Neutral and Cationic Methyl Complexes of Platinum(II) with 6-Substituted 2,2′-Bipyridines: Synthesis, Characterisation and Reactivity with Carbon Monoxide − Molecular Structures of [PtCl(methyl)(6-ethyl-2,2′-bipyridine)] and of [Pt(methyl)(acetonitrile)(6-ethyl-2,2′-bipyridine)][BF_4]

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The complex *trans*-[PtCl(Me)(SMe_2)$_2$] reacts with 6-R-substituted 2,2′-bipyridine, HL^n (n = 1, R = H; n = 2, R = Me; n = 3, R = Et; n = 4, R = *i*Pr; n = 5, R = CH_2Ph; n = 7, R = Ph), to afford the neutral complexes [PtCl(Me)(HL^n)]. Only one isomer is formed (R *cis* to Cl) with all the ligands, but one (R = Ph). When R = $C(Me)_2Ph$ (HL^6), only an (N–N–C) cyclometallated species is formed. The stereoselectivity observed is interpreted in terms of the nature of the substituent R, and of the hydrogen bond formed between H–C(α) of the R substituent and the chloride ion bound to the platinum center. The molecular structure of [PtCl(Me)(HL^3)] has been resolved by an X-ray analysis and shows that the above-mentioned hydrogen bond length is 2.28 Å. The reactivity of three representative complexes (R = H, Et, CH_2Ph) with carbon monoxide has been studied. The reaction affords the ionic species [Pt(Me)(CO)(HL^n)]$^+$[$PtCl_2$(Me)(CO)]$^-$ and the free ligand. There is evidence of the formation of an acyl species, which does not contain the bipyridine ligand, only when working at high pressures of CO. The above cations are also obtained by direct carbonylation of the solvent species, [Pt(Me)(MeCN)(HL^n)][BF_4], achieve by halide abstraction from the neutral complexes. The molecular structure of [Pt(Me)(MeCN)(HL^3)][BF_4] has been resolved by an X-ray analysis.

Introduction

Palladium complexes [PdX(R)(N−N)], where X is a halide, R an alkyl or aryl group and (N−N) a bidentate nitrogen ligand, have been widely studied because of their potential in organic syntheses.[1] Many studies have focused their attention on the reaction of these Pd complexes with carbon monoxide. This is of fundamental interest in industrial processes, e.g., hydroformylation and copolymerisation of olefins and carbon monoxide.[2] As a result, there is a lot of experimental and theoretical data available on the insertion of carbon monoxide, as well as of alkenes, into the palladium−carbon σ bonds.[3] The analogous platinum complexes [PtX(R)(N−N)] also have been the subject of many studies concerning intra- and intermolecular C−H activation,[4] oxidative addition reactions[5] and addition of neutral ligands to give coordinatively saturated 18-electron species.[6] Great efforts have been devoted to the electronic and steric requirements which could stabilise pentacoordinated derivatives: in this context, in the case of bipyridine or phenanthroline derivatives, reactions with olefins have been widely investigated.[7] Surprisingly, reactions with CO, as well as the related migratory−insertion reactions into metal−carbon σ bonds, have been less investigated in spite of the extensively developed chemistry of alkylplatinum(II) and -platinum(IV) compounds[8] with nitrogen donors and being interesting as models for the catalytic species in the palladium systems.

Herein we report the synthesis and the spectroscopic characterisation of a series of alkylplatinum(II) derivatives of the type: [PtX(Me)(HL^n)] (X = Cl or I, HL^n = unsymmetric 2,2′-bipyridine 6-alkyl-, benzyl- or aryl-substituted), as well as their reactivity with carbon monoxide. Furthermore, some X-ray structural determinations are given.

Results and Discussion

Synthesis of the Adduct Species

The ligands HL^n and the platinum complexes are depicted in Scheme 1; the index n indicates the ligand.

The complex **1a** (HL^1 = 2,2′-bipyridine) is well known, it can be prepared in an almost quantitative yield by reaction of [PtCl(Me)(COD)] (COD = 1,5-cyclooctadiene) with HL^1 in CH_2Cl_2.[9] The 6-substituted-2,2′-bipyridines HL^{2-7} show a different reactivity, in spite of several attempts under a variety of experimental conditions, we were unable to achieve displacement of COD. Nevertheless, the adducts of all the ligands but one (HL^6, see later), can easily be obtained by reaction of *trans*-[PtCl(Me)(SMe_2)$_2$], an intermediate used in the synthesis of other species with (N−N) ligands.[5b,7b] The adducts can be isolated in good yields, they

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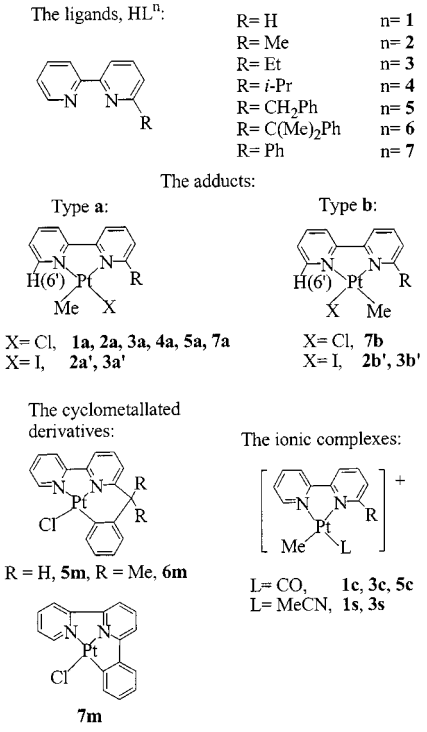


Scheme 1

are stable in the solid state and in all cases but one (**5a**) also in solutions of chlorinated solvents at room temperature. They are not electrolytes in acetone. Owing to the ligand asymmetry, two stereoisomers are possible (Scheme 1).

In the case of the alkyl- or benzyl-substituted ligands HL^{2-5} only one isomer is formed. ^1H NMR spectroscopic data are consistent with isomer **a**; in particular the assessment relies on the chemical shift of H(6′) proton and its coupling constant to ^{195}Pt. The resonance is known to be influenced by the neighbouring ligands,[10] halides having a stronger deshielding effect than a methyl ligand. The values observed for **2a**−**5a** and **7a** (see Table 1) indicate that the methyl group is in close proximity to H(6′). This is supported by NOE difference experiments on **2a** and **3a** ($CDCl_3$ solution), irradiation of the H(6′) resonance gives enhancement of the signal of the methyl group bound to the platinum center, and vice versa. The extent of the coupling between H(6′) and ^{195}Pt is related to the nature of the ligand *trans* to the nitrogen atom N(1) of the unsubstituted pyridine ring. The relatively high values of $^3J_{Pt-H}$ indicate that the ligand has a low *trans* influence, like a chloride ligand.[11] It is worth noting that in **1a**, one H(6) is close to the chloride ion and the other to the methyl group. Indeed, one of the resonances is strongly deshielded (δ = 9.65) with $^3J_{Pt-H} \approx 17$ Hz, whereas the other one (δ = 9.23) has a larger $^3J_{Pt-H}$ value (60.3 Hz). The latter values are very similar to those found for **2a**−**5a** and **7a**.

As stated above, two stereoisomers **7a** and **7b** (ca. 1:1) are formed, only in the case of the ligand HL[7]. Evidence for the formation of two isomers is given by ^1H NMR spectra. There are two methyl signals at δ = 1.26 ($^2J_{Pt-H}$ = 82.3 Hz) and δ = 0.32 ($^2J_{Pt-H}$ = 77.2 Hz) and two H(6′) resonances. The upfield methyl signal can be assigned to **7b**, taking into account the anisotropic shielding effect of the phenyl substituent. The H(6′) resonance in **7b** (δ = 9.58) is, as expected, more deshielded than in **7a** (δ = 9.10); the extent of the $^{195}Pt-^1H$ coupling reflects the difference in the *trans* influence between the chloride ($^3J_{Pt-H(6')}$ = 60.0 Hz, **7a**) and the methyl group (coupling not observable, **7b**). One of the isomers, **7b**, can be isolated in a pure form from the mixture by column chromatography, the other one is converted during elution through the column to the cyclometallated species **7m** (see later). The structure of **3a** has been resolved by an X-ray analysis.

Molecular Structure of [PtCl(Me)(HL^3)] (3a)

The structure consists of the packing of discrete [PtCl(Me)(HL^3)] molecules. An ORTEP[12] view of the molecule is shown in Figure 1. Selected bond lengths and angles are reported in Table 2.

Table 1. ^1H NMR spectroscopic data of the adduct and the cyclometallated species, room temperature, solvent $CDCl_3$ unless otherwise stated, coupling constants in Hz, J_{Pt-H} in brackets, J_{H-H} in parentheses, chemical shift in ppm from internal TMS.

	Pt−Me	Me	CH_2 or CH	H(6′)	Other Aromatics
1a	1.23 s [76.9]			9.23 d (5.6) [60.3] H(6′) 9.65 d (5.9) [ca. 17] H(6)	7.5−8.2 {6 H}
2a	1.37 s [80.8]	3.17 s		9.09 d (5.4) [61.5]	7.4−8.1 {6 H}
3a	1.37 s [81.3]	1.41 t (7.6)	3.73 q (7.6)[a]	9.06 d (6.1) [62.8]	7.4−8.1 {6 H}
4a	1.39 s [82.3]	1.36 d (6.9)	5.02 m (6.9)[b]	9.07 dd (5.4) [61.8]	7.4−8.2 {6 H}
5a	1.42 s [80.8]		5.17 s[a]	9.10 dd (5.1) [61.8]	7.2−8.2 {11 H}
7a	1.26 s [82.3]			9.10 d (6.3) [60.0]	7.4−8.2 {11 H}
7b	0.32 s [77.2]			9.58 d (6.0)	7.4−8.2 {11 H}
2a′	1.44 s [78.1]	3.28 s		8.92 d (5.7) [59.3]	7.4−8.4 {6 H}
2b′	1.48 s [78.6]	2.87 s [ca. 6]		9.90 dd (5.4) [ca. 23]	7.4−8.4 {6 H}
3a′	1.45 s [77.2]	1.37 t (7.6)	3.80 q (7.6)[a]	8.90 d (5.4) [58.8]	7.4−8.2 {6 H}
3b′	1.45 s [77.0]	1.35 t (7.6)	3.30 q (7.6)[a]	9.87 dd (5.1) [ca. 20]	7.4−8.2 {6 H}
5m			4.29 s[a]	9.55 d (5.4)	7.0−8.1 {10 H}
6m[c]		2.13 s		9.60 dd (7.1)	6.9−8.2 {10 H}
7m				9.01 dd (6.1) [ca. 18]	7.0−8.1 {10 H}

[a] CH_2. − [b] CH. − [c] Solvent CD_2Cl_2.

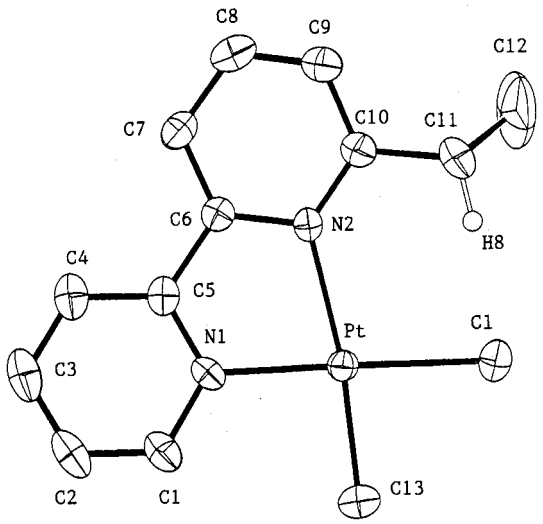


Figure 1. ORTEP view of compound **3a**; ellipsoids are drawn at the 30% probability level

Table 2. Selected bond lengths [Å] and angles [°] with e.s.d.s in parentheses for compound **3a**

Pt−Cl	2.299(2)	Pt−N1	2.022(4)
Pt−N2	2.188(4)	Pt−C13	2.043(6)
Cl···H8	2.28		
Cl−Pt−N1	176.1(1)	Cl−Pt−N2	103.1(1)
Cl−Pt−C13	83.8(2)	N1−Pt−N2	78.7(2)
N1−Pt−C13	94.4(2)	N2−Pt−C13	173.0(2)
C11−H8···Cl	160.4		

The platinum atom displays a square-planar coordination with a slight square-pyramidal distortion; maximum deviations from the best plane are +0.033(1) and −0.034(4) Å for Pt and N1, respectively. The Pt−Cl and Pt−N1 bond lengths, 2.299(2) and 2.022(4) Å, respectively, are normal and in good agreement with the corresponding values, 2.289(2) and 2.030(6) Å found in $[PtCl_2(HL)]$[13] [HL = diphenyl(2-pyridylmethyl)phosphane oxide]. The Pt−N2 distance, 2.188(4) Å, is rather long even after taking into account the *trans* influence of the Me ligand; compare Pt−N1 = 2.117(7) Å in [PtCl(L)][14] (HL = 6-*tert*-butyl-2,2′-bipyridine), where the pyridine N atom is *trans* to an alkyl group. The Pt−C13 bond length, 2.043(6) Å, is in good agreement with the corresponding value, 2.037(3) Å, found in $[Pt\{HOB(C_6F_5)_3\}(Me)(HL)]$[8b] (HL = 4,4′-di-*tert*-butyl-2,2′-bipyridine). The Cl−Pt−N2 angle, 103.1(1)°, is very large and is probably a result of the steric hindrance of the ethyl substituent on the bipyridine ligand. However, it must be observed that there is a clear intramolecular hydrogen bond between H8, bonded to C11, and the Cl atom (see Figure 1, Cl···H8 = 2.28 Å, C11−H8···Cl angle = 160.4°). The two pyridine rings are strictly planar and are twisted 9.8(2)° with respect to each other. A rather short distance (2.78 Å) between the chlorine atom of one molecule and the hydrogen atom H2, bonded to C2, of a neighbouring molecule, suggests the possibility of a weak intermolecular hydrogen bond.

The isolation of only one isomer (type **a**) for the adducts of the ligands HL^{1-5} deserves comments. Several factors can play a role in making isomer **a** the preferred one: *i*) in **a**, the Me group, more bulky than Cl, is far away from the R substituent; *ii*) owing to the higher *trans* influence of the methyl group with respect to the chloride ion, a methyl group *trans* to N2 can lengthen the Pt−N2 bond, thus relieving the steric effects of the R substituent; *iii*) the **a**-type isomer can be more stable due to the hydrogen bond between the chloride ion and the hydrogen atom on C(α) of the R substituent. The hydrogen bond could be responsible, at least in part, also for the deshielding of the α-hydrogen signals observed in the solution ^1H NMR: $[\delta_{complex} - \delta_{ligand}]$ = 0.54 (**2a**, 3 α-H), 0.82 (**3a**, 2 α-H), 1.92 (**4a**, 1 α-H), 0.92 (**5a**, 2 α-H).

The ligand HL^7 (R = Ph) lacks α-hydrogen atoms on the substituent, thus preventing the formation of a hydrogen bond with the chloride ion. Furthermore, the phenyl ring is sterically less demanding, owing to the ability of setting itself perpendicular to the coordination plane. Indeed, in this case both isomers **a** and **b** are formed in about a 1:1 ratio.

In order to obtain an insight into the role of the α-hydrogen atoms in driving the reaction selectively towards isomer **a**, several attempts were carried out to obtain the adduct of the *tert*-butyl-substituted ligand. No adduct was isolated and no evidence was provided by ^1H NMR spectra for its existence in solution. Actually, the reaction affords an unusual C(3)-metallated (C−N) species, $[PtCl(SMe_2)(L)]$ (HL = 6-*tert*-butyl-2,2′-bipyridine), with the loss of methane. The X-ray structure of this complex has recently been reported.[15]

Replacement of the chloride by an iodide ion has been carried out on **2a** and **3a** by reaction with LiI. Alternatively, these products can be obtained by reaction of the ligands HL^2 and HL^3 with *trans*-$[PtI(Me)(SMe_2)_2]$. The two procedures give the same products, the latter one in lower yield. Both isomers are obtained, **2a′**, **2b′** and **3a′**, **3b′**, the **a**-type isomers being the major products (77% for **2a′** and 79% for **3a′**). Therefore, it seems that both *α*-hydrogen atoms and a chloride ligand are required to make isomer **a** the more favoured isomer.

Cyclometallated Species

The synthesis of the adduct species is straightforward with all the ligands but HL^6 (R = $C(Me)_2Ph$). It behaves like an (N−N−C) tridentate ligand, affording only the cyclometallated species **6m** which arises from aromatic C−H activation and elimination of methane. Similar cyclometallated species are also obtained with HL^5 and HL^7 (Scheme 1). The adduct **5a** is not stable in chlorinated solvents, and slowly converts at room temperature to the cyclometallated species **5m**; **7m** is formed during the chromatographic separation of the mixture of isomers **7a** and **7b**.

Reaction with Carbon Monoxide

The reaction of the neutral adducts **1a**, **3a** and **5a** with carbon monoxide (p_{CO} = 1 atm) did not afford the corres-

ponding acyl derivatives, either at room temperature, or in refluxing chloroform. Only when working under high pressures of CO (ca. 100 atm) there is some evidence for slow formation of an acyl species (see later). Under mild conditions, the reaction proceeds to give the ionic species in accordance with Equation (1) of Scheme 2.

$$2\,[PtCl(Me)(HL^n)] + 2\,CO \longrightarrow [Pt(Me)(CO)(HL^n)][PtCl_2(Me)(CO)] + HL^n \quad (1)$$

$$[Pt(Me)(CO)(HL^n)][PtCl_2(Me)(CO)] + Na[BAr'_4] \longrightarrow [Pt(Me)(CO)(HL^n)][BAr'_4] + Na[PtCl_2(Me)(CO)]\downarrow \quad (2)$$

$$[\{PtCl(Me)(CO)\}_2(N\text{–}N)] \rightleftharpoons [Pt(Me)(CO)(N\text{–}N)][PtCl_2(Me)(CO)] \quad (3)$$

$$[PtCl(Me)(HL^n)] + AgBF_4 + MeCN \longrightarrow [Pt(Me)(MeCN)(HL^n)][BF_4] + AgCl$$
$$[Pt(Me)(MeCN)(HL^n)][BF_4] + CO \longrightarrow [Pt(Me)(CO)(HL^n)][BF_4] \quad (4)$$

$$\mathbf{3a} \xrightarrow{CO,\ 1\ atm} [Pt(Me)(CO)(HL^3)]\,[PtCl_2(Me)(CO)] \xrightarrow{CO,\ 100\ atm} [Pt(Me)(CO)(HL^3)]\,[PtCl_2(COMe)(CO)] \quad (5)$$

Scheme 2

The free ligand was recovered almost quantitatively from the reaction mixture. The ionic nature of the products was confirmed, by conductivity measurements in dichloromethane and acetone, and by FAB mass spectroscopy (positive and negative ions). The IR spectra show two strong absorptions at ca. 2100 and 2060 cm^{-1} due to the stretching vibrations of the terminal carbonyl groups (Table 3). The lower frequency can be assigned to the CO ligand of the anionic complex. The ^1H NMR spectra (Table 3) show two methyl signals; the more shielded one at $\delta = 0.87$ [$(CD_3)_2CO$ solution] is assigned to the anion and is unaffected by the type of the cation (**1c**, **3c**, **5c**), further supporting the hypothesis of two independent ions, one of which does not contain the (N−N) ligand. Indeed, the cations **1c**, **3c** and **5c** could be isolated as $[BAr'_4]^-$ salts {$[BAr'_4]^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate} by exchange with Na[BAr'_4] [Equation (2), Scheme 2] in CH_2Cl_2 solution. The sodium salt of the anion could not be isolated owing to rapid decomposition.

It is worth noting that [**1c**] $[PtCl_2(Me)(CO)]$ is obtained in two forms that differ in colour, one is yellow and the other one red. Analytical and spectroscopic (^1H NMR, IR and MS) data support their identical composition, while UV spectra ($CHCl_3$ solution) show that the colour difference is due to an absorption at 410 nm (λ_{max}, $\varepsilon \approx 1500$ M^{-1} cm^{-1}) present in the red form. The absorption is concentration-dependent and disappears upon dilution, thus supporting stacking interactions between the anion and the cation and leading to charge-transfer phenomena.[16] Unfortunately, in spite of several attempts, we were unable to grow crystals suitable for X-ray determinations.

Tetraalkylammonium salts of $[PtCl_2(Me)(CO)]^-$ have previously been described[17] as having a *cis* configuration for the anion and our experimental data confirm this arrangement. In particular, the IR spectra show two Pt−Cl stretching frequencies at ca. 320 and 260 cm^{-1}.

A behaviour somewhat reminiscent of that observed in our complexes is described in the literature.[18] In the case of a complex with a 6-R-pyridine-2-carbaldehyde imine, carbonylation of pentacoordinated [PtCl(Me)(ethylene)-(N−N)] (N−N = 6-Me-py-2-CH=NPh) gave a mixture of products, in which free (N−N) and square-planar mono- and dinuclear complexes were detected. The main species is described as a dinuclear complex having a bridging (N−N) ligand; it is not an electrolyte in chloroform, but does dissociate in nitromethane according to the equilibrium shown in Equation (3), Scheme 2.

Cationic Species

The cationic complexes $[Pt(Me)(CO)(HL^n)]^+$ can also be obtained by halide abstraction from the neutral complexes with $AgBF_4$ and subsequent carbonylation of the solvent species [Equation (4), Scheme 2].

The ^1H NMR spectra of the cations obtained in this way are "exactly" superimposable on the spectra of the products obtained by direct carbonylation of the neutral complexes (Table 3), except for the methyl resonance of the anion $[PtCl_2(Me)(CO)]^-$. Although two isomers are possible for **3c** and **5c**, the carbonylation reaction is stereospecific affording only the **a**-type isomer, as confirmed by NOE difference experiment on **3c**[BF_4] (CD_3CN solution). Irradiation of H(6′) at $\delta = 8.90$ gives enhancement of the signal at $\delta = 1.40$ (Me) and vice versa. The linear structure of CO, which does not cause steric hindrance, most likely favours isomer **a**. The solvent species are obtained in good yields and can be isolated and characterised in the solid state. The structure of **3s**[BF_4] has been resolved by an X-ray analysis.

Molecular Structure of [Pt(Me)(MeCN)(HL^3)][BF_4] (**3s**[BF_4])

The structure consists of the packing of $[Pt(Me)(MeCN)(HL^3)]^+$ cations and $[BF_4]^-$ anions in the molar ratio 1:1. An ORTEP view of the molecule is shown in Figure 2. Selected bond lengths and angles are reported in Table 4.

The platinum atom displays a square-planar coordination with a slight square-pyramidal distortion; maximum deviations from the best plane are +0.011(1) and −0.005(4) Å for atoms Pt and C13, respectively. The Pt−N1, Pt−N2 and Pt−C13 bond lengths, 2.013(2), 2.173(3) and 2.036(4) Å, respectively, are very similar to the corresponding values, discussed above, observed in **3a**, 2.022(4), 2.188(4) and 2.043(6) Å. The Pt−N3 distance, 1.971(3) Å, can be com-

Table 3. ^{1}H NMR and selected IR data [cm^{-1}] of the ionic species

Cation	Anion	Solvent	MeCN	^{1}H NMR[a] Pt−Me	Me	CH_2	H(6′)	Other aromatics	IR (CO)
1c	$[BF_4]$	$(CD_3)_2CO$		1.35 s [68.1]			9.15 d (5.8) [40] 9.25 d (5.1) [20]	8.0−8.9	2119 vs[b]
1c	$[BAr'_4]$	$CDCl_3$		1.27 s [67.1]			8.68 dd (5.4) [20] 8.78 dd (5.7) [42]	7.5−8.0	2100 vs[b]
		$(CD_3)_2CO$		1.35 s [68.1]			9.10−9.30 b {2 H}	7.7−9.0	
1c	$[PtCl_2(Me)(CO)]$	$(CD_3)_2CO$		0.87 s [78.4] 1.35 s [68.1]			9.20 b {2 H}	8.0−8.9	2104 vs, 2060 vs[c] 2093 vs, 2045 vs[b]
1s	$[BF_4]$	CD_3CN	2.61 s [14.7]	0.99 s [76.4]			8.88 dd (5.1) [15] 8.92 d (6.6) [60]	7.6−8.4	
3c	$[BF_4]$	$(CD_3)_2CO$		1.48 s [68.9]	1.54 t (7.6)	3.33 q (7.6)	9.17 dd (5.6) [43]	8.0−8.9	2100 vs[c] 2109 vs[b]]
3c	$[BAr'_4]$	$(CD_3)_2CO$		1.48 s [68.9]	1.54 t (7.5)	3.34 q (7.5)	9.18 d (5.6) [43]	7.6−8.9	2100 vs[b]
3c	$[PtCl_2(Me)(CO)]$	$(CD_3)_2CO$		0.87 s [78.6] 1.48 s [68.9]	1.54 t (7.5)	3.34 q (7.5)	9.17 d (5.4) [42]	8.0−8.9	2099 vs, 2059 vs[c] 2084 vs, 2043 vs[b]
3s	$[BF_4]$	CD_3CN	2.58 s [15.6]	1.15 s [77.9]	1.41 t (7.6)	3.13 q (7.6)	8.90 dd (5.4) [63]	7.6−8.3	
5c	$[PtCl_2(Me)(CO)]$	$(CD_3)_2CO$		0.87 s [78.6] 1.45 s [68.9]		4.80 s	9.18 dd (5.6) [42]	7.3−8.9	2100 vs, 2060 vs[c] 2081 vs, 2055 vs[b]

[a] Room temperature, coupling constants in Hz, J_{Pt-H} in square brackets, J_{H-H} in round brackets, chemical shift in ppm from internal TMS. − [b] Nujol mull. − [c] CH_2Cl_2 solution.

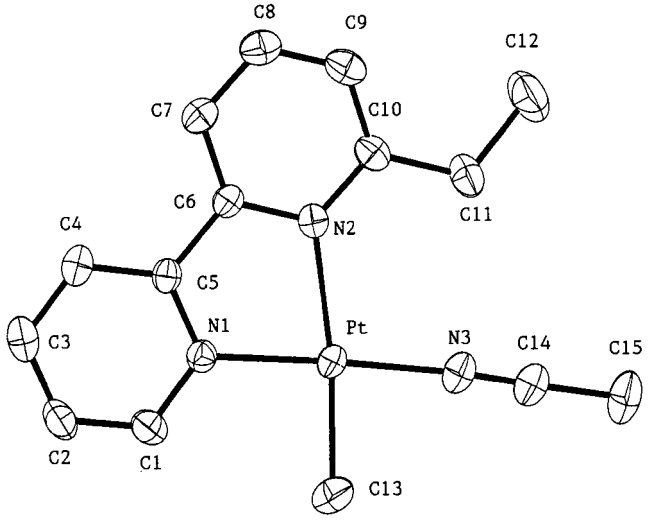


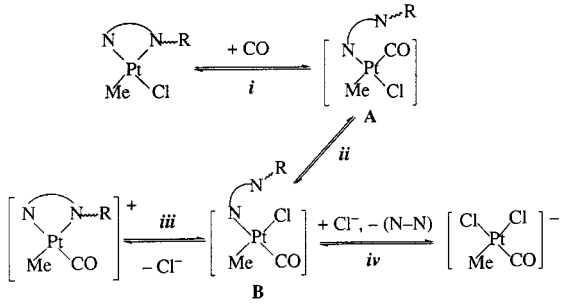
Figure 2. ORTEP view of the cation in compound **3s**$[BF_4]$; ellipsoids as in Figure 1

Table 4. Selected bond lengths [Å] and angles [°] with e.s.d.s in parentheses for compound **3s**$[BF_4]$

Pt−N1	2.013(2)	Pt−N2	2.173(3)
Pt−N3	1.971(3)	Pt−C13	2.036(4)
N3−C14	1.128(5)	C14−C15	1.456(6)
N1−Pt−N2	79.0(1)	N1−Pt−N3	177.2(1)
N1−Pt−C13	93.7(1)	N2−Pt−N3	103.7(1)
N2−Pt−C13	172.6(1)	N3−Pt−C13	83.7(2)
Pt−N3−C14	175.5(4)	N3−C14−C15	178.0(4)

pared with the Pt−NCMe bond length, 1.955(4) Å, found in the cation $[Pt(Me)(MeCN)(Ar_2DAB)]^+$ [19] (Ar_2DAB = diaryldiazabutadiene). It is interesting also to observe that the N2−Pt−N3 angle, 103.7(1)°, is very similar to the N2−Pt−Cl angle, 103.1(1)°, found in **3a**, thus confirming the hypothesis that it is a result of the bulkiness of the ethyl substituent on the bipyridine ligand. The existence of intramolecular hydrogen bonds in this cation is more dubious, because the two hydrogen atoms bonded to C11 are 2.51 and 2.72 Å apart from atom N3, whereas one of the hydrogen atoms bonded to C13 lies 2.35 Å from N3. The two pyridine rings are strictly planar and are twisted 3.9(1.2)° with respect to each other. Four rather short interionic F···H interactions in the range 2.41−2.48 Å suggest the possibility of weak interionic hydrogen bonds.

A plausible reaction pathway that accounts for Equation (1) is shown in Scheme 3. The reaction implies (*i*) Addition of CO with displacement of a coordinated nitrogen and (*ii*) isomerisation of **A** to species **B**, having the chloride *trans* to the methyl group. Isomer **B** can re-establish the pentacycle with the bipyridine (*iii*) loosing a chloride ion or (*iv*) detach completely the bipyridine in the presence of chloride produced in step *iii*. Partial evidence for the formation of the



Scheme 3

cation **nc** and the anion $[PtCl_2(Me)(CO)]^-$ through **B** is provided by the reaction of **3c**$[BF_4]$ with LiCl in acetone, monitored by NMR spectroscopy. With excess LiCl, the ^1H NMR spectrum shows the total conversion of **3c** into $[PtCl_2(Me)(CO)]^-$ and free ligand, in an equimolecular ratio. If the reaction is carried out in the absence of excess LiCl, only the stoichiometric amount of **3c** reacts and there is no evidence of the presence of the species **B**, which seems to be very labile.

High-Pressure Carbonylation

As stated previously, we observe formation of an acyl species only when working under high pressures of CO. The acylation is indeed very slow, for example, in the case of complex **3a**, partial conversion (ca. 80%) of the ionic intermediate to an acyl species is obtained after 20 d [$p_{CO} \approx 100$ atm, Equation (5), Scheme 2].

The ^1H NMR spectra ($CDCl_3$ solution) clearly indicate that only the anion is involved in the acylation. In fact, the signals due to the cation species are not changed, while the intensity of the methyl signal (of the anion) is reduced and a new signal with satellites ($^3J_{Pt-H} = 10.3$ Hz) appears at $\delta = 2.49$; the intensities of the latter two resonances integrate to 3 protons. The IR spectra, in addition to strong bands in the region of terminal carbonyl groups, show a strong absorption at 1650 cm^{-1} and a new Pt−Cl stretch at 347 cm^{-1}.

Experimental Section

General: The unsymmetric 6-R-2,2′-bipyridine HL^{3-7} ligands were obtained through not trivial syntheses according to a procedure previously described,[20] the ligand HL^2 according to Kauffmann et al.[21] The compounds *trans*-$[PtCl(Me)(SMe_2)_2]$,[22] *trans*-$[PtI(Me)(SMe_2)_2]$[22] and $Na[BAr'_4]$[23] {sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate} were prepared as reported elsewhere. All solvents were freshly distilled prior to use. Reactions with CO under pressure were performed with a Pyrex bottle in a stainless steel autoclave. − Elemental analyses were performed with a Perkin−Elmer Elemental Analyzer 240B by Mr A. Canu (Dipartimento di Chimica, Università di Sassari). − Conductivities were measured with a Philips PW 9505 conductimeter. − Infrared spectra (Nujol mull or CH_2Cl_2 solution) were recorded in the range 4000−180 cm^{-1} with a Perkin−Elmer 983 spectrophotometer. − UV spectra ($CHCl_3$ solution) were determined with a Hitachi 2010 spectrophotometer. − ^1H NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 299.9 MHz and the selected data are collected in Table 1 and Table 3; the chemical shifts are given in ppm relative to internal TMS and were determined by reference to the residual ^1H solvent peaks. − Mass spectra were obtained with a VG 7070EQ instrument operating under FAB conditions with 3-nitrobenzyl alcohol as a supporting matrix.

[PtCl(Me)(HL^1)] (1a): A solution of the ligand (46.4 mg, 0.297 mmol) in CH_2Cl_2 (10 mL) was added to a solution of *trans*-$[PtClMe(SMe_2)_2]$ (100.0 mg, 0.270 mmol), in the same solvent (20 mL). The solution was stirred for 3 h and then concentrated under vacuum to a small volume, hexane was added dropwise affording a yellow solid adduct. Yield 102.0 mg (94%); m.p. 250 °C. − $C_{11}H_{11}ClN_2Pt$: calcd. C 32.88, H 2.77, N 6.97; found C 32.55, H 2.89, N 6.72. − FAB-MS; *m/z*: 401 $[M]^+$, 386 $[M - Me]^+$, 366 $[M - Cl]^+$, 351 $[M - Cl - Me]^+$. − IR (Nujol): $\tilde{\nu}$ = 1599 s, 1555 m, 333 s cm^{-1}.

The other adduct species were obtained according to the same procedure but with different reaction times.

[PtCl(Me)(HL^2)] (2a): 30 min, orange. Yield 97%, m.p. 176−177 °C. − $C_{12}H_{13}ClN_2Pt$: calcd. C 34.66, H 3.16, N 6.74; found C 34.43, H 3.05, N 6.38. − FAB-MS; *m/z*: 415 $[M]^+$, 400 $[M - Me]^+$, 380 $[M - Cl]^+$, 365 $[M - Cl - Me]^+$. − IIR (Nujol): $\tilde{\nu}$ = 1600 s, 1556 m, 320 s cm^{-1}.

[PtI(Me)(HL^2)] (2a′+2b′): LiI (43.4 mg, 0.325 mmol) was added to a solution of **2a** (45.0 mg, 0.108 mmol) in acetone (20 mL). The solution was stirred for 20 h at room temperature. It was then concentrated to dryness and the residue dissolved in CH_2Cl_2, filtered and concentrated to a small volume. Addition of hexane gave an orange analytical sample. Yield 45.0 mg (82%); m.p. 134−136 °C (mixture). The reaction between *trans*-$[PtIMe(SMe_2)_2]$ and the ligand in CH_2Cl_2 gave the products in 32% yield. − $C_{12}H_{13}ClN_2Pt$: calcd. C 28.41, H 2.59, N 5.52; found C 28.25, H 2.35, N 5.30. − IR (Nujol): $\tilde{\nu}$ = 1597 s, 1556 m cm^{-1}.

[PtCl(Me)(HL^3)] (3a): 30 min, yellow. Yield 84%; m.p. 142−144 °C. − $C_{13}H_{15}ClN_2Pt$: calcd. C 36.32, H 3.52, N 6.52; found C 35.95, H 3.64, N 6.27. − FAB-MS; *m/z*: 414 $[M - Me]^+$, 379 $[M - Cl - Me]^+$. − IR (Nujol): $\tilde{\nu}$ = 1599 s, 1565 m, 321 s cm^{-1}.

[PtI(Me)(HL^3)] (3a′ + 3b′): The title compounds were prepared according to the two procedures described for **2a′** and **2b′**. Orange. Yields: 80−40%; m.p. 97−100 °C (dec., mixture). − $C_{13}H_{15}IN_2Pt$: calcd. C 29.95, H 2.91, N 5.38; found C 30.08, H 2.76, N 5.32. − IR (Nujol): $\tilde{\nu}$ = 1595 s, 1556 m cm^{-1}.

[PtCl(Me)(HL^4)] (4a): 4.5 h. Pale yellow. Yield 68%; m.p. 85−89 °C (dec. with gas evolution). − $C_{14}H_{17}ClN_2Pt$: calcd. C 37.88, H 3.87, N 6.31; found C 37.60, H 3.55, N 5.95. − FAB-MS; *m/z*: 443 $[M]^+$, 428 $[M - Me]^+$, 393 $[M - Cl - Me]^+$. − IR (Nujol): $\tilde{\nu}$ = 1599 s, 1562 m, 317 s cm^{-1}.

[PtCl(Me)(HL^5)] (5a): 30 min. Orange. Yield 73%; m.p. 147−150 °C. − $C_{18}H_{17}ClN_2Pt$: calcd. C 43.95, H 3.49, N 5.70; found C 43.69, H 3.38, N 5.52. − FAB-MS; *m/z*: 476 $[M - Me]^+$, 456 $[M - Cl]^+$, 441 $[M - Cl - Me]^+$. − IR (Nujol): $\tilde{\nu}$ = 1596 s, 1562 m, 702 s, 322 s cm^{-1}.

[PtCl(L^5)] (5m): A solution of **5a** in CH_2Cl_2 was stirred at room temperature for 4 d. It was then concentrated under vacuum to a small volume and diethyl ether was added dropwise, affording the title complex in a quantitative yield. The product was a yellow solid; m.p. 247−249 °C. − $C_{17}H_{13}ClN_2Pt$: calcd. C 42.91, H 2.76, N 5.89; found C 42.71, H 2.51, N 5.67. − FAB-MS; *m/z*: 475 $[M]^+$, 440 $[M - Cl]^+$. − IR (Nujol): $\tilde{\nu}$ = 1600 s, 340 s, 319 s cm^{-1}.

[PtCl(L^6)] (6m): A solution of the ligand (89.8 mg, 0.327 mmol) in CH_2Cl_2 (10 mL) was added to a solution of *trans*-[PtClMe(SMe_2)$_2$] (110.0 mg, 0.297 mmol), in the same solvent (20 mL). The solution was stirred for 2 h and then concentrated under vacuum to a small volume. Hexane was added dropwise to afford the cyclometallated species as an orange solid. Yield 94.4 mg (63%);. m.p. stable at 280 °C. − $C_{19}H_{17}ClN_2Pt$: calcd. C 45.28, H 3.41, N 5.56; found C 45.00, H 3.51, N 5.34. − FAB-MS; *m/z*; 503 $[M]^+$, 468 $[M - Cl]^+$. − IR (Nujol): $\tilde{\nu}$ = 1595 s, 1568 m, 339 s cm^{-1}.

[PtCl(Me)(HL^7)] (7a + 7b): 4 h. Orange. Yield 84%; m.p. 258 °C (mixture). − $C_{17}H_{15}ClN_2Pt$: calcd. C 42.72, H 3.17, N 5.86; found C 42.45, H 3.07, N 5.71. − IR (Nujol): $\tilde{\nu}$ = 1595 s, 1573 s, 697 s, 337 s cm^{-1}.

[PtCl(L^7)] (7m): The two isomers, **7a + 7b**, were separated by chromatography on neutral Al_2O_3 (activity II) by elution with dichloromethane. **7b** was recovered in the first fraction, whereas **7a** underwent a decomposition affording the cyclometallated species **7m**: red-orange; m.p. stable at 280 °C. − $C_{16}H_{11}ClN_2Pt$: calcd. C 41.61, H 2.41, N 6.07; found C 41.53, H 2.33, N 6.08. − IR (Nujol): $\tilde{\nu}$ = 1590 s, 1570 m, 328 s cm^{-1}.

1c[PtCl$_2$(Me)(CO)]: CO was bubbled through a stirred orange solution of **1a** (110.0 mg, 0.274 mmol) in CH_2Cl_2 (20 mL) at room temperature. After 2.5 h, the solution became pale yellow. It was concentrated under vacuum to a small volume, diethyl ether was then added dropwise affording a yellow solid which was filtered and collected (67.0 mg, m.p. 149 °C). The filtrate was concentrated to dryness and the oily residue washed with diethyl ether several times to give a red solid which was recrystallised from CH_2Cl_2/diethyl ether (14.0 mg, m.p. 148 °C). Yield 81.0 mg (84%). From the mother liquor, some ligand was recovered (20.0 mg, 0.128 mmol). − $C_{14}H_{14}Cl_2N_2O_2Pt_2$: calcd. C 23.91, H 2.01, N 3.98; found C 23.75, H 2.12, N 4.36. (the microanalysis refers to the yellow form, the one of the red form is very similar). − FAB-MS; *m/z*: 394 $[M]^+$, 379 $[M - Me]^+$, 366 $[M - CO]^+$, 351 $[M - Me - CO]^+$, 308 $[N]^-$, 293 $[N-Me]^-$, 280 $[N-CO]^-$, 265 $[N-Me-CO]^-$. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2104 vs, 2060 vs; (Nujol) 2093 vs, 2045 vs, 1602 s, 318 m, 262 m cm^{-1}(the spectroscopic data are identical for the yellow and the red form). − UV ($CHCl_3$): λ_{max} (yellow form) = 335 nm ($c = 10^{-3}$ M); red form: 335 nm, 410 nm ($c = 10^{-3}$ M), 300 nm ($c = 2{\cdot}10^{-5}$ M).

1s[BF$_4$]: A solution of $AgBF_4$ (48.5 mg, 0.249 mmol) in MeCN (5 mL) was added dropwise to a stirred orange solution of **1a** (100.0 mg, 0.249 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred in the absence of light for 0.5 h at room temperature, it was then filtered through a Celite filter aid, affording a yellow filtrate. The solvent was removed in vacuo to give an orange-yellow solid, which was recrystallised from CH_2Cl_2/diethyl ether, affording a brick-red solid. Yield 110.7 mg (90%); m.p. 218−226 °C (dec.). − $C_{13}H_{14}BF_4N_3Pt$: calcd. C 31.60, H 2.86, N 8.50; found C 31.49, H 2.81, N 8.25. − FAB-MS; *m/z*: 407 $[M]^+$, 392 $[M - Me]^+$, 366 $[M - MeCN]^+$, 351 $[M - Me - MeCN]^+$. − IR (Nujol): $\tilde{\nu}$ = 2359−2303 vw, 1600 m, 1058 vs cm^{-1}.

1c[BF$_4$]: CO was bubbled through a stirred orange solution of **1s**[BF_4] (200.0 mg, 0.405 mmol) in CH_2Cl_2 (50 mL) at room temperature. After 20 h, the solution was lemon-yellow, it was concentrated under vacuum to a small volume and diethyl ether was then added dropwise, affording a pale yellow solid in a quantitative yield (193.7 mg); m.p. 260−270 °C (dec.). − $C_{12}H_{11}BF_4N_2OPt$: calcd. C 29.95, H 2.31, N 5.82; found C 29.60, H 2.11, N 5.59. − IR (Nujol): $\tilde{\nu}$ = 2119 vs, 1598 s, 1060 vs cm^{-1}.

1c[BAr′$_4$]: Na[BAr′$_4$] (62.9 mg, 0.071 mmol) was added to a stirred solution of **1c**[$PtCl_2$(Me)(CO)] (50.9 mg, 0.072 mmol) in CH_2Cl_2 (5 mL). After a few minutes, the solution was filtered through a Celite filter aid, concentrated to dryness and then dried in vacuo. The off-white solid was recrystallised from CH_2Cl_2/hexane. Yield 89.3 mg (quantitative). m.p. 139−141 °C. − $C_{44}H_{23}BF_{24}N_2OPt$: calcd. C 42.02, H 1.85, N 2.23; found C 41.70, H 1.67, N 2.38. − FAB-MS; *m/z*: 394 $[M]^+$, 379 $[M - Me]^+$, 366 $[M - CO]^+$, 351 $[M - Me - CO]^+$, 863 $[N]^-$. − IR (Nujol): $\tilde{\nu}$ = 2100 s, 1600 m, 1120 vs cm^{-1}.

3c[PtCl$_2$(Me)(CO)]: CO was bubbled through a deep yellow solution of **3a** (52.0 mg, 0.121 mmol) in CH_2Cl_2 (20 mL) at room temperature. After 1 h, the resulting pale yellow solution was concentrated to dryness and the oily residue washed with diethyl ether to afford a pale-yellow solid which was recrystallised from CH_2Cl_2/diethyl ether. The free ligand (9.9 mg, 0.054 mmol) was recovered from the mother liquor. Yield 41.1 mg (93%). m.p. 153 °C (dec.). − $C_{16}H_{18}Cl_2N_2O_2Pt_2$: calcd. C 26.27, H 2.48, N 3.83; found C 26.37, H 2.16, N 3.64. − FAB-MS; *m/z*: 422 $[M]^+$, 407 $[M - Me]^+$, 379 $[M - Me - CO]^+$, 308 $[N]^-$, 293 $[N-Me]^-$, 280 $[N-CO]^-$, 265 $[N-Me-CO]^-$, 258 $[N-Me-Cl]^-$. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2099 vs, 2059 vs; (Nujol) 2084 vs, 2043 vs, 1601 s, 1568 m, 320 s, 262 m cm^{-1}.

3s[BF$_4$]: The title complex was prepared in the same manner as **1s**[BF_4]. A bright-yellow solid was obtained (the dropwise addition of diethyl ether caused the precipitation of a bright-red solid which was rapidly converted into a bright-yellow one). Yield 81%. m.p. 215 °C (dec.). − $C_{15}H_{18}BF_4N_3Pt$: calcd. C 34.49, H 3.48, N 8.05; found C 34.41, H 3.32, N 7.97. − FAB-MS; *m/z*: 435 $[M]^+$, 420 $[M - Me]^+$, 394 $[M - MeCN]^+$, 379 $[M - Me - MeCN]^+$. − IR (Nujol): $\tilde{\nu}$ = 2358−2332 vw, 1600 m, 1563 m, 1052 vs cm^{-1}

3c[BF$_4$]: The title complex was prepared in the same manner as **1c**[BF_4]. 10 h, colourless solution. Quantitative yield; m.p. 235−238 °C. − $C_{14}H_{15}BF_4N_2OPt$: calcd. C 33.02, H 2.98, N 5.50; found C 32.74, H 2.60, N 5.39. − FAB-MS; *m/z*: 422 $[M]^+$, 407 $[M - Me]^+$, 394 $[M - CO]^+$, 379 $[M - Me - CO]^+$. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2100 vs, (Nujol) 2109 vs, 1599 s, 1566 m, 1057 vs cm^{-1}.

3c[BAr′$_4$]: The title complex was prepared in the same manner as **1c**[BAr′$_4$]. Yield: quantitative; m.p. 129 °C. − $C_{46}H_{27}BF_{24}N_2OPt$: calcd. C 42.97, H 2.12, N 2.18; found C 42.64, H 2.02, N 2.38. − FAB-MS; *m/z*: 422 $[M]^+$, 407 $[M - Me]^+$, 394 $[M - CO]^+$, 379 $[M - Me - CO]^+$. − IR (Nujol): $\tilde{\nu}$ = 2100 s, 1600 m, 1120 vs cm^{-1}.

5c[PtCl$_2$(Me)(CO)]: The title complex was prepared in the same manner as **3c**[$PtCl_2$(Me)(CO)]. Pale-yellow. Yield 90%; m.p. 154−158 °C (dec.). − $C_{21}H_{20}Cl_2N_2O_2Pt_2$: calcd. C 31.78, H 2.54, N 3.53; found C 32.04, H 2.29, N 3.74. − FAB-MS; *m/z*: 484 $[M]^+$, 468 $[M - CH_4]^+$, 440 $[M - CH_4 - CO]^+$, 308 $[N]^-$, 293 $[N-Me]^-$, 280 $[N-CO]^-$, 265 $[N-Me-CO]^-$, 258 $[N-Me-Cl]^-$. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2100 vs, 2060 vs; (Nujol) 2081 vs, 2055 vs, 1605 s, 1568 m, 702 s, 323 s, 274 s cm^{-1}.

X-ray Data Collections and Structure Determinations: Crystal data and other experimental details are summarised in Table 5. The diffraction experiments were carried out with a Siemens SMART CCD area detector diffractometer at room temperature using Mo-K_α radiation (λ = 0.71073 Å) with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrices were obtained from the least-squares refinement of 83 (for **3a**) and 52 (for **3s**[BF_4]) reflections measured in three different sets of 15 frames each, in the range $3° < \theta < 23°$. At the end of the data collections the first 50 frames, containing 251 (for **3a**) and 180 (for **3s**[BF_4]) reflections, were recollected in order to monitor the crystal

Table 5. Crystallographic data

Compound	**3a**	**3s**[BF_4]
Empirical formula	$C_{13}H_{15}ClN_2Pt$	$C_{15}H_{18}BF_4N_3Pt$
M	429.82	522.23
Colour	yellow	Yellow
Crystal system	orthorhombic	Triclinic
Space group	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no.2)
a [Å]	6.984(1)	8.223(1)
b [Å]	9.860(1)	8.969(1)
c [Å]	19.111(2)	12.936(1)
α [°]		103.29(1)
β [°]		105.87(1)
γ [°]		102.68(1)
V [Å^3]	1316.0(3)	851.5(2)
Z	4	2
F(000)	808	496
$D_{calcd.}$ [g cm^{-3}]	2.17	2.03
T [K]	293	293
Crystal size [mm]	0.11 × 0.23 × 0.25	0.11 × 0.23 × 0.39
μ (Mo-K_α) [cm^{-1}]	109.6	83.6
Min. and max. transm. factors	0.50−1.00	0.50−1.00
Scan mode	ω	ω
Frame width [°]	0.30	0.30
Time per frame [s]	15	20
No. of frames	2450	2450
Detector−sample distance [cm]	5.00	5.00
θ range [°]	3−26	3−26
Reciprocal space explored (*h*, *k*, *l*)	±9, ±13, ±24	±10, ±12, ±17
No. of reflections (total; independent)	15516; 3192	9996; 3987
R_{int}	0.051	0.033
Final R_2 and R_{2w} indices[a] (F^2, all reflections)	0.042, 0.054	0.035, 0.044
Conventional R_1 index [$I > 2\sigma(I)$]	0.024	0.020
Reflections with $I > 2\sigma(I)$	2735	3265
No. of variables	154	217
Goodness of fit[b]	1.06	0.95

[a] $R_2 = [\Sigma(|F_o^2 - kF_c^2|)/\Sigma F_o^2]$, $R_{2w} = [\Sigma w(F_o^2 - kF_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. − [b] $[\Sigma w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (0.04F_o^2)^2]^{1/2}$, N_o is the number of observations and N_v the number of variables.

decay, which was not observed, so that no time-decay correction was needed. The 2450 (for both **3a** and **3s**[BF_4]) collected frames were processed with the software SAINT,[24] and an empirical absorption correction was applied (SADABS[25]) to the 15516 collected reflections of **3a**, 3192 of which are unique with $R_{int} = 0.051$ ($R_{int} = \Sigma|F_o^2 - F_{mean}^2|/\Sigma F_o^2$), and to the 9996 collected reflections of **3s**[BF_4], 3987 of which are unique with $R_{int} = 0.033$. Scattering factors and anomalous dispersion corrections were taken from ref.[26] The calculations were performed with an AST Power Premium 486/33 computer using the Personal Structure Determination Package[27] and the physical constants tabulated therein. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares, using all reflections and minimising the function $\Sigma w(F_o^2 - k|F_c^2|)^2$ (refinement on F^2). Anisotropic thermal factors were refined for all the non-hydrogen atoms. The hydrogen atoms of the methyl group bonded to the platinum center and those of the methyl group belonging to the acetonitrile ligand were detected in the final Fourier maps and not refined. All the other hydrogen atoms were placed in their ideal positions (C−H = 0.97 Å, *B* 1.10 times that of the carbon atom to which they are attached) and not refined. For the noncentrosymmetric compound **3a**, full refinement of the reported structure model led to $R_2 = 0.042$ and $R_{2w} = 0.054$, full refinement of the structure enantiomorph led to $R_2 = 0.056$ and $R_{2w} = 0.094$. The final Fourier maps show maximum residuals of 1.7(4) e/Å^3 at 0.85 Å from Pt for **3a**, and of 0.88(30) e/Å^3 at 1.06 Å from Pt for **3s**[BF_4]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142180 (**3a**) and -142181 (**3s**[BF_4]). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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