resonances at 123.3 and 127.2 ppm. IR showed ν_{C-S} at 1158 cm^{-1} (ppy) and (tpy), $\nu_{C=C}$ at 1460 cm^{-1} (ppy) and at 1475 cm^{-1} (tpy) and $\nu_{C=N}$ at 2205 cm^{-1} (ppy) and at 2215 cm^{-1} (tpy). These frequencies are close to those observed by Zuleta *et al.*[48] in [Pt(bpy)mnt]; 1157, 1471 and 2203 cm^{-1}.

Configurational considerations. In the compounds considered so far the two additional ligand atoms are equal, and the *cis–trans* configurational problem will not arise. In the remaining two classes of compounds, however, [<N–C>Pt(CO)Cl] and [<N–C>Pt(mor_3P)Cl], CO and mor_3P may be *trans* to the nitrogen or to the carbon atom in the *N,C*-chelate.

Owing to solubility problems the former compounds are not readily attacked by NMR techniques. The spectra obtained in acetone-d_6 did indicate, however, that the cyclometalated products had been obtained, that the Bu_4N^+ cation was absent and that the complexes were pure. Since Craig and Watts [39] concluded that the carbonyl group in [Pd(ppy)(CO)Cl] is *trans* to the nitrogen atom, one may assume that the corresponding Pt compounds have the same configuration.

The [<N–C>Pt(mor_3P)Cl] complexes are quite soluble in many solvents and were the subject of a detailed NMR study. The very large Pt–P coupling constants, 5636 Hz (ppy) and 5540 Hz (tpy), readily suggest the mor_3P ligand to be *trans* to the nitrogen atom in the <N–C> ligand,[44] a suggestion that most recently was confirmed by a crystallograpic study.[34]

At this stage one may return to the synthesis of *trans-N,P*-[<N–C>Pt(mor_3P)Cl]. These compounds can be prepared from both Bu_4N[<N–C>$PtCl_2$] by displacement of Cl^- and from [<N–C>Pt(CO)Cl] in which CO is presumably *trans* to the nitrogen atom.[39] With excess 2-phenylpyridine and $[Pt(ppy)Cl_2]^-$ one obtains *trans-N,N*-[Pt(ppy)(Hppy)Cl].[26] $(PhSeCH_2\text{-})_2$, acting as a monodentate ligand, links two [<N–C>PtCl] moieties with the selenium atoms *trans* to the nitrogen atoms.[49] In short, the *trans-N* products seem to be the favoured ones, contrary to what is expected from the relative *trans* effect of the nitrogen and carbon donors. These observations seem to indicate that the *trans* effect in a *N,C*-chelate ring may not follow the usual rules or, alternatively, the rate of conversion from the expected *trans-C* compound to the *trans-N* compound is high in complexes in which the metal atom is part of a *N,C*-chelate ring. Recent studies by Tobe *et al.*[50] indicate that the *cis* labilizing effect of particularly the cyanide ligand has to be taken into account when rates of substitution reactions of *cis* and *trans* $[Pt(NR_3)_2(CN)_2]$ are considered.

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References

1. Adamson, A. W. and Fleischauer, P. D., Eds., *Concepts of Inorganic Photochemistry,* Wiley, New York 1975.
2. Ferraudi, G. J. *Elements of Inorganic Photochemistry,* Wiley, New York 1988.
3. Sandrini, D., Maestri, M., Ciano, M., Maeder, U. and von Zelewsky, A. *Helv. Chim. Acta 73* (1990) 1306.
4. Craig, C. A., Garces, F. O., Watts, R. J., Palmans, R. and Frank, A. J. *Coord. Chem. Rev. 97* (1990) 193.
5. Maestri, M., Balzani, V., Deuschel-Cornioley, C. and von Zelewsky, A. In: Vohnan, D., Hammond,G. S. and Neckers, D. C., Eds., *Advances of Photochemistry,* Wiley-Interscience, New York 1991, No. 17.
6. Maestri, M., Sandrini, D., Balzani, V., Chassot, L., Jolliet, P. and von Zelewsky, A. *Chem. Phys. Lett. 122* (1985) 375.
7. Maestri, M., Deuschel-Cornioley, C. and von Zelewsky, A. *Coord. Chem. Rev. 111* (1991) 117.
8. Ivanova, M. E. and Shagisultanova, G. A. *Zh. Fiz. Khim. (Russia) 68* (1991) 1516.
9. Juris, A., Balzani, V., Barigelletti, F., Campagna, S., Belser, P. and von Zelewsky, A. *Coord. Chem. Rev. 84* (1988) 85.
10. Miskowski, V. M., Houlding, V. H., Che, C.-M. and Wang, Y. *Inorg. Chem. 32* (1993) 2518.
11. Zuleta, J. A., Bevilacqua, J. M., Proserpio, D. M., Harvey, P. D. and Eisenberg, R. *Inorg. Chem. 31* (1992) 2396.
12. King, K. A., Spellane, P. J. and Watts, R. J. *J. Am. Chem. Soc. 107* (1985) 1431.
13. Gratsch, P. A. and Kutal, C. *J. Am. Chem. Soc. 108* (1986) 3105.
14. Ryabov, A. D. *Chem. Rev. 90* (1990) 403.
15. Chassot, L., Müller, E. and von Zelewsky, A. *Inorg. Chem. 23* (1984) 4249.
16. Chan, C.-W., Lai, T.-F., Che, C.-M. and Peng, S.-M. *J. Am. Chem. Soc. 115* (1993) 11245.
17. Kasahara, A. *Bull. Chem. Soc. Jpn. 41* (1968) 1272.
18. Cope, A. C. and Friedrich, E. C. *J. Am. Chem. Soc. 90* (1968) 909.
19. Giordano, T. J. and Rasmussen, P. G. *Inorg. Chem. 14* (1975) 1628.
20. Chassot, L. and von Zelewsky, A. *Inorg. Chem. 26* (1987) 2814.
21. Garces, F. O. and Watts, R. J. *Magn. Res. Chem. 31* (1993) 529.
22. Davison, A. and Holm, R. H. In: Muetterties, E. L., Ed., *Inorganic Synthesis,* McGraw-Hill, New York 1967, Vol. 10, pp. 8-26.
23. Bell, E. V. and Bennett, G. M. *J. Chem. Soc.* (1928) 3189.
24. Rømming, C. and Songstad, J. *Acta Chem. Scand., Ser. A32* (1978) 689.
25. Derome, A. E. *Modern NMR Techniques for Chemistry Research,* Pergamon Press 1987.

26. Kvam, P.-I., Engebretsen, T., Maartmann-Moe, K. and Songstad, J. *To be published.*
27. Knop, J. V., Trinajstic, N., Milun, M. and Pejakovic, S. *Rev. Roum. Chim. 23* (1978) 103.
28. Fromholtz, K. M., Kvam, P.-I., Sætre, L. and Songstad, J. *To be published.*
29. Angelici, R. J. *Coord. Chem. Rev. 105* (1990) 61.
30. Amari, C., Ianelli, S., Pelizzi, C., Pelizzi, G. and Predieri, G. *Inorg. Chim. Acta 211* (1993) 89.
31. Constable, E. C., Henney, R. P. G., Raithby, P. R. and Sousa, L. R. *Angew. Chem., Int. Ed. Engl. 30* (1991) 1363.
32. Bouwhuis, E. and Janssen, M. J. *Tetrahedron Lett. 3* (1972) 233.
33. Sergejev, G. B., Polyakov, V. A., Smirnow, V. V. and Rostovschekova, T. N. *Zh. Fiz. Khim. 53* (1979) 1946.
34. Kvam, P.-I., Maartmann-Moe, K. and Songstad, J. *To be published.*
35. Cheng, J., Xenopoulos, A. and Wunderlich, B. *Magn. Reson. Chem. 30* (1992) 917.
36. Orellana, G., Ibarra, C. A. and Santoro, J. *Inorg. Chem. 27* (1988) 1025.
37. Lavallee, D. K., Baughman, M. D. and Phillips, M. P. *J. Am. Chem. Soc. 99* (1977) 718.
38. Sprouse, S., King, K. A., Spellane, P. J. and Watts, R. J. *J. Am. Chem. Soc. 106* (1984) 6647.
39. Craig, C. A. and Watts, R. J. *Inorg. Chem. 28* (1989) 309.
40. Brown, C., Heaton, B. T. and Sabounchei, J. *J. Organomet. Chem. 142* (1977) 413.
41. Andersen, R., Kvam, P.-I., and Songstad, J. *To be published.*
42. Che, C.-M., He, L.-Y., Poon, C.-K. and Mak, T. C. W. *Inorg. Chem. 28* (1989) 3081.
43. Appleton, T. G., Chisholm, M. H., Clark, H. C. and Manzer, L. E. *Inorg. Chem. 11* (1972) 1786.
44. Crociani, B., Bianca, F. D. and Giovenco, A. *J. Organomet. Chem. 361* (1989) 255.
45. Erickson, L. E., Sarneski, J. E. and Reilley, C. N. *Inorg. Chem. 14* (1975) 3007.
46. Kuyper, J. *Inorg. Chem. 16* (1977) 2171.
47. Pesek, J. J. and Mason, W. R. *J. Magn. Reson. 25* (1977) 519.
48. Zuleta, J. A., Burberry, M. S. and Eisenberg, R. *Coord. Chem. Rev. 97* (1990) 47.
49. Kvam, P.-I., Maartmann-Moe, K. and Songstad, J. *Unpublished data.*
50. Cattalini, L., Guidi, F. and Tobe, M. L. *J. Chem. Soc., Dalton Trans.* (1993) 233.

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