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# Carbene complexes of cycloplatinated 1*H*-indole-1-methyl-2-(2′-pyridine). The crystal and molecular structure of σ-{Pt[1*H*-indole-1-methyl-2-(2′-pyridinyl-$C^3$,N′]-(DMSO)Cl} and of σ-{Pt[1*H*-indole-1-methyl-2-(2′-pyridinyl-$C^3$,N′)][=C($OCH_2CH_3$)($CH_2C_6H_5$)]Cl}

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**Abstract**

Reaction of 1-methyl-2-(2′-pyridinyl)-1*H*-indole (**1**) with $PtCl_2(DMSO)_2$ (DMSO = dimethylsulfoxide) gave the cycloplatinated product **2**; X-ray structure determination of **2** showed a metallation to platinum via the C3 carbon of the indole nucleus, which is chelated to the metal via the pyridine nitrogen atom. Compound **2** reacts with neutral ligands such as CO, Bu′NC, styrene and phenylacetylene, to give compounds **3**–**6** respectively, where DMSO is replaced by the neutral ligands. The phenylacetylene derivative **6** reacts with ethanol to give the carbene complex **7**, whose X-ray structure has been determined. Related carbene complexes with other alcohols and other acetylenic derivatives have also been synthesised. 

*Keywords:* 1*H*-indole-1-methyl-2-(2′-pyridinyl); Ligand substitution; Platinum carbene complexes

## 1. Introduction

Terminal alkynes and alkynyl ligands coordinated to electrophilic metal centres react with alcohols to give (alkoxy)alkyl carbene complexes of the type $L_nM\{=C(OR'')CH_2R'\}$ [1]. It has been pointed out recently that the reactions of cationic solvento platinum(II) species of the type $[PtR(PPh_3)_2(solv)]BF_4$ with terminal alkynes and alcohols are strongly influenced by the electronic properties of the alkyl ligand present in the cation [2]. When alkyl is a methyl group, the reaction leads to cationic carbene complexes of platinum, whereas the corresponding trifluoromethyl complex gives a β-alkoxyalkenyl derivative [2,3]. It has been argued that in this latter case, the more electrophilic nature of the reacting complex would stabilise a π-alkyne intermediate rather than a vinylidene, which would explain the observed product. As part of a program to study the cyclometallation reactions of indole derivatives [4], we have studied the reactions of $Pt(DMSO)_2Cl_2$ with 1-methyl-2-(2′-pyridinyl)-1*H*-indole (**1**), obtaining the {Pt[1*H*-indole-1-methyl-2-(2′-pyridinyl-$C^3$,N′](DMSO)Cl} derivative **2**. The presence in this complex of a chelated C,N ligand and of a labile DMSO species, prompted us to investigate its reactivity towards neutral ligands, in particular terminal alkynes, and the following reactions with alcohols in order to verify the influence of the metallated indole derivative on the outcome of the reactions.

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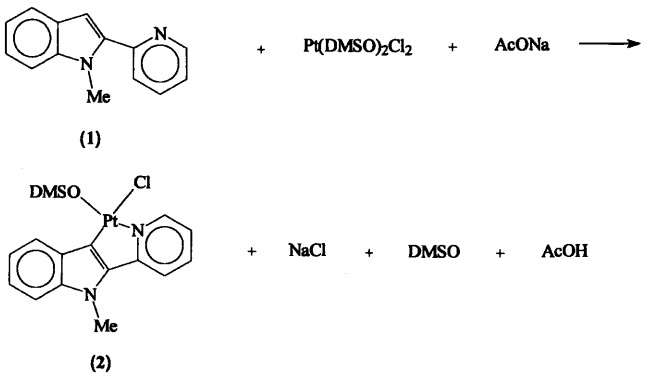
## 2. Results and discussion

### 2.1. Cyclometallated compounds

Reaction of 1-methyl-2-(2′-pyridinyl)-1*H*-indole (**1**) with $Pt(DMSO)_2Cl_2$ in propan-2-ol and in the presence of AcONa, readily gave the monomeric, cycloplatinated product **2** (Eq. (1)):




(1)

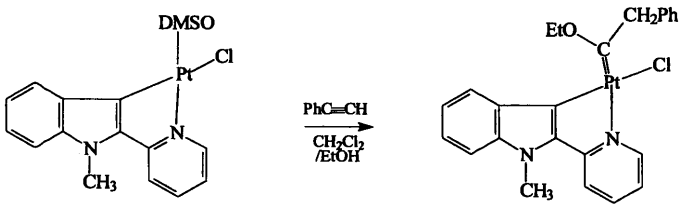
The halogen ligand in **2** is in a *trans* position with respect to the carbon σ-donor, as evidenced by the low frequency of $\nu_{(Pt-Cl)}$ at 278 $cm^{-1}$ which confirms unequivocally the X-ray structural determination (see below). When reaction (1) was conducted with 2-(2′-pyridinyl)-1*H*-indole, where the indole nitrogen is not protected by the methyl group against electrophilic attack by the metal, a monomeric $\eta^2$-*N*,*N*′-bonded 2-(2′-pyridinyl)-indolyl derivative was obtained [5,6].

When CO was bubbled into a solution of **2** in methylene chloride at room temperature overnight, the complex **3** was isolated by silica gel flash-chromatography of the reaction mixture.

A strong and sharp absorption at 2102 $cm^{-1}$ in the IR spectrum (nujol) as well as a signal at 176.86 ppm in the $^{13}$C-NMR spectrum indicate a terminal carbonyl ligand. An additional absorption at 293 $cm^{-1}$ in the spectrum of **3** is consistent with a Pt–Cl bond *trans* to the indole ring.

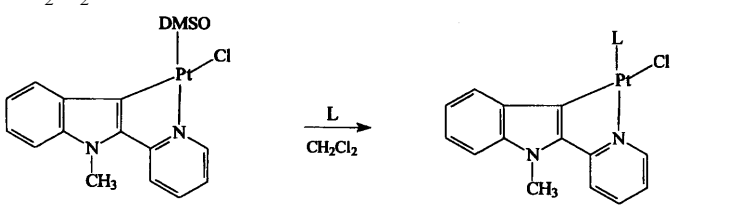
Similarly, in the IR spectrum of **4** absorptions were observed at 2207 $cm^{-1}$ ($\nu_{(-N\equiv C)}$) and 291 $cm^{-1}$ ($\nu_{(Pt-Cl)}$). The presence in complex **5** of $^1$H-NMR signals for three protons at 6.39 ppm (dd, $J = 13.2$, 7.9 Hz), 5.33 ppm (d, $J = 13.2$ Hz) and 4.91 ppm (d, $J = 7.9$ Hz) and two signals at 75.02 and 94.28 ppm in the $^{13}$C-NMR spectrum indicate the coordination of styrene to the metal through the double bond. In compound **6** the position of $\nu_{(C\equiv C)}$ was observed at 1781 $cm^{-1}$ in the IR spectrum together with a broad absorption at 4.15 ppm in the $^1$H-NMR spectrum, and signals at 64.61 and 71.64 ppm in the $^{13}$C-NMR spectrum. These data support a coordination of the 1-alkyne to platinum via the triple bond. Finally, in compounds **5** and **6** absorptions in the IR spectra at 291 and 298 $cm^{-1}$, respectively, confirm the presence of a Pt–Cl bond *trans* to the cyclometallated indole ring.

When the reaction of **2** with phenylacetylene was conducted in a $CH_2Cl_2$–ethanol mixture we obtained the platinum(II) carbene complex **7** (Eq. (3)):




(3)

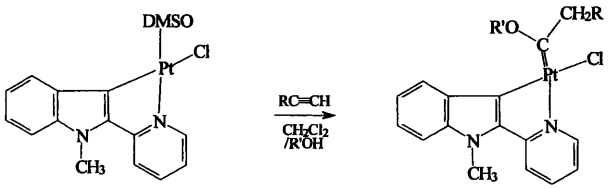
Complex **2** reacts at room tempeature with neutral ligands such as carbon monoxide and Bu$^t$-NC, leading to the substitution products **3** and **4** (Eq. (2)) and similar products with L = Ph–CH=$CH_2$ (**5**) and L = Ph–C≡CH (**6**) have been obtained analogously in warm $CH_2Cl_2$:




(2)

The benzyl methylene group of the alkoxy(benzyl)carbene gives rise to an AB pattern ($^2J_{H-H} = 17.4$ Hz), with only one of these protons showing coupling to $^{195}$Pt ($J_{Pt-H} = 4.5$ Hz) in agreement with that reported in ref. [7] and this is indicative of hindered

Table 1
Series of products synthesised under the same reaction conditions




| | | |
|---|---|---|
| **7** | $R = -C_6H_5$ | $R' = -CH_2CH_3$ |
| **8** | $R = -C_6H_5$ | $R' = -CH(CH_3)_2$ |
| **9** | $R = -C_6H_5$ | $R' = -C(CH_3)_3$ |
| **10** | $R = -(CH_2)_5CH_3$ | $R' = -CH_2CH_3$ |
| **11** | $R = -Si(CH_3)_3$ [a] | $R' = -CH_2CH_3$ |
| **12** | $R = -Si(CH_3)_3$ [a] | $R' = -CH_2(CH_3)_{14}CH_3$ |
| **13** | $R = -(CH_2)_4C{\equiv}CH$ | $R' = -CH_2CH_3$ |
| **14** | $R = -C(CH_3)_3$ | $R' = -CH_2CH_3$ |
| **15** | $R = -C(CH_3){=}CH_2$ | $R' = -CH_2CH_3$ |
| **16** | $R = -C(CH_3)_2OH$ | $R' = -CH_2CH_3$ |

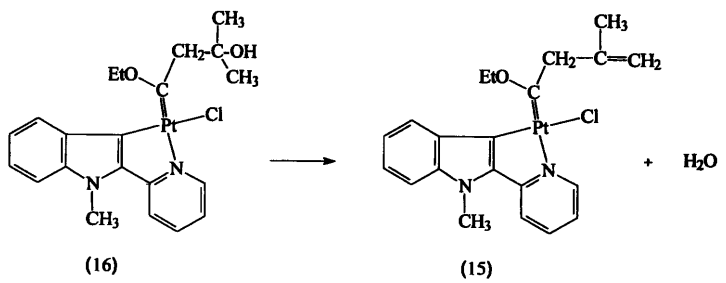
[a] In the platinum carbene complex R = H.

rotation about the Pt–C bond in solution. The $OCH_2$ protons of the ethoxy–carbene complexes are diastereotopic. The chemical shift difference between the two methylene protons is significant (ca. 0.5 ppm), suggesting that on average they occupy very different magnetic environments. The presence of a singlet at 278.35 ppm in the $^{13}$C-NMR spectrum is indicative of the presence of a Pt=C group and, finally, the X-ray determination confirms unequivocally the structure of **7**. Attempted reactions of **6** with ethanol, in the presence of $AgBF_4$, gave a complex mixture of products.

A series of analogous products was synthesised from different alkynes and alcohols under the same reaction conditions (Table 1).

When we used the (trimethylsilyl)acetylene as alkyne we were unable to isolate the corresponding platinum carbene derivative. The NMR spectrum of the crude reaction mixture showed the presence of a trimethylsilyl group, but after flash chromatography the final product was the corresponding methyl derivative, arising from protonolysis of the C–Si bond (products **11** and **12**). In the case of the alkynes $HC{\equiv}CC(CH_3){=}CH_2$ and $HC{\equiv}CC(CH_3)_2OH$ we obtained the same platinum carbene complex (**15**), probably via dehydration of the initial hydroxyplatinum carbene (Eq. (4)):

Analytical and IR data of compounds **2**–**15** are shown in Table 2.




(4)

Table 2
Analytical and IR data

| Complex | Colour | M.p. (°C) | Analysis [a] (%) | Yield (%) | IR $\nu_{Pt-Cl}$ [b] ($cm^{-1}$) |
|---|---|---|---|---|---|
| **2** | Orange | 197–199 | C 37.1 (37.2), H 3.3 (3.3), N 5.7 (5.4) | 71 | 278 |
| **3** | Yellow–orange | 185–186 | C 38.8 (38.7), H 2.5 (2.4), N 6.1 (6.0) | 81 | 2102 [c], 293 |
| **4** | Yellow–orange | 143–144 | C 43.7 (43.8), H 3.7 (3.9), N 7.9 (8.1) | 51 | 2207 [d], 291 |
| **5** | Orange | >290 | C 48.5 (48.8), H 3.4 (3.5), N 5.0 (5.2) | 53 | 291 |
| **6** | Orange | 245–247 | C 48.7 (48.9), H 3.1 (3.2), N 5.1 (5.2) | 61 | 1781 [e], 298 |
| **7** | Orange | 189–190 | C 49.0 (49.2), H 3.9 (4.0), N 4.7 (4.8) | 65 | 288 |
| **8** | Orange | 195–197 (dec) | C 49.9 (50.0), H 4.0 (4.2), N 4.6 (4.7) | 39 | 291 |
| **9** | Orange | 193–195 | C 50.8 (50.9), H 4.3 (4.4), N 4.5 (4.6) | 68 | 293 |
| **10** | Orange | | | 50 | 287 |
| **11** | Yellow–orange | 178–179 | C 41.9 (42.4), H 3.5 (3.8), N 5.2 (5.5) | 61 | 292 |
| **12** | Yellow–orange | 158–159 | C 54.1 (54.4), H 6.6 (6.7), N 3.8 (3.9) | 54 | 287 |
| **13** | Orange | 163–165 (dec) | C 48.3 (48.9), H 4.3 (4.6), N 4.6 (4.7) | 34 | 291 |
| **14** | Yellow–orange | 173–174 | C 46.2 (46.7), H 4.4 (4.8), N 4.7 (4.9) | 48 | 289 |
| **15** | Orange | 130–132 (dec) | C 45.2 (45.9), H 4.0 (4.2), N 5.0 (5.1) | 45 | 291 |

[a] Given as found (required).
[b] Nujol mull.
[c] $\nu_{CO}$.
[d] $\nu_{NC}$.
[e] $\nu_{C=C}$.

Table 3
Crystallographic data

| | | |
|---|---|---|
| Compound | $C_{16}H_{17}ClN_2OPtS$ | $C_{24}H_{23}ClN_2OPt$ |
| FW (amu) | 515.93 | 586.00 |
| Space group | $P2_1/c$ (no. 14) | $P\bar{1}$ (no. 2) |
| Unit cell dimensions | | |
| $a$ (Å) | 10.533(6) | 8.583(3) |
| $b$ (Å) | 16.167(8) | 9.379(2) |
| $c$ (Å) | 9.956(3) | 14.106(2) |
| $\alpha$ (°) | 90 | 74.82(1) |
| $\beta$ (°) | 94.43(3) | 79.26(2) |
| $\gamma$ (°) | 90 | 78.03(2) |
| $V$ (Å$^3$) | 1690(1) | 1061.5(5) |
| $Z$ | 4 | 2 |
| $F(000)$ | 984 | 568 |
| $D_{calc}$ (g cm$^{-3}$) | 2.027 | 1.833 |
| $\mu$(Mo–K$_\alpha$) (cm$^{-1}$) | 85.85 | 67.53 |
| Scan mode | $\omega$ | $\omega$ |
| Scan speed (° min$^{-1}$) | 2–3 | 2–3 |
| Scan width (°) | 1.8+0.350 tan $\theta$ | 1.0+0.35 tan $\theta$ |
| $\theta$ range (°) | 3–25 | 3–23 |
| Independent reflections | 2969 | 2584 |
| Observed reflections [$I>2\sigma(I)$] | 1827 | 1881 |
| Transmission factors | 0.36–1.00 | 0.55–1.00 |
| Parameters refined | 199 | 262 |
| Final $R$ and $wR_2$ indices [a] | 0.060, 0.144 | 0.045, 0.106 |
| Largest difference peak and hole (e Å$^{-3}$) | 1.95, −1.14 | 1.85, −1.61 |

[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$, $wR_2 = [\Sigma w(F_o^2 - k|F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

In conclusion, a series of carbene complexes of platinum(II) can be easily obtained from a precursor having an alkyne and a chelated C,N compound as ligand. To the best of our knowledge, these are the first examples of carbene complexes having such a co-ligand. The isolation of compound **6** having a π-bonded alkyne, and its easy transformation into carbene complexes by reaction with alcohols, seems to exclude that the stabilisation of a π-alkyne intermediate, rather than a vinylidene, is a situation which favours the formation of β-alkoxyalkenyl derivatives by reaction with alcohols [2,3]. At the moment we have no evidence that the π-alkyne intermediate evolves to a hydride-acetylide species prior to the reaction with alcohol, a step which seems to be essential 'en route' to vinylidene [8] and carbene complexes [9].

### 2.2. Crystal structure determination of **2** and **7**

A summary of the crystallographic data and details of the refinement procedure are given in Table 3. Intensity data were collected on a Enraf–Nonius CAD4 diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation. Lorentz, polarisation and an empirical absorption correction [11] were applied to the data. Both structures were solved by Patterson and Fourier methods and refined with full-matrix least-squares (SHELX-93) [12]. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogens were riding on their carbon atoms.

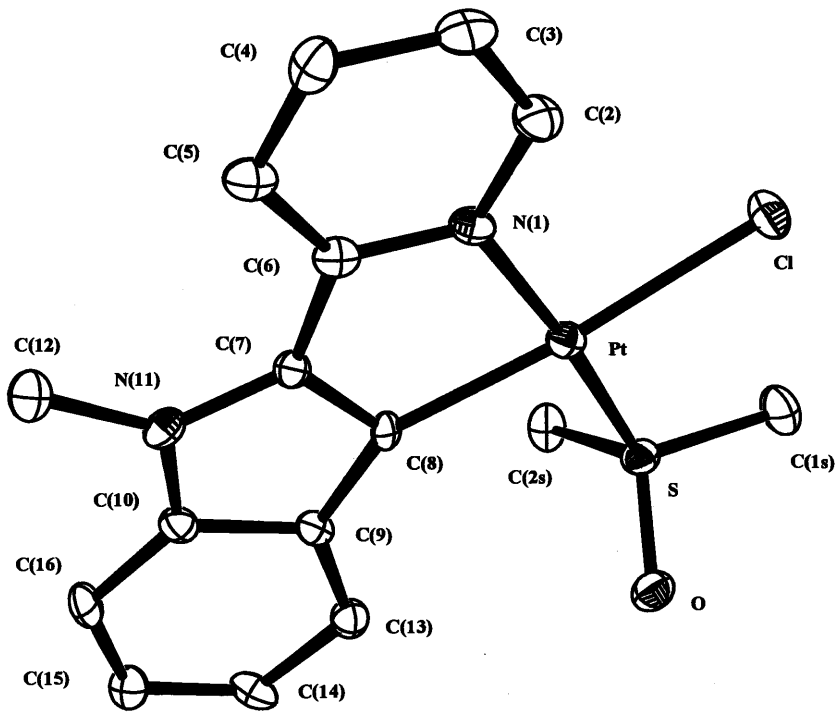



Fig. 1. A perspective view of compound **2**. Hydrogen atoms have been omitted for clarity.

Table 4
Selected interatomic distances (Å) and angles (°) for compound **2**

| | | | |
|---|---|---|---|
| Pt–Cl | 2.398(5) | Cl–Pt–S | 91.6(2) |
| Pt–S | 2.207(5) | Cl–Pt–N1 | 93.2(4) |
| Pt–N1 | 2.063(16) | Cl–Pt–C8 | 172.9(4) |
| Pt–C8 | 2.038(14) | S–Pt–N1 | 175.1(4) |
| S–O | 1.465(14) | S–Pt–C8 | 95.4(5) |
| S–C1s | 1.728(21) | N1–Pt–C8 | 79.7(6) |
| S–C2s | 1.796(21) | Pt–N1–C2 | 124.7(12) |
| N1–C2 | 1.378(25) | Pt–N1–C6 | 117.0(12) |
| N1–C6 | 1.345(24) | C2–N1–C6 | 118.2(16) |
| N11–C7 | 1.388(22) | C7–N11–C10 | 106.6(14) |
| N11–C10 | 1.391(22) | C7–N11–C12 | 130.5(15) |
| C2–C3 | 1.373(29) | C10–N11–C12 | 122.9(15) |
| C3–C4 | 1.409(31) | N1–C6–C5 | 121.5(18) |
| C4–C5 | 1.362(29) | N1–C6–C7 | 111.6(15) |
| C5–C6 | 1.431(28) | C5–C6–C7 | 127.0(16) |
| C6–C7 | 1.451(25) | N11–C7–C6 | 128.0(16) |
| C7–C8 | 1.382(24) | N11–C7–C8 | 112.3(15) |
| C8–C9 | 1.404(21) | C6–C7–C8 | 119.5(16) |
| C9–C10 | 1.437(24) | Pt–C8–C7 | 111.9(11) |
| | | Pt–C8–C9 | 143.0(12) |
| | | C7–C8–C9 | 105.0(14) |
| | | C8–C9–C10 | 108.9(14) |
| | | C8–C9–C13 | 133.9(15) |
| | | C10–C9–C13 | 117.2(15) |
| | | N11–C10–C9 | 107.0(14) |
| | | N11–C10–C16 | 129.1(16) |
| | | C9–C10–C16 | 123.9(16) |

### 2.3. Structure of compound *2*

A perspective view of compound **2** is shown in Fig. 1. Selected interatomic distances and angles are reported in Table 4. The complex contains a Pt atom in square planar coordination surrounded by a chloride ion and a dimethylsulfoxide molecule respectively *trans* to the indolic C8 (C3 atom in indole ring) and pyridinic N1 atoms of the ligand; the metal atom is essentially in the coordination plane (0.006(1) Å out of the plane). The platinum environment can be compared with that found in a similar indole-fused platinacycle, σ-[Pt($C_8H_4NHCH_2NMe_2$)(DMSO)Cl] [4]. Here a Pt–N1 distance of 2.063(16) Å with respect to 2.124(5) Å in σ-[Pt($C_8H_4NHCH_2NMe_2$)(DMSO)Cl] is observed; this shortening is probably due to π-back donation from the metal to the pyridinic moiety, which is absent in the case of the aminic nitrogen atom. Accordingly, the Pt–S distance is slightly but significantly elongated, 2.207(5) versus 2.180(2) Å. The Pt–Cl distance is the same in both compounds (2.398(4) and 2.394(2) Å), whereas an elongation of the Pt–C interaction is observed here (2.038(14) versus 1.973(7) Å) probably due to electron withdrawing performed by the pyridinic ring, which renders the electron pair on C8 (C3 atom in the 1-methyl-2-(2′-pyridinyl)-1*H*-indole ring) less available, as well as to the conformational rigidity of the two different moieties. The metal atom is 0.020(1) Å out of the platinacycle ring. All the rings of the pyridinyl-indolyl ligand are planar within experimental error; the torsion angle C8–C7–C6–N1 (respectively C3, C2, C2′ and N1 atoms in the 1-methyl-2-(2′-pyridinyl)-1*H*-indole ring) is 5.6(24)°.

### 2.4. Structure of compound *7*

A perspective view of compound **7** is shown in Fig. 2. Selected interatomic distances and angles are reported

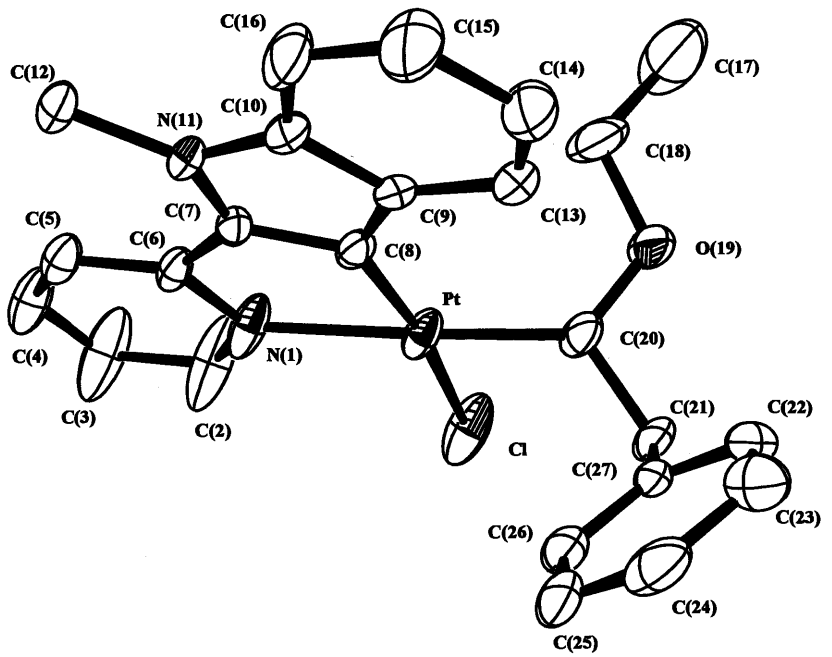



Fig. 2. A perspective view of compound **7**. Hydrogen atoms have been omitted for clarity.

Table 5
Selected interatomic distances (Å) and angles (°) for compound **7**

| | | | |
|---|---|---|---|
| Pt–Cl | 2.370(5) | Cl–Pt–C20 | 87.2(5) |
| Pt–C20 | 1.869(14) | Cl–Pt–N1 | 93.9(4) |
| Pt–N1 | 2.120(11) | Cl–Pt–C8 | 171.8(5) |
| Pt–C8 | 1.977(15) | C20–Pt–N1 | 177.8(5) |
| C20–O19 | 1.322(23) | C20–Pt–C8 | 100.8(6) |
| O19–C18 | 1.449(34) | N1–Pt–C8 | 78.2(5) |
| C20–C21 | 1.501(26) | Pt–N1–C2 | 124.0(11) |
| N1–C2 | 1.326(28) | Pt–N1–C6 | 115.9(8) |
| N1–C6 | 1.357(17) | C2–N1–C6 | 119.9(15) |
| N11–C7 | 1.375(20) | C7–N11–C10 | 106.3(16) |
| N11–C10 | 1.353(23) | C7–N11–C12 | 127.4(13) |
| C2–C3 | 1.388(29) | C10–N11–C12 | 126.0(13) |
| C3–C4 | 1.372(28) | N1–C6–C5 | 118.6(12) |
| C4–C5 | 1.345(26) | N1–C6–C7 | 111.1(14) |
| C5–C6 | 1.392(19) | C5–C6–C7 | 130.3(13) |
| C6–C7 | 1.426(21) | N11–C7–C6 | 129.3(16) |
| C7–C8 | 1.377(18) | N11–C7–C8 | 111.6(12) |
| C8–C9 | 1.428(25) | C6–C7–C8 | 119.1(13) |
| C9–C10 | 1.397(23) | Pt–C8–C7 | 115.7(10) |
| | | Pt–C8–C9 | 139.2(15) |
| | | C7–C8–C9 | 105.2(13) |
| | | C8–C9–C10 | 106.5(17) |
| | | C8–C9–C13 | 135.4(18) |
| | | C10–C9–C13 | 118.1(14) |
| | | N11–C10–C9 | 110.4(14) |
| | | N11–C10–C16 | 127.1(21) |
| | | C9–C10–C16 | 122.4(20) |
| | | Pt–C20–O19 | 127.0(12) |
| | | Pt–C20–C21 | 125.1(10) |
| | | O19–C20–C21 | 107.8(15) |

in Table 5. The structure of complex **7** contains a Pt atom in square planar coordination surrounded by a chloride ion and the alkoxy(benzyl)carbene ligand respectively *trans* to indolic C8 (C3 atom in the 1-methyl-2-(2′-pyridinyl)-1*H*-indole ring) and the pyridinic N1 of the ligand; the metal atom is essentially in the coordination plane. The orientation of the carbene ligand around the Pt–C20 bond is similar to that generally found in other platinum complexes containing non-chelating carbene ligands with the C8–Pt–C20–O19 torsion angle of $-70.4(16)°$. The values of the bond distances and angles within the carbene moiety are very similar to those found in *cis*-[$PtCl_2$-($PMe_2Ph$)(C(OEt)-($CH_2Ph$))] [13].The C20–C21 and O19–C18 distances are indicative of single bond character and that for the C20–O19 interaction shows double bond character; the ligand displays a *trans* arrangement about the C20–O19 bond, the C21–C20–O19–C18 torsion angle being 178.8(17)°. The Pt–C20 bond length (1.869(14) Å) is substantially in line with the corresponding distances found in analogous complexes, where values in the range 1.92–2.02 Å have been observed, according to the different extent of Pt→C backbonding. The Pt–N1 distance is significantly longer than that found in complex **2** due to the different *trans* influence of the carbene ligand. The geometrical features of the indolic ligand are very similar to those found in complex **2**.

## 3. Experimental

### 3.1. General

All reactions were carried out under a dinitrogen atmosphere. All starting materials were used as received. Compound **1** was prepared according to a literature procedure [10]. IR: Perkin–Elmer 1310, Nicolet MX-1FTIR. MS: VG 7070/EQ (70 eV). MR: Varian XL-200 (200 MHz and 50.3 MHz, for $^1H$ and $^{13}C$, respectively). For $^1H$- and $^{13}C$-NMR, $CDCl_3$ was used as solvent, and TMS as internal standard.

### 3.2. σ-{Pt[1H-1-methyl-2-(2′-pyridinyl)-indolyl-$C^3$,N′](DMSO)Cl} (2)

208 mg of **1** ($1 \times 10^{-3}$ mol) were suspended in 10 ml of degassed propan-2-ol under dinitrogen and 422 mg of $Pt(DMSO)_2Cl_2$ ($1 \times 10^{-3}$ mol) with 80 mg ($1 \times 10^{-3}$ mol) of sodium acetate were added. The reaction was refluxed for 1 h. The solution became orange and after cooling to room temperature an orange product **2** precipitated. It was filtered off, washed with propan-2-ol ($3 \times 5$ ml), then dried in vacuo. $^1H$-NMR $\delta$ (ppm): 3.52 (s, 3H, S–$CH_3$, $J_{Pt-H} = 22$), 3.85 (s, 3H, N–$CH_3$), 7.01–8.05 (m, 7H, aromatic), 9.56 (dt, 1H, H-6′, $J_{H-H} = 7.2$, $J_{Pt-H} = 40$). $^{13}C$-NMR $\delta$ (ppm): 32.56, 48.75 ($J_{Pt-C} = 63$), 109.98, 118.01, 121.01, 124.69, 125.13, 125.36, 127.65, 130.25, 137.98, 141.37, 150.79, 154.03, 157.12.

### 3.3. σ-{Pt[1H-1-methyl-2-(2′-pyridinyl)-indolyl-$C^3$,N′](CO)Cl} (3)

129 mg ($0.25 \times 10^{-3}$ mol) of **2** dissolved in 20 ml of dichloromethane were carbonylated under magnetic stirring, overnight at room temperature with CO at atmospheric pressure in the presence of 0.2 ml of triethylamine. The solution became red and the solvent was evaporated to dryness. The residue was purified on silica gel column eluting with dichloromethane–chloroform (2:8). $^1H$-NMR $\delta$ (ppm): 3.98 (s, 3H, N–$CH_3$), 6.89–7.85 (m, 7H, aromatic), 9.49 (dt, 1H, H-6′, $J_{H-H} = 7.2$, $J_{Pt-H} = 40$). $^{13}C$-NMR $\delta$ (ppm): 32.11, 110.7, 121.11, 124.19, 124.93, 125.66, 128.65, 131.55, 137.78, 141.01, 142.36, 150.71, 153.93, 156.18, 176.86 (CO).

### 3.4. σ-{Pt[1H-1-methyl-2-(2′-pyridinyl)-indolyl-$C^3$,N′](Bu$^t$NC)Cl} (4)

To a solution of 154 mg ($0.3 \times 10^{-3}$ mol) of **2** in 20 ml of dichloromethane under dinitrogen, were added 34

mg ($0.4 \times 10^{-3}$ mol) of *tert*-butyl isocyanide. The solution became deep-orange and was stirred at room temperature for 2 h. The solvent was evaporated to dryness and the residue was purified on silica gel column eluting with dichloromethane. $^1$H-NMR $\delta$ (ppm): 1.71 (s,9H,C–$CH_3$), 4.02 (s, 3H, N–$CH_3$), 6.82–7.85 (m, 7H, aromatic), 9.51 (dt, 1H, H-6′, $J_{H-H} = 7.1$, $J_{Pt-H} = 40$). $^{13}$C-NMR $\delta$ (ppm): 30.94, 31.32, 32.38, 117.34, 119.85, 120.36, 123.65, 124.61, 131.45, 140.99, 142.1, 144.53, 151.18, 153.41, 155.8.

### 3.5. σ-{Pt[1H-1-methyl-2-(2′-pyridinyl)-indolyl-$C^3$,N′]($C_6H_5$–CH=$CH_2$)Cl} (5)

To a stirred solution of 154 mg ($0.3 \times 10^{-3}$ mol) of **2** in 20 ml of dichloromethane under dinitrogen, were added 42 mg ($0.4 \times 10^{-3}$ mol) of styrene. The solution was refluxed under stirring for 2 h and gave an orange solution. The solvent was evaporated to dryness and the residue was purified on silica gel column eluting with dichloromethane. $^1$H-NMR $\delta$ (ppm): 3.95 (s, 3H, N–$CH_3$), 4.91 (d, 1H, = CH, $J = 7.9$), 5.33 (d, 1H, = CH, $J = 13.3$), 6.39 (dd, 1H, =CH, $J = 7.9$, 13.2), 7.65–8.01 (m, 12H, aromatic), 9.49 (dt, 1H, H-6′, $J_{H-H} = 7.2$, $J_{Pt-H} = 40$). $^{13}$C-NMR $\delta$ (ppm): 31.04, 75.02, 94.28, 110.45, 117.24, 120.46, 120.72, 122.55, 124.31, 127.96, 129.19, 131.18, 132.33, 132.77, 134.03, 140.14, 141.6, 143.25, 150.48, 156.78.

### 3.6. σ-{Pt[1H-1-methyl-2-(2′-pyridinyl)-indolyl-$C^3$,N′]($C_6H_5$–CH≡CH)Cl} (6)

To a stirred solution of 154 mg ($0.3 \times 10^{-3}$ mol) of **2** in 20 ml of dichloromethane under dinitrogen, were added 41 mg ($0.4 \times 10^{-3}$ mol) of phenylacetylene. The solution was refluxed under stirring for 2 h. The solvent was evaporated to dryness and the residue was purified on silica gel column eluting with dichloromethane. $^1$H-NMR $\delta$ (ppm): 3.98 (s, 3H, N–$CH_3$), 4.15 (brs, 1H, ≡CH), 6.78–7.98 (m, 12H, aromatic), 9.45 (dt, 1H, H-6′, $J_{H-H} = 7.3$, $J_{Pt-H} = 40$). $^{13}$C-NMR $\delta$ (ppm): 32.51, 64.61, 71.64, 110.34, 117.31, 120.36, 120.75, 122.51, 124.41, 127.91, 129.21, 131.21, 132.25, 132.74, 133.92, 140.24, 141.58, 143.21, 150.51, 156.65.

### 3.7. General synthesis of cyclometallated platinum(II) carbenes (7–15)

To a stirred solution of $0.3 \times 10^{-3}$ mol of **6** in 10 ml of dichloromethane–alcohol (1:1) under dinitrogen, were added ($0.9 \times 10^{-3}$ mol) of the corresponding alkyne. The solution was stirred for 2–10 h until starting material disappeared in TLC (eluent $CH_2Cl_2$–hexane). The solvent was evaporated to dryness and the residue was purified on silica gel column eluting with the same eluent.

$^1$H-NMR, $^{13}$C-NMR and MS spectra data for the compounds obtained are as follows.

**7**. $^1$H-NMR $\delta$ (ppm): 1.22 (t, 3H, $OCH_2CH_3$), 4.04 (s, 3H, N–$CH_3$), 4.54 (d, 1H, Pt–C=$CH_2$–Ph, $J_{H-H} = 17.4$), 4.68 (dt, 1H, Pt–C=$CH_2$–Ph, $J_{H-H} = 17.4$, $J_{H-Pt} = 4.5$), 5.25 (dq, 1H, O$CH_2$–$CH_3$, $J_{H-H} = 10.4$, $J_{H-Pt} = 7.2$), 5.61 (dq, 1H, O$CH_2$–$CH_3$, $J_{H-H} = 10.4$, $J_{H-Pt} = 7.2$), 6.75–7.75 (m, 12H, aromatic), 9.38 (dt, 1H, H-6′, $J_{H-H} = 8.2$, $J_{Pt-H} = 14.7$). $^{13}$C-NMR $\delta$ (ppm): 14.41, 32.54, 64.21 ($J_{C-Pt} = 52$), 82.37 ($J_{C-Pt} = 58$), 110.06, 117.01, 119.27, 119.92, 120.43, 122.53, 124.06, 127.52, 128.85, 130.9, 131.9, 133.83, 139.88, 141.34, 144.21, 150.23, 156.37, 278.35 (Pt=C). MS $m/z$ (%): 586 (25), 466 (34), 438 (100), 430 (32), 401 (45), 386 (65), 206 (54), 130 (22), 91 (13).

**8**. $^1$H-NMR $\delta$ (ppm): 1.37 (d, 3H, OCH($CH_3$)$_2$), 1.64 (d, 3H, OCH($CH_3$)$_2$), 4.03 (s, 3H, N–$CH_3$), 4.51 (d, 1H, Pt–C=$CH_2$–Ph, $J_{H-H} = 17.4$), 4.61 (dt, 1H, Pt–C=$CH_2$–Ph, $J_{H-H} = 17.4$, $J_{H-Pt} = 4.5$), 6.54 (sept, 1H, O$CH$($CH_3$)$_2$), 6.75–7.75 (m, 12H, aromatic), 9.38 (dt, 1H, H-6′, $J_{H-H} = 8.6$, $J_{Pt-H} = 14.7$). $^{13}$C-NMR $\delta$ (ppm): 21.09, 22.05, 32.04, 68.81 ($J_{C-Pt} = 52$), 91.9 ($J_{C-Pt} = 58$), 109.76, 117.71, 119.27,119.9, 120.43, 122.53, 123.96, 127.13, 128.55, 130.55, 130.91, 133.53, 139.48, 141.01, 144.11, 149.22, 156.18, 277.28 (Pt=C). MS $m/z$ (%): 466 (41), 438 (91), 414 (100), 401 (41), 386 (51), 372 (43), 207 (24), 130 (22).

**9**. $^1$H-NMR $\delta$ (ppm): 1.55 (s, 9H, OC ($CH_3$)$_3$), 4.04 (s, 3H, N–$CH_3$), 4.61 (d, 1H, Pt–C=$CH_2$–Ph, $J_{H-H} = 17.3$), 4.69 (dt, 1H, Pt–C=$CH_2$–Ph, $J_{H-H} = 17.3$, $J_{H-Pt} = 4.4$), 6.75–7.75 (m, 12H, aromatic), 9.38 (dt, 1H, H-6′, $J_{H-H} = 8.4$, $J_{Pt-H} = 14.7$). $^{13}$C-NMR $\delta$ (ppm): 20.03, 32.04, 68.81 ($J_{C-Pt} = 52$), 92.01 ($J_{C-Pt} = 57$), 109.21, 118.01, 119.21,119.87, 120.15, 122.21, 124.01, 127.32, 128.05, 130.75, 134.11, 133.53, 139.02, 141.05, 144.32, 149.01, 156.28, 279.12 (Pt=C). MS $m/z$ (%): 614 (83), 557 (100), 549 (48), 466 (91), 430 (80), 401 (41), 386 (51), 209 (33), 131 (25).

**10**. $^1$H-NMR $\delta$ (ppm): 0.95 (t, 3H, –$(CH_2)_5$–$CH_3$), 1.27 (m, 10H, –$(CH_2)_5$–$CH_3$), 1.62 (t, 3H, $OCH_2CH_3$), 3.15 (t, 1H, Pt=C$CH_2$–$(CH_2)_5$–$CH_3$, $J_{H-H} = 17.1$), 3.19 (t, 1H, Pt=C$CH_2$–$(CH_2)_5$–$CH_3$, $J_{H-H} = 17.1$), 4.05 (s, 3H, N–$CH_3$), 5.38 (dq, 1H, $OCH_2$–$CH_3$, $J_{H-H} = 10.2$, $J_{H-Pt} = 7.4$), 5.58 (dq, 1H, $OCH_2$–$CH_3$, $J_{H-H} = 10.2$, $J_{H-Pt} = 7.4$), 6.75–7.75 (m, 7H, aromatic), 9.46 (dt, 1H, H-6′, $J_{H-H} = 8.5$, $J_{Pt-H} = 14.6$). $^{13}$C-NMR $\delta$ (ppm): 13.34, 14.31, 26.48, 32.04, 36.23, 37.18, 38.7, 63.98 ($J_{C-Pt} = 52$), 109.91, 118.32, 124.12, 125.13, 125.34, 128.45, 129.43, 138.91, 141.22, 151.33, 154.33, 156.92, 276.38 (Pt=C). MS $m/z$ (%): 594 (66), 512 (100), 466 (91), 437 (22), 386 (45), 332 (24), 207 (13), 130 (48).

**11**. $^1$H-NMR $\delta$ (ppm): 1.21 (t, 3H, $OCH_2$–$CH_3$), 2.99 (t, 3H, Pt=C–$CH_3$, $J_{H-Pt} = 13.2$), 4.02 (s, 3H, N–$CH_3$), 5.37 (dq, 1H, O$CH_2$–$CH_3$, $J_{H-H} = 10.2$, $J_{H-Pt} = 7.3$),

5.41 (dq, 1H, O$CH_2$–$CH_3$, $J_{H-H} = 10.2$, $J_{H-Pt} = 7.3$), 6.81–7.77 (m, 7H, aromatic), 9.39 (dt, 1H, H-6′, $J_{H-H} = 8.2$, $J_{Pt-H} = 14.1$). $^{13}$C-NMR $\delta$ (ppm): 15.32, 26.91, 33.15, 64.21 ($J_{C-Pt} = 52$), 110.67, 120.31, 124.46, 125.01, 125.93, 128.91, 131.42, 136.68, 141.51, 142.06, 150.22, 154.05, 155.97, 276.38 (Pt=C). MS $m/z$ (%): 509 (42), 466 (100), 438 (41), 430 (23), 414 (31), 401 (13), 387 (45), 207 (24), 130 (29).

**12**. $^1$H-NMR $\delta$ (ppm): 0.94 (t, 3H, $OCH_2$–$(CH_2)_{14}$–$CH_3$), 1.26 (m, 28H, $OCH_2$–$(CH_2)_{14}$–$CH_3$), 2.98 (t, 3H, Pt=C–$CH_3$, $J_{H-Pt} = 13.4$), 4.08 (s, 3H, N–$CH_3$), 5.34 (dq, 1H, O$CH_2$–$(CH_2)_{14}$–$CH_3$, $J_{H-H} = 10.3$, $J_{H-Pt} = 7.1$), 5.49 (dq, 1H, O$CH_2$–$(CH_2)_{14}$–$CH_3$, $J_{H-H} = 10.3$, $J_{H-Pt} = 7.1$), 6.81–7.71 (m, 7H, aromatic), 9.39 (dt, 1H, H-6′, $J_{H-H} = 8.2$, $J_{Pt-H} = 14.1$). $^{13}$C-NMR $\delta$ (ppm): 15.8, 23.08, 26.14, 28.94, 29.54, 29.79, 30.06, 32.36, 45.66, 64.35 ($J_{C-Pt} = 52$), 110.13, 116.99, 120.03, 120.42, 122.27, 124.11, 132.01, 139.84, 141.41, 150.14, 156.37, 275.8 (Pt=C). MS $m/z$ (%): 706 (53), 466 (100), 444 (22), 430 (32), 401 (23), 386 (41), 206 (31), 130 (26).

**13**. $^1$H-NMR $\delta$ (ppm): 1.27 (m, 8H $CCH_2$–$(CH_2)_4$–C≡CH), 1.62 (t, 3H, $OCH_2CH_3$), 3.17 (t, 1H, Pt=C$CH_2$–$(CH_2)_4$–C≡CH, $J_{H-H} = 17.1$), 3.19 (t, 1H,, Pt=C$CH_2$–$(CH_2)_4$ –C≡CH, $J_{H-H} = 17.1$), 3.84 (s,1H, $CCH_2$–$(CH_2)_4$–C≡C$H$), 4.1 (s, 3H, N–$CH_3$), 5.48 (dq, 1H, O$CH_2$–$CH_3$, $J_{H-H} = 10.2$, $J_{H-Pt} = 7.4$), 5.61 (dq, 1H, O$CH_2$–$CH_3$, $J_{H-H} = 10.2$, $J_{H-Pt} = 7.4$), 6.81–7.79 (m, 7H, aromatic), 9.41 (dt, 1H, H-6′, $J_{H-H} = 8.5$, $J_{Pt-H} = 14.6$). $^{13}$C-NMR $\delta$ (ppm): 14.31, 26.48, 32.04, 36.23, 37.18, 38.7, 44.13, 46,18, 63.98 ($J_{C-Pt} = 52$), 109.91, 118.32, 124.12, 125.13, 125.34, 128.45, 129.43, 138.91, 141.22, 151.33, 154.33, 156.92, 276.38 (Pt=C). MS $m/z$ (%): 466 (100), 436 (34), 386 (57), 207 (21), 130 (41).

**14**. $^1$H-NMR $\delta$ (ppm): 1.21 (s, 9H $C(CH_3)_3$), 1.67 (t, 3H, $OCH_2CH_3$), 2.98 (d, 1H, Pt=C$CH_2$–$C(CH_2)_3$, $J_{H-H} = 16.1$), 3.60 (t, 1H, Pt=C$CH_2$–$C(CH_2)_3$, $J_{H-H} = 16.4$), 4.04 (s, 3H, N–$CH_3$), 5.49(dq, 1H, O$CH_2$–$CH_3$, $J_{H-H} = 10.4$, $J_{H-Pt} = 7.2$), 5.51 (dq, 1H, O$CH_2$–$CH_3$, $J_{H-H} = 10.4$, $J_{H-Pt} = 7.2$), 6.71–7.79 (m, 7H, aromatic), 9.38 (dt, 1H, H–6′, $J_{H-H} = 8.9$, $J_{Pt-H} = 14.7$). $^{13}$C-NMR $\delta$ (ppm): 14.71, 32.4, 33.91, 71.25, 82.19 ($J_{C-Pt} = 51$), 110.14, 116.99, 118.32, 123.99, 124.12, 125.34, 128.45, 129.43, 138.81, 141.02, 151.33, 153.63, 156.52, 275.18 (Pt=C). MS $m/z$ (%): 566 (53), 530 (67), 514 (56), 466 (100), 438 (29), 430 (45), 401 (54), 387 (51), 207 (16), 130 (45).

**15**. $^1$H-NMR $\delta$ (ppm): 1.63 (t, 3H, $OCH_2CH_3$), 1.96 (s, 3H, –C($CH_3$)=$CH_2$), 3.87 (d, 1H, –$CH_2$C($CH_3$)=$CH_2$, $J_{H-H} = 7.8$), 3.98 (d, 1H, –$CH_2$C($CH_3$)=$CH_2$, $J_{H-H} = 7.8$), 4.06 (s, 3H, N–$CH_3$), 5.03 (s, 1H, –C($CH_3$)=C$H_2$), 5.28 (s, 1H, –C($CH_3$)=C$H_2$), 5.38 (dq, 1H, O$CH_2$–$CH_3$, $J_{H-H} = 10.4$, $J_{H-Pt} = 7.2$), 5.51 (dq, 1H, O$CH_2$–$CH_3$, $J_{H-H} = 10.4$, $J_{H-Pt} = 7.2$), 6.99–7.77 (m, 7H, aromatic), 9.38 (dt, 1H, H-6′, $J_{H-H} = 8.7$, $J_{Pt-H} = 14.7$). $^{13}$C-NMR $\delta$ (ppm): 14.56, 21.89, 33.87, 64.21 ($J_{C-Pt} = 48$), 78.19 ($J_{C-Pt} = 51$), 109.21, 110.21, 117.0, 118.03, 123.79, 124.22, 125.23, 128.42, 129.66, 138.93, 139.07, 150.12, 151.43, 156.02, 271.31 (Pt=C). MS $m/z$ (%): 550 (37), 513 (27), 484 (32), 466 (100), 430 (31), 401 (57), 208 (26), 130 (68).

## 4. Supplementary material

Tables giving details of the data collection and refinement, atomic coordinates, displacement parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 142060 and 142061. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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