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Platinum(II) Benzophenone Imine Complexes and the Crystal Structure of *trans*-(*N,N*)-(Benzophenone imine)chloro-[2-(1-imino-1-phenylmethyl)phenylido]-platinum(II)–Acetone (2/1)

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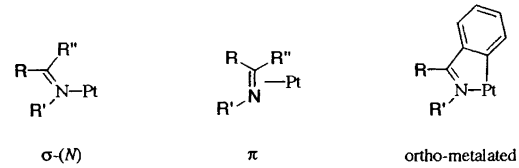
Syntheses and characterisation by ^{1}H NMR and IR of the platinum(II) complexes $[PtI_2(Ph_2C{=}NH)_2]$, $[PtCl_2(Ph_2C{=}NH)_2]$, $[PtCl(Ph(Ph{-}H)C{=}NH)(NH_2CH_2CH_2NH_2)]$ and *trans*-(*N,N*)-$[PtCl(Ph(Ph{-}H)C{=}NH)(Ph_2C{=}NH)]$ are described. Absorption and emission spectra at room temperature for the latter complex are reported. The crystal structure of *trans*-(*N,N*)-$[PtCl(Ph(Ph{-}H)C{=}NH)(Ph_2C{=}NH)]\cdot 1/2\{(CH_3)_2CO\}$ was determined by X-ray diffraction methods. Space group $C2/c$, $a = 14.318(4)$ Å, $b = 22.854(4)$ Å, $c = 15.212(3)$ Å and $\beta = 108.42(2)°$, using 10 368 reflections in the refinement of 291 parameters gave $R = 0.037$ and $wR2 = 0.074$ (for all data). The ligands surround platinum in a planar configuration with bond lengths of Pt–Cl 2.404(1) Å, Pt–N (monodentate imine ligand) 2.004(3) Å, Pt–N (bidentate imine ligand) 1.979(3) Å and Pt–C 1.988(3) Å. The chemical shifts in the ^{1}H NMR spectrum of *trans*-(*N,N*)-$[PtCl(Ph(Ph{-}H)C{=}NH)(Ph_2C{=}NH)]$ (in $CDCl_3$) display variations with concentration of the complex that indicate dimerisation. The dimerisation constant was determined from the change in chemical shift for the NH proton of the ortho-metalated ligand, $K = 1.25(4)$ M^{-1} at 300 K. The structure of the dimer in solution is proposed to resemble one of the types of interactions that are encountered between platinum complexes in the solid state.

The study of transition metal complexes containing coordinated imines was initiated by Bright and Mills with the preparation of $Fe_2(CO)_6(Ph_2C{=}NH)_2$ in 1967.[1] Since then a large number of imine complexes have been reported.[2–4] Imine ligands with an aromatic group on the carbon atom can coordinate to a metal in three ways, i.e. σ-(*N*), π or ortho-metalated (Scheme 1).



Scheme 1. Coordination modes of aromatic imine ligands.

Formation of σ-(*N*) coordination compounds and/or ortho-metalation are often competing processes.[5] It has been shown that changes in the reaction conditions by varying the metal to ligand ratio or choosing different starting material or solvent can alter the product distribution significantly. Reacting PhCH=NPh with $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMe_2Ph)_2]$ in $CHCl_3$ yielded *trans*-$[PtCl_2(PhCH{=}NPh)(PMe_2Ph)]$,[6] whereas reaction of the same imine with Na_2PtCl_4 in CH_2Cl_2 yielded the ortho-metalated complex, $[Pt_2(\mu\text{-}Cl)_2((Ph{-}H)CH{=}NPh)_2]$.[7]

Platinum(II) complexes with σ-(*N*)-coordinated ketimines are of particular interest owing to their structural similarity to the recently reported iminoether complexes,[8] which exhibit interesting biological properties. Whereas antitumor activity of bis(amine)platinum(II) complexes has been solely connected with their *cis*-configuration, the *trans*-isomers being useless in that respect, *trans*-bis(iminoether) complexes show promising antitumor activity,[9,10] leaving their *cis*-isomers significantly less active in bio-assays.[9–11]

Platinum(II) complexes with σ-(*N*)-coordinated ket-

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imines are typically synthesised by one of the following procedures: (i) reaction between a suitable platinum(II) starting complex, and an imine which is either stabilised by aromatic groups or part of a conjugated system;[6,12–17] (ii) condensation reactions between an amine and a ketone of which one may be coordinated to the metal in the starting material;[18–23] (iii) reaction of a carbanion with a coordinated nitrile.[24–26] In most of the reported complexes the imine is part of a bidentate system. When a monodentate imine is used as ligand, complexes with one imine ligand only have been isolated.

In this paper we describe the synthesis and characterisation of bis-imine complexes of the monoimine benzophenone imine as well as complexes containing ortho-metalated benzophenone imine.

Experimental

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker AC 250 MHz spectrometer using TMS or the solvent peak as internal standard (CD_2Cl_2 at 5.35 ppm, D_2O at 4.70 ppm). IR spectra were recorded on a Perkin Elmer SPECTRUM 2000 FT-IR spectrometer in KBr tablets (4000–450 cm^{-1}) and in polyethylene tablets (700–30 cm^{-1}). UV/Vis spectra were recorded on a Shimadzu MPS-2000 spectrometer using 1 and 10 mm cuvettes.

Syntheses. All reagents were of analytical grade. Benzophenone imine was from Aldrich and K_2PtCl_4 from Johnson Matthey. Toluene was dried over NaH and *trans*-$[PtCl_2(CH_3CN)_2]$ was prepared according to published procedures.[27] Calcium chloride drying tubes were used to keep out moisture from reaction mixtures in organic solvents.

[PtI$_2${Ph$_2$C=NH}$_2$] (**1**). Solutions of K_2PtCl_4 (0.196 g, 0.467 mmol, in 2.5 ml water) and KI (0.65 g, 3.98 mmol, in 0.7 ml water) were mixed and stirred at room temperature for 20 min. Benzophenone imine (200 µl, 1.19 mmol) in acetone (2 ml) was added drop by drop over 3 min and a yellow precipitate formed. After stirring for 20 min the precipitate was collected and washed with water and ice-cold acetone and dried in air. The crude material (340 mg) was recrystallised by dissolving it in a minimum amount of chloroform (35 ml) and fitting the bottle with a loose stopper to allow for slow evaporation of the solvent. The yellow crystals were collected and washed with ether and dried in air. Yield 230 mg (60%). Calc. for $C_{26}H_{22}N_2I_2Pt$: C, 38.49; H, 2.73; N, 3.45%. Found: C, 38.40; H, 2.76; N, 3.38. ^{1}H NMR (CD_2Cl_2): 6.61 (d), 7.30 (t), 7.52 (t), 7.71 (t), 7.86 (t), 8.27 (d), 8.56 (NH), ($CDCl_3$): 6.51 (d), 7.24 (t), 7.46 (t), 7.63 (t), 7.80 (t), 8.29 (d), 8.52 (NH). IR (selected frequencies): 1591 (m), 1565 (m), 1449 (m), 784 (m), 696 (s), 598 (w), 437 (w), 202 (w), 187 (w).

trans-*(*N,N*)-[PtCl{(Ph–H)PhC=NH}{Ph$_2$C=NH}]·1/2((CH$_3$)$_2$CO)* (**2**) *from* K_2PtCl_4. Potassium tetrachloroplatinate (1.0 g, 2.4 mmol) and benzophenone imine (1.2 ml, 7.2 mmol) in toluene (60 ml) were refluxed for 14 days. A white precipitate of KCl (340 mg) was removed. The red solution was evaporated to dryness. The crude product was dissolved in acetone and shortly after a pure product precipitated. The orange crystals were collected and washed with ice-cold acetone and ether and dried in air. From the mother liquor an additional batch of crystals was obtained. Yield 1.1 g (54%). Calc. for $C_{27.5}H_{24}N_2ClO_{0.5}Pt$: C, 53.19; H, 3.90; N, 4.51%. Found: C, 52.96; H, 3.67; N, 4.40%. ^{1}H NMR ($CDCl_3$, 10.2 mg, 0.016 mmol, in 500 µl): 6.8–7.1 (m), 7.35–7.7 (m), 8.28 (d), 8.87 (NH, J_{Pt-H}=30 Hz), 10.13 (NH, J_{Pt-H}=29 Hz). IR (selected frequencies): 1704 (m), 1597 (m), 1584 (m), 1577 (m), 1560 (m), 1450 (s), 1431 (m), 1387 (m), 1253 (m), 789 (s), 731 (s), 695 (vs), 600 (m), 273 (m).

[PtCl$_2${Ph$_2$C=NH}$_2$] (**3**). Benzophenone imine (200 µl, 1.19 mmol), *trans*-$[PtCl_2(CH_3CN)_2]$ (200 mg, 0.574 mmol, only sparingly soluble in the solvent) and dichloromethane (25 ml) were stirred at room temperature until all starting material was dissolved and or reacted, 10 days. The yellow solution was evaporated to dryness and the residue was treated with acetone and chloroform. The resulting suspension was cooled on ice and the yellow crystals were collected, washed with ether and dried in air. Yield 70 mg (20%). Calc. for $C_{26}H_{22}N_2Cl_2Pt$: Pt, 31.04; C, 49.68; H, 3.52; N, 4.46%. Found: Pt, 31.00; C, 49.25; H, 3.35; N, 4.36%. ^{1}H NMR ($CDCl_3$): 6.59 (d), 7.23 (t), 7.45 (t), 7.60 (t), 7.77 (t), 8.24 (d), 8.90 (NH). IR (selected frequencies): 1591 (m), 1567 (m), 1450 (m), 786 (m), 697 (s), 602 (m), 340 (s), 331 (s), 324 (s). The mother liquor contained yet unidentified complexes.

[PtI$_2${Ph$_2$C=NH}$_2$] (**1**) *from [PtCl$_2${Ph$_2$C=NH}$_2$]* (**3**). A solution of **3** (7.3 mg, 0.012 mmol) and KI (30 mg, 0.18 mmol) in acetone (50 ml) was stirred at room temperature for 10 days. The solution was evaporated to dryness and the residue extracted with chloroform. In the yellow solution, $[PtI_2\{(Ph)_2C=NH\}_2]$ was identified by ^{1}H NMR spectroscopy as the only product.

trans-*(*N,N*)-[PtCl{(Ph–H)PhC=NH}{Ph$_2$C=NH}]* (**2**) *and [PtCl$_2${Ph$_2$C=NH}$_2$]* (**3**) *from [PtI$_2${Ph$_2$C=NH}$_2$]* (**1**). To a solution of $[PtI_2\{Ph_2C=NH\}_2]$ (100 mg, 0.123 mmol, in 4 ml acetone) were added $AgNO_3$ (0.25 ml 1.0 M) and water (4 ml). The resulting yellow solution was heated on an oil bath (70 °C) for 10 min. The grey precipitate which formed was removed and washed thoroughly with acetone (20 ml). Conc. HCl (0.18 ml) was added to the orange filtrate. The resulting solution was left at room temperature for slow evaporation of acetone. Orange crystals and a black oil formed. Filtration and a quick wash with acetone isolated orange crystals of **2**. Yield 10 mg (13%). The mother liquor was evaporated to dryness, and the residue was treated with

chloroform, which led to an orange solution and yellow crystals of **3**. Yield 6 mg (8%).

[PtCl{(Ph–H)PhC=NH}($NH_2CH_2CH_2NH_2$)]·1/2$CHCl_3$ (**4**). To a solution of **2** (29.3 mg, 0.047 mmol, in 0.5 ml $CHCl_3$) was added 1,2-ethanediamine (3.1 μl, 0.046 mmol) and an orange precipitate immediately formed. The precipitate was isolated, washed with ether and dried in air. Yield 21 mg (97%). Anal. calc. for $C_{15.5}H_{18.5}N_3Cl_{2.5}Pt$: C, 35.10; H, 3.49; N, 7.92; Cl(ionic), 6.68; Pt, 36.78%. Found: C, 34.82; H, 3.41; N, 7.81; Cl(ionic), 6.79; Pt, 35.86. ^{1}H NMR (D_2O): 2.87 (CH_2, J_{Pt-H}=32 Hz), 7.16–7.22 (t, 1 H), 7.30–7.42 (m, 3 H), 7.60–7.68 (m, 5 H).

Reaction of **2** *with amines.* To a solution of **2** (10.2 mg, 0.016 mmol, in 0.5 ml) in $CDCl_3$ was added ten equivalents of cyclohexylamine. ^{1}H NMR spectroscopy investigation indicated the presence of [Pt{(Ph–H)PhC=NH}-($C_6H_{11}NH_2$)Cl] complexes (2.1 (d, CH_2), 2.35 (d, CH_2) 2.8 (s, CH), 4.95 (NH_2), 5.55 (NH_2), 6.55 (d), 6.8–7.6 (m), 10.14 (NH), Ph_2C=NH [7.34–7.50 (m), 7.58 (d)] and $C_6H_{11}NH_2$ [1.19 (m, CH_2), 1.53 (m, CH_2), 2.61 (m, CH)]. In similar experiments, solutions of **2** were treated with one equivalent of cyclohexylamine or tributylamine.

[Pt{Ph_2C=NH}$_2$($NH_2CH_2CH_2NH_2$)]I_2 (**5**). A solution of **1** (0.15 g, 0.185 mmol) and 1,2-ethanediamine (50 μl, 0.74 mmol) in 30 ml of $CHCl_3$ was stirred overnight at room temperature in the dark. The resulting white crystals were separated from a colourless solution, washed with ether, and air dried. Yield 0.13 g (80%). Calc. for $C_{28}H_{30}N_4I_2Pt$: C, 38.59; H, 3.47; N,6.43; Pt, 22.39% Found: C, 38.42; H, 3.15; N, 6.37; Pt, 22.15%

Association constant determination for **2**. Solutions were made by diluting stock $CDCl_3$ solutions of **2** with $CDCl_3$. To avoid evaporation of solvent, solutions were cooled on ice prior to the measurement. The final concentrations of **2** ranged from 0.002 52 to 0.0945 M. The ^{1}H NMR spectra were recorded at 300 K; the chemical shifts of the resonances were relative to TMS. Analysis of the data was performed by linear regression using the program KaleidaGraph,[28] and using an iterative method described by Horman and Dreux.[29] Here the basic equations, $\delta_i=\delta_0([m]/[C]_0)+\delta_\infty(2[d]/[C]_0)$, $K=[d]/[m]^2$ and $[C]_0=[m]+2[d]$, are rearranged to a straight-line equation. K is the equilibrium constant for dimerisation, [m], [d] and $[C]_0$ are the concentrations of the monomer, dimer and total complex, respectively, δ_i is the observed chemical shift, δ_0 is the chemical shift for the pure monomer and δ_∞ is the chemical shift for the pure dimer.

Crystal structure determination of [PtCl{(Ph–H)PhC=NH}{Ph_2C=NH}]·1/2{$CO(CH_3)_2$} (**2**). Crystals were prepared by dissolving **2** in acetone and adding water until a slightly clouded solution was obtained. Acetone was added to reproduce a clear solution which was left for slow evaporation of acetone until orange crystals, suitable for X-ray diffraction experiments, had formed on the surface. The diffraction data were collected with an Enraf Nonius CAD-4 diffractometer (graphite-monochromated Mo Kα radiation, λ=0.710 73 Å) operating in the ω/2θ-scan mode. The crystal was cooled by an Enraf-Nonius gas-flow low-temperature device to 122.0(5) K. Lattice parameters were determined from the setting angles of 22 reflections with θ in the range 19.8–24.3°. The intensities of five standard reflections were measured every 10^4 s. The orientation of the crystal was checked after every 600 reflections. Data reduction was performed by use of the DREADD programs.[30] Corrections were made for Lorentz, polarisation, background and absorption effects, the latter by the Gaussian integration procedure. The data were corrected for a total intensity loss of up to 8.9% monitored for the five standard reflections. Reflections related by the symmetry of the crystal class (2/*m*) were averaged. The structure was solved by the Patterson method using SHELXS-86, and refined by full matrix least-squares with SHELXL-93 minimising $\Sigma\omega(F_o^2-F_c^2)^2$. Scattering factors were taken from Ref. 31 and were used as contained in the programs. After anisotropic displacement parameters were introduced for the non-hydrogen atoms, all hydrogen atoms were localised in the difference Fourier and introduced in their idealised positions. The final maxima in the difference electron density were found to be close to platinum. Crystallographic data are summarised in Table 1. Atomic fractional coordinates for all non-hydrogen atoms are listed in Table 2.

Results

Syntheses. Synthetic pathways for the reported complexes are given in Scheme 2. Substitution reactions in **2** with monodentate amines were followed by ^{1}H NMR, as no precipitation occurred. When complex **2** was treated with one equivalent of tributylamine no substitution occurred within 3 days, as indicated by the lack of change in the ^{1}H NMR spectrum. By contrast, one equivalent of cyclohexylamine immediately lead to some substitution. The resulting ^{1}H NMR spectrum indicated that several complexes were formed. When ten equivalents of cyclohexylamine were added a much simpler ^{1}H NMR spectrum appeared. This indicated that the monodentate imine ligand in **2** was substituted by cyclohexylamine, leaving the ortho-metalated ligand untouched. Only the low-field imine NH frequency was present after substitution and could be assigned as arising from the ortho-metalated ligand. The NH frequency of the free imine which was liberated in the substitution reaction is very broad and could not be detected in the concentration range studied. Two resonances (4.95 and 5.55 ppm) for coordinated NH_2 were present. The large difference in these chemical shifts might be due to the presence of the two geometric isomers *cis*- and *trans*-(*N*,*N*)-(cyclohexyl-

Table 1. Crystallographic data for [PtCl{(Ph–H)PhC=NH}-{Ph_2C=NH}] · 1/2{$CO(CH_3)_2$}.

Empirical formula	$C_{26}H_{21}$ Cl N_2Pt · 1/2{$CO(CH_3)_2$}
Formula weight/g mol^{-1}	621.039
Space group	Monoclinic, *C*2/*c*
Temperature/K	122.0(5)
a/Å	14.318(4)
b/Å	22.854(4)
c/Å	15.212(3)
β/°	108.42(2)
V/Å^3	4723(2)
Z	8
d_{calcd}/g cm^{-3}	1.747
m/cm^{-1}	6.075
F(000)	2416
Crystal size	0.15 × 0.12 × 0.07
Range/Θ°	1.7–35
Range of indices	$-10 < h < 23$ $-36 < k < 36$ $-24 < l < 23$
No. of reflections	
collected	15629
independent [*R*(int) = 0.0460]	10368
observed, $I > 2\sigma(I)$	10355
No. of variables	291
Max. Min. transmission coefficient	0.651 0.306
Goodness-of-fit on F^2	1.669
Final *R* [$I > 2\sigma(I)$]	*R*1 = 0.0372, *wR*2 = 0.0718
R (all data)	*R*1 = 0.0533, *wR*2 = 0.0744
Max./Min Δρ/e Å^{-3}	3.783/−2.755

amine)chloro-[2-(1-imino-1-phenylmethyl)-phenylido]-platinum(II).

Characterisation. The identity of the products was established by IR and ^{1}H NMR spectroscopy. The crystal structure of *trans*-(*N*,*N*)-(benzophenone imine)chloro-[2-(1-imino-1-phenylmethyl)phenylido]platinum(II) – acetone(2/1) (**2**) established its coordination geometry. In the IR spectra of complexes **1**–**3** the ν(C=N) frequencies were 1591 cm^{-1} (**1**), 1597 cm^{-1} (**2**) and 1591 cm^{-1} (**3**), which may be compared to the frequency of the free ligand at 1605 cm^{-1}.[32] The ν(Pt–Cl) frequencies in **3** were around 330 cm^{-1}, in accordance with simple coordination compounds.[33,34] The presence of more than one IR band in the Pt–Cl region is normally indicative of the *cis*-isomer; the fact that two such signals appear in the spectrum of **3** is in favour of its *cis*-configuration. However, more than one signal has been observed for *trans*-[$PtCl_2$(imine)PMe_2Ph] complexes.[6] In **2** the ν(Pt–Cl) frequency was 273 cm^{-1}, indicating a strong *trans* influencing ligand such as a carbanion.[33] Owing to low intensities of ν(Pt–I) frequencies they are difficult to assign. In **1** these are assigned to 202 and/or 187 cm^{-1}. This could be similar to *cis*-[$PtI_2(py)_2$], for which 178 and 167 cm^{-1} is found, or to *trans*-[$PtI_2(py)_2$], for which ν(Pt–I) = 183 cm^{-1} is reported.[35] In [PtI_2L_2] complexes (L = butane-1-amine or hexane-1-amine) it was found that the *cis*-isomers had strong-intensity Pt–I signals at 178 or 176 cm^{-1} and that the *trans* isomers had medium-intensity Pt–I signals at 191 cm^{-1}.[36]

The ^{1}H NMR spectra of **1** and **3** consist of two sets of phenyl groups which show 2D coupling patterns. The peaks are well separated and are identified as 2,6 (low field, doublet) 4 (triplet) 3,5 (triplet), 4′ (triplet), 3′,5′ (triplet) and 2′,6′ (high-field doublet). All five protons in one set are at higher field than all the five protons of the other set. This phenyl coupling pattern is in agreement with σ-(*N*) imine coordination. The chemical shifts for the imine proton in $CDCl_3$ are 8.52 ppm for **1** and 8.90 ppm for **3**.

2D NMR COSY and TOCSY spectra of **2** show that signals between 6.8 and 7.1 ppm arise from one type of phenyl group, the triplet around 7.38 ppm and a signal near 7.5 ppm together with the doublet at 8.28 ppm arise from another phenyl group, whereas the remaining signals between 7.45 and 7.7 ppm show mutual couplings. From the integrals of the 1D spectra the first of the above group of signals contained 4 H, the 7.38 ppm plus the 8.28 ppm signals represented 4H and therefore one phenyl group together with the signal near 7.5 ppm. The signals between 7.45 ppm and 7.7 ppm represented 11 H, i.e two phenyl groups plus one proton from the second phenyl. We assign the phenyl protons in the following way: the signals between 6.8 and 7.1 ppm arrise from the C-bound phenyl group, and the triplet around 7.38 and the signal near 7.5 ppm together with the doublet at 8.25 ppm arise from one of the phenyl groups of the monodentate ligand. The signals between 7.45 and 7.7 ppm arise from one phenyl group of the monodentate imine overlapping with the non-C bound phenyl group of the orthometalated ligand. The imine NH protons were assigned by comparison with the spectrum of **2** added ten equivalents of cyclohexylamine; thus, the low-field NH frequency arises from the orthometalated ligand and the high-field NH frequency form the monodentate imine.

The ultraviolet/visible absorption features of **2** are listed in Table 3. The absorption spectra have a long tail into the visible region, with molar absorptivities at 500 nm of 150 M^{-1} cm^{-1} in acetone and 120 M^{-1} cm^{-1} in dichloromethane, thus explaining the orange colour of the complex. The ultraviolet and visible absorption spectrum follows the Lambert–Beer law over a concentration range of 9.71×10^{-5} to 9.71×10^{-3} M in dichloromethane and 1.95×10^{-5} to 1.95×10^{-3} M in acetone. Furthermore, a Gaussian analysis[37] of the visible absorption spectra obtained for solutions with different concentrations of **2** yielded curves at identical positions and with identical widths and relative heights.

Compound **2** is emissive at room temperature (Table 3), an interesting feature when considering that ortho-metalated platinum(II) complexes have been studied extensively in order to search for long-lived emission, preferably at room temperature.[38–40]

Crystal structure of [PtCl{(Ph–H)PhC=NH}-{Ph_2C=NH}] · 1/2{$CO(CH_3)_2$}. A perspective view of

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (in Å^2) for [PtCl{(Ph–H)PhC=NH}{Ph_2C=NH}] · 1/2{$CO(CH_3)_2$}.

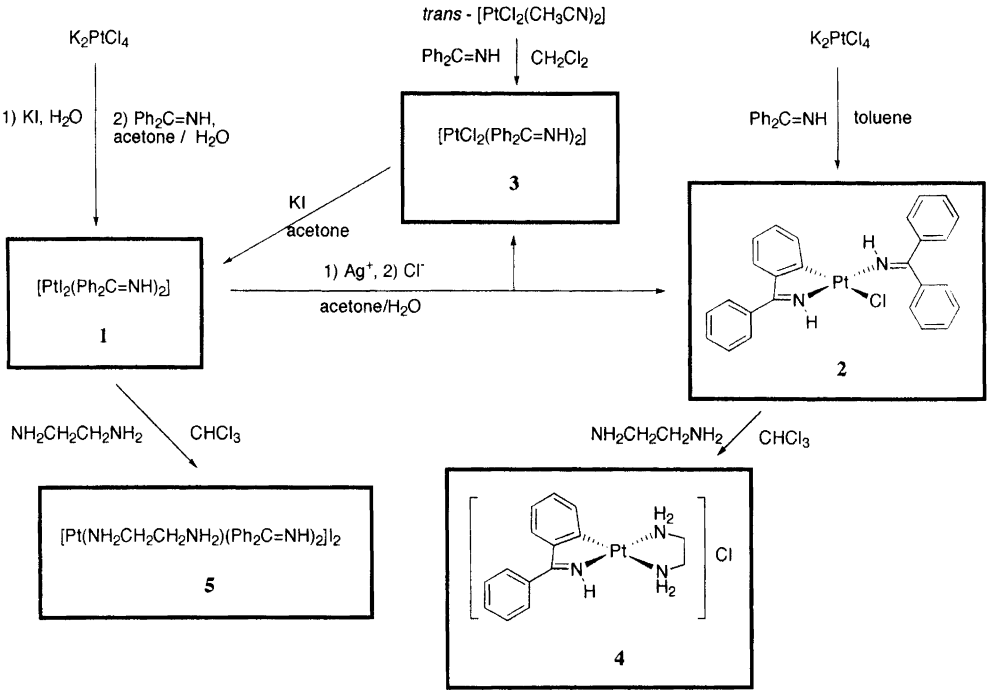
Atom	*x*	*y*	*z*	*U*(eq)[a]
Pt	0.1044(1)	0.0101(1)	0.3566(1)	0.0013(1)
Cl	0.0095(1)	−0.0667(1)	0.3951(1)	0.0017(1)
N1	0.0392(2)	0.0707(1)	0.4097(2)	0.0016(1)
N2	0.1704(2)	−0.0434(1)	0.2901(2)	0.0015(1)
C1A	0.0635(2)	0.1249(1)	0.4059(2)	0.0016(1)
C2A	0.1427(2)	0.1336(1)	0.3660(2)	0.0016(1)
C3A	0.1770(2)	0.0806(1)	0.3372(2)	0.0015(1)
C4A	0.2571(2)	0.0854(2)	0.3038(2)	0.0017(1)
C5A	0.2994(2)	0.1396(2)	0.2975(2)	0.0019(1)
C6A	0.2630(3)	0.1907(2)	0.3238(2)	0.0021(1)
C7A	0.1843(3)	0.1874(2)	0.3584(2)	0.0020(1)
C8A	0.0101(2)	0.1723(1)	0.4364(2)	0.0016(1)
C9A	0.0582(3)	0.2159(2)	0.4980(2)	0.0021(1)
C10A	0.0050(3)	0.2594(2)	0.5245(3)	0.0024(1)
C11A	−0.0973(3)	0.2596(2)	0.4894(3)	0.0025(1)
C12A	−0.1458(3)	0.2159(2)	0.4286(3)	0.0025(1)
C13A	−0.0925(3)	0.1727(2)	0.4018(2)	0.0022(1)
C1B	0.2556(2)	−0.0685(1)	0.3115(2)	0.0015(1)
C2B	0.2908(2)	−0.0916(2)	0.2362(2)	0.0017(1)
C3B	0.2658(2)	−0.0618(2)	0.1516(2)	0.0022(1)
C4B	0.2978(3)	−0.0821(2)	0.0798(3)	0.0032(1)
C5B	0.3547(3)	−0.1322(2)	0.0922(3)	0.0033(1)
C6B	0.3800(3)	−0.1618(2)	0.1759(3)	0.0029(1)
C7B	0.3490(2)	−0.1419(2)	0.2483(3)	0.0022(1)
C8B	0.3182(2)	−0.0736(1)	0.4095(2)	0.0016(1)
C9B	0.4203(2)	−0.0681(2)	0.4343(2)	0.0021(1)
C10B	0.4777(3)	−0.0729(2)	0.5270(3)	0.0028(1)
C11B	0.4347(3)	−0.0840(2)	0.5944(3)	0.0030(1)
C12B	0.3332(3)	−0.0899(2)	0.5703(2)	0.0028(1)
C13B	0.2745(3)	−0.0848(2)	0.4782(2)	0.0021(1)
O	0.5000	0.2134(2)	0.2500	0.0044(1)
C1X	0.5000	0.2665(2)	0.2500	0.0027(1)
C2X	0.5926(3)	0.3017(2)	0.2801(3)	0.0034(1)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

the platinum(II) complex is given in Fig. 1; selected bond lengths and angles are listed in Table 4. The platinum(II) complex contains one ortho-metalated benzophenone imine, one *N*-coordinated monodentate benzophenone imine ligand and a chloride ligand bound *trans* to the coordinated carbon atom. The coordination geometry around platinum is close to planar, but displays a small tetrahedral distortion. The deviations from the average coordination plane are: C3A 0.066(1), Cl 0.049(1), N1 −0.062(1) and N2 −0.053(1) Å, whereas Pt is only 0.021(1) Å from the least-squares plane. Both imine nitrogen protons are on the same side of the coordination plane. Bond lengths and angles are very similar to those found in a related complex, [Pt(L)(LH)Cl] (LH = diazapam).[41] The Pt–Cl distance of 2.4036(9) Å is longer than the Pt–Cl distance of 2.32 Å found in *cis*-diamine complexes and *cis*(bithioxane) complexes[42,43] in accordance with the lower ν(Pt–Cl). The bond lengths in the ortho-metalated ligand show variations (Table 4) that imply a small delocalisation of charge. A shortening is observed for the C1A–C2A [1.459(5)] single bond compared to C1B–C2B [1.486(4)]. The C2A–C3A distance [1.472(4)] is longer, and the C7A–C2A distance [1.388(5)] is shorter than the normal values for C–C bonds in phenyl groups. The ortho-metalated phenyl group is almost coplanar with the coordination plane, the interplanar angle being 3.41(2)̀. The interplanar angle between the phenyl groups of the neutral ligand is 60.67(1)̀. In the negatively charged ligand the corresponding angle is significantly smaller, 47.78(1)̀, probably due to steric hindrance.

Complexes related by the crystallographic two-fold axis form dimers with a Pt–Pt distance of 3.6496(10) Å. The interaction is further stabilised by strong intermolecular hydrogen bonds between the imine nitrogen of the neutral ligand (N2) and the coordinated chloride (Table 5 and Fig. 2). These dimers interact through weaker hydrogen bonds between the N1 imine nitrogen and the chloride (Table 5) to complexes related by inversion symmetry. Through these N1–H···Cl hydrogen bonds another type of dimer interaction is achieved, resulting in layers of platinum complexes perpendicular to the *b*-axis.

The platinum complex crystallises as an acetone solvate. The crystal packing leaves cavities between the coordination compounds and these are occupied by the



Scheme 2. Synthetic parthways for the reported complexes.

Table 3. UV/visible absorption (with molar absorptivities) and emission features for **2** at 298 K.

Solvent	λ_{max}/nm	$\varepsilon/10^3\ M^{-1}\ cm^{-1}$
Absorption:		
Acetone[a]	391	5.40
	370	5.30
CH_2Cl_2	388	6.3
	370	6.1
	315 (sh)	8.5
	290 (sh)	13.0
Emission:		
CH_2Cl_2	560[b]	

[a]Solvent cut-off at 350 nm. [b]Excitation wavelength of 460 nm.

acetone molecules which are found on the crystallographic twofold axis. The positions of the acetone molecules are stabilised by interactions of the acetone oxygen with H5A from two platinum complexes related by a two-fold axis. This is in accordance with the fact that the negative charge on C3A increases the acidity of the hydrogen atoms attached to C5A and C7A compared to normal phenyl protons.

Association constant. The resonances in the ^1H NMR spectrum at 300 K of **2** in $CDCl_3$ are dependent on the concentration of the complex. In the aromatic region small chemical shifts (± 0.005 to ± 0.07 ppm) resulted in collapse of some signals and very differently looking spectra appeared. The imine protons shifted 0.08 and 0.365 ppm for the high field (monodentate imine ligand) and low field resonance (ortho-metalated imine ligand), respectively. An analysis of the chemical shift of the imine proton at low field yielded a binding constant of $K = 1.22$–$1.29\ M^{-1}$ (Fig. 3), which corresponds to a variation in the degree of dimerisation from about 0.3 to 9% for the concentration interval used. Values for the chemical shift for the pure monomer and for the pure dimer were estimated to be $\delta_0 = 9.97$ ppm and $\delta_\infty = 12.27$ ppm, respectively.

Analysis of the high-field NH proton ($\Delta\delta = 0.08$ ppm) and the CH proton which showed the largest shift in chemical shift ($\Delta\delta = 0.07$ ppm), yielded binding constants of the same magnitude but with a much lower certainty.

Discussion

In studies of geometric isomerisation in square planar platinum(II) complexes, $[PtX_2L_2]$ (X = halide or pseudo-halide, L = N-donor ligand) there are numerous examples of *cis* to *trans* isomerisations.[36,44–46] A general rule is that the *cis* isomers are favoured by enthalpy but the *trans* isomers are favoured by entropy.[47]

We aimed to synthesise *cis*-bis(benzophenone imine)diiodoplatinum(II) by a slightly modified procedure (directed by solubility properties of the imine) to that used for synthesising *cis*-dichlorodi(amine)platinum(II) complexes.[48] In the latter, addition of amine to a solution of tetraiodoplatinate yields the isomeric pure *cis*-diiododi(amine)platinum(II) complex as a precipitate, directed by the *trans*-effect. With benzophenone imine in place of the amine we expected the same result. Indeed, the synthesis proceeded in the usual way indicated by the very fast formation of a yellow precipitate

Table 4. Selected bond lengths (in Å) and angles (in °) for [PtCl{(Ph–H)PhC=NH}{Ph_2C=NH}] · 1/2{$CO(CH_3)_2$}.

Pt–Cl	2.4036(9)	Pt–C3A	1.988(3)
Pt–N1	1.979(3)	Pt–N2	2.004(3)
N1–C1A	1.295(4)	N2–C1B	1.293(4)
C1A–C2A	1.459(4)	C1B–C2B	1.486(4)
C2A–C3A	1.427(4)	C2B–C3B	1.399(5)
C3A–C4A	1.399(4)	C3B–C4B	1.391(5)
C4A–C5A	1.395(5)	C4B–C5B	1.384(6)
C5A–C6A	1.388(5)	C5B–C6B	1.385(6)
C6A–C7A	1.389(5)	C6B–C7B	1.389(5)
C2A–C7A	1.388(5)	C2B–C7B	1.396(5)
C1A–C8A	1.482(4)	C1B–C8B	1.482(4)
C8A–C9A	1.393(5)	C8B–C9B	1.396(5)
C9A–C10A	1.388(5)	C9B–C10B	1.394(5)
C10A–C11A	1.392(5)	C10B–C11B	1.378(6)
C11A–C12A	1.389(5)	C11B–C12B	1.388(6)
C12A–C13A	1.386(5)	C12B–C13B	1.393(5)
C8A–C13A	1.394(5)	C8B–C13B	1.400(4)
C3A–Pt–Cl	171.90(9)	N1–Pt–N2	172.53(11)
C1A–N1–Pt	118.9(2)	C1B–N2–Pt	134.5(2)
N1–Pt–Cl	92.00(9)	N2–Pt–Cl	94.01(8)
N1–Pt–C3A	80.24(13)	N2–Pt–C3A	93.9(12)
N1–C1A–C2A	113.8(3)	N2–C1B–C2B	119.1(3)
N1–C1A–C8A	120.8(3)	N2–C1B–C8B	120.7(3)
C2A–C3A–Pt	113.3(2)	C4A–C3A–Pt	130.2(2)
C1A–C2A–C3A	113.6(3)	C1B–C2B–C3B	119.0(3)
C2A–C3A–C4A	116.5(3)	C2B–C3B–C4B	120.5(4)
C3A–C4A–C5A	121.2(3)	C3B–C4B–C5B	119.7(4)
C4A–C5A–C6A	121.1(3)	C4B–C5B–C6B	120.1(3)
C5A–C6A–C7A	119.2(3)	C5B–C6B–C7B	120.9(4)
C2A–C7A–C6A	120.0(3)	C2B–C7B–C6B	119.5(4)
C7A–C2A–C1A	124.4(3)	C7B–C2B–C1B	121.6(3)
C8A–C1A–C2A	125.3(3)	C8B–C1B–C2B	120.2(3)
C9A–C8A–C1A	122.6(3)	C9B–C8B–C1B	120.8(3)
C13A–C8A–C1A	118.3(3)	C13B–C8B–C1B	119.7(3)

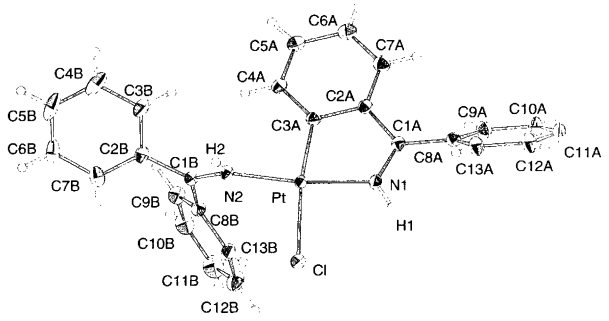


*Fig. 1. ORTEP*II[51] drawing showing the molecular geometry of [PtCl{(Ph–H)PhC=NH}{Ph_2C=NH}] · 1/2{$CO(CH_3)_2$} (the thermal ellipsoids are scaled to include 50% probability). The hydrogen atoms are drawn as spheres with a fixed radius.

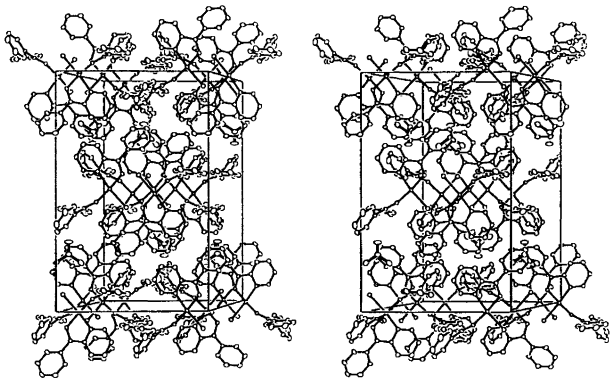


Fig. 2. Stereo pair illustrating the packing in [PtCl{(C_6H_5)(C_6H_4)C=NH}{(C_6H_5)$_2$C=NH}] · 1/2{$CO(CH_3)_2$}, seen along the *c*-axis.

Table 5. Hydrogen bonding interactions in [PtCl{(Ph–H)PhC=NH}{Ph_2C=NH}] · 1/2{$CO(CH_3)_2$}.

Atoms			D···A/Å	H···A/Å	D–H···A/°
N1	H1	Cl[a]	3.258(3)	2.597	133
N2	H2	Cl[b]	3.204(3)	2.361	161
C13B	H13B	Cl	3.624(4)	2.708	162

[a] $(-x, -y, 1-z)$. [b] $(-x, y, 1/2-z)$.

(Scheme 2). Also, when the yellow diiodo complex (**1**) was treated with 1,2-ethanediamine in chloroform at room temperature, white crystals with the same composition as bis(benzophenone imine)-1,2-ethanediamineplatinum(II) iodide (**5**) were formed almost quantitatively. The colour change clearly indicates that a substitution of iodide with the diamine in the coordination sphere has taken place. Although the formulation of this compound as a monomer is likely (strongly suggesting a *cis*-configuration)

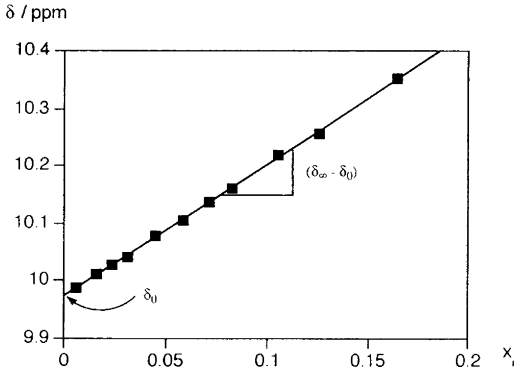


Fig. 3. Plot of δ (observed chemical shift) for the ortho-metalated imine proton in [PtCl{(Ph–H)PhC=NH}{Ph_2C=NH}] as a function of x_i, $x_i=(1+y_i/2)-[(1+y_i/2)^2-1]^{1/2}$, $y_i=1/(2K[C]_0)$; 300 K.

it can not be excluded that it is a polymer in which 1,2-ethanediamine bridge two platinum centres each having two imines *trans* to each other.

A puzzling fact, however, is that the dichloro complex (**3**) prepared from *trans*-diacetonotriledichloro-platinum(II) presumably is the same geometric isomer as the diiodo complex (**1**), since the two dihalogeno complexes (**1**) and (**3**) can be generated from each other by classical methods, cf. Scheme 2. A simple *trans* to *cis* (or *vice versa*) conversion in these reactions is unlikely.

Substitution of monodentate imines by amines or by CO is observed for a number of platinum(II) complexes.[6,14,40,41] In the ortho-metalated complex *trans*-(*N*,*N*)-(benzophenone imine)chloro-[2-(1-imino-1-phenylmethyl)-phenylido]-platinum(II) (**2**) substitution of the monodentate imine was accomplished with cyclohexylamine and with 1,2-ethanediamine, Scheme 2. Thus, **2** is a useful starting material for preparing complexes with one ortho-metalated benzophenone imine and an array of ligands on the remaining coordination sites.

The dimerisation constant for **2** of $K=1.25(4)\ M^{-1}$ implies weak binding. The most obvious structure of a self-association of **2** is either through a stacking interaction, or an interacting through hydrogen bond formation. Both types of dimer interactions were observed in the solid state. In one dimer two units related by two-fold symmetry are sitting on top of each other resulting in a short Pt–Pt distance; the other dimer interaction involves hydrogen bonds between the chloride and the imine proton of the ortho-metalated ligand where the two units are side by side. It is a general observation that all protons which are affected by the association, both in hydrogen-bonded interactions and in stacked interactions, show approximately the same change in chemical shift.[49] In the present case, only the imine proton of the ortho-metalated benzophenone imine showed a significant variation in chemical shift. If stacking is the origin of the dimerisation in **2** one would expect the aromatic protons as well as the proton of the monodentate imine to be strongly affected, but not the imine proton of the ortho-metalated benzophenone imine. It is therefore likely that the dimer

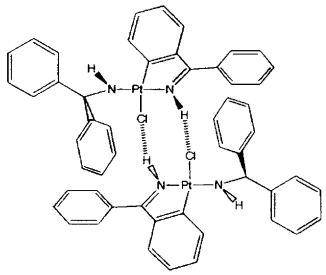


Fig. 4. Proposed hydrogen bonding interaction in the [PtCl{(Ph–H)PhC=NH}{Ph_2C=NH}] dimer in $CDCl_3$ solution.

observed in solution is similar to the dimer found in the solid state, where two molecules related by inversion symmetry form intermolecular hydrogen bonds between the proton of the ortho-metalated ligand and a coordinated chloride (Fig. 4).

Dimers with strong Pt–Pt interactions are known to have very different UV/visible spectra relative to the corresponding monomers, and accordingly, solutions of such compounds are expected to exhibit changes in their UV/visible spectra with concentration. With compound **2**, no changes in the UV/visible spectrum were observed in acetone or chloroform when looking in a concentration range in which it would be expected if dimers with strong Pt–Pt interactions were present.[40] Also, the ^1H NMR spectra of **2** showed no significant shifts for the phenyl protons. An apparent lack of Pt–Pt interaction in solution despite a short Pt–Pt distance (3.65 Å) in the solid state has also been observed for the [Pt(2,2′-bipyridine)(1,2-ethanediamine)]$(PF_6)_2$ salt.[50]

Conclusion

With benzophenone imine another example of an ortho-metalated luminescent platinum(II) complex emerged. Furthermore, the ease with which a monodentate benzophenone imine is substituted by amines makes the ortho-metalated complex suitable as a starting material for an array of new complexes. Dimerisation for the ortho-metalated platinum(II) complex was observed and was found to be due to a hydrogen-bond interaction rather than a Pt–Pt interaction, despite both such interactions being observed in the solid state. The reported bis complexes are to the best of our knowledge the first examples of bis-imine platinum(II) complexes of a monodentate imine. The original goal of studying the ligand chemistry of imines relative to amines and iminoethers in simple bis complexes was not possible with this ligand since only one geometric isomer of the dichloro complex could be isolated.

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