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First example of an imine addition to coordinated isonitrile

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Dedicated to Professor Bernhard Lippert as a sign of appreciation of his contributions to the platinum group metal chemistry.

Abstract

The interplay between *cis*-[$PtCl_2\{CNC_6H_3(2,6\text{-}Me_2)\}_2$] and $Ph_2C{=}NH$ results in the addition of benzophenone imine to one isonitrile ligand to yield the aminoimino-carbene *cis*-[$PtCl_2\{CNC_6H_3(2,6\text{-}Me_2)\}\{C(N{=}CPh_2)N(H)C_6H_3(2,6\text{-}Me_2)\}$]. The formulation of the latter compound is based on the coherent ^1H and $^{13}C\{^1H\}$ NMR and ESI-MS data. This adduct is not stable in solution even at room temperature leading to diamino-carbene *cis*-[$PtCl_2\{CNC_6H_3(2,6\text{-}Me_2)\}\{C(NH_2)N(H)C_6H_3(2,6\text{-}Me_2)\}$], which is, formally, the product of the addition of ammonia to one isonitrile ligand in *cis*-[$PtCl_2\{CNC_6H_3(2,6\text{-}Me_2)\}_2$].

Keywords: Isonitriles; Platinum(II) complexes; Imine; Nucleophilic addition; Aminoimino-carbene; Diamino-carbene

1. Introduction

Activation of unsaturated substrates by their coordination to metal centers, especially those molecules whose reactivity is not strongly pronounced, e.g., dinitrogen, nitriles or isonitriles, is currently a research area of a paramount importance [1–9]. The activation provided by metal centers can promote chemical transformations that are not feasible for the metal-free species [4–9].

Among the reactions of coordinated nitriles and isonitriles, special attention has been dedicated to their coupling with various types of nucleophiles, for instance, bearing HN donor centers; these reactions give a great variety of new ligated species with C–N bonds [4]. In this context, the additions of ammonia, primary or secondary amines to metal-complexed RCN [4] and RNC molecules [8] are well documented and this interplay brings about formation of the amidine $NH{=}C(R)NR'R''$ and the amino-carbene $C(NR'R'')N(H)R$ ligands, respectively.

In contrast to the additions of nucleophiles with sp^3-N donor centers, interaction of RCN and RNC ligands with sp^2-N nucleophiles such as imines is much less explored. Indeed, although the coupling between nitriles and imines [10–14] and heteroimines [15–19] at Pt centers has recently been observed by some of us, the corresponding reactions of metal-bound *isonitriles and imines* have never been reported up to date. In this work, we extended our previous studies on the addition of sp^2-N nucleophiles to platinum-bound nitriles to other Pt-ligated unsaturated substrates, *viz.* isonitriles $RN{\equiv}C$, and found the first example of RNC–imine integration to furnish an imino-carbene moiety. Isonitriles are isoelectronic with nitriles and since long have been the object of attention of some of us, namely toward their activation by coordination [7–9,20–30].

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2. Experimental

2.1. Materials and instrumentation

Solvents were obtained from commercial sources and used as received, while chloroform was conventionally dried over $CaCl_2$. Benzophenone imine (Aldrich) was used without additional purification. The complex *cis*/*trans*-$[PtCl_2(EtCN)_2]$ was prepared as previously described [31]. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ESI^+ mass-spectra were obtained on VARIAN 500-MS LC ion trap mass spectrometer. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. 1D (^1H, $^{13}C\{^1H\}$, ^{195}Pt) NMR spectra and 2D ($^1H,^1H$-COSY, $^1H,^{13}C$-HMQC, $^1H,^{13}C$-HSQC and $^1H,^{13}C$-HMBC) NMR correlation experiments were recorded on Bruker Avance II+ 400 and 500 MHz (UltraShield™ Magnets) spectrometers at ambient temperature. ^{195}Pt NMR chemical shifts are given relatively to $K_2[PtCl_6]$ (0.0 ppm).

2.2. Synthetic work

2.2.1. Synthesis of cis-$[PtCl_2\{CNC_6H_3(2,6\text{-}Me_2)\}_2]$ (**II**)

A suspension of *cis*/*trans*-$[PtCl_2(EtCN)_2]$ (0.38 g, 1 mmol) in $CHCl_3$ (20 mL) was refluxed for *ca.* 5 min until complete dissolution of the starting material, whereupon a solution of $C{\equiv}NC_6H_3(2,6\text{-}Me_2)$ (0.26 g, 2 mmol) in $CHCl_3$ (5 mL) was added. In *ca.* 5 min after the addition, a bright yellow precipitate started to release. The reaction mixture was refluxed for 3 h giving a bright yellow precipitate under a yellow supernatant solution. The precipitate was filtered off, washed with one portion of cold acetone (10 °C; 5 mL) and with three 15-mL portions of diethyl ether and dried *in vacuo* at 20–25 °C. An additional amount of **II** was obtained upon evaporation of the filtrate from the reaction mixture to *ca.* 1/2 and followed by the addition of diethyl ether (5 mL). Total yield is 90%, based on Pt. *Anal.* Calc. for $C_{18}H_{18}N_2Cl_2Pt$: C, 40.92; H, 3.43; N, 5.30. Found: C, 40.80; H, 3.24; N, 5.42%. ESI^+-MS, *m*/*z*: 529 [M+H]. IR spectrum (selected bands), cm^{-1}: 2920 m ν(C–H), 2205, 2230 s ν(C≡NR), 830 m δ(C–H) (aryl). ^1H NMR spectrum in $CDCl_3$, δ: 2.50 and 2.51 (s, 6*H*, Me), 7.17–7.33 (m, 3*H*, aryls). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 18.8 (Me), 128.5, 128.6, 130.7, 131.1, 136.2 (aryls), 117.4 (br, C≡NR). ^{195}Pt NMR in $CDCl_3$, δ: −2230 (120 Hz).

2.2.2. Reaction between **II** and $Ph_2C{=}NH$ taken in equimolar amounts

A solution of $Ph_2C{=}NH$ (0.018 g, 0.10 mmol) in $CHCl_3$ (5 mL) was added to a suspension of **II** (0.053 g, 0.10 mmol) in $CHCl_3$ (10 mL) and the reaction mixture was refluxed for *ca.* 2 h until homogenization forming a bright yellow solution with some opalescence. The solution was filtered off from small undissolved impurities, evaporated to dryness at 20–25 °C under a stream of dry N_2, and the yellow residue formed was washed with two 10-mL portions of diethyl ether and dried in air at 20–25 °C. The obtained solid residue (mixture of **III** and **IV**) was analyzed by ESI-MS, NMR and IR methods. ESI^+-MS, *m*/*z*: 748 $[M_{III}+K]^+$, 728 $[M_{IV}+H]^+$, 691 $[M_{III}-Cl+OH]^+$, 545 $[M_{IV}]$. ESI^-, *m*/*z*: 748 $[M_{III}+K]^-$, 708 $[M_{III}-H]^-$, 364 $[M_{III}+OH]^{2-}$. ^1H NMR spectrum in $CDCl_3$, δ: 2.08 (s, Me), 2.12 (s, Me), 6.10–7.54 (m, aryls). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 9.5 (Me), 11.5 (Me), 127.8, 128.3, 128.4, 128.5, 128.7, 128.8, 129.6, 130.0, 131.7, 132.4, 134.3, 135.7 (aryls; Supplementary Fig. 1S), 172.4 (N=*C*Ph_2), 196.2 (C=N). IR spectrum (selected bands), cm^{-1}: 3228 mw ν(N–H), 3187 mw ν(N–H), 2220 s ν(C≡N), 2196 s ν(C≡N), 1652 s ν(C=N), 1619 s ν(C=N), 1605 s ν(C=N), 1598 s ν(C=N), 1475 s ν(C=C), 782 s δ(C–H), 775 s δ(C–H). Slow evaporation of an acetone solution of the obtained solid in air at 20–25 °C for 1 d gives crystals of **IV** suitable for X-ray diffraction along with some non-crystalline material.

2.2.3. Interaction of cis-$[PtCl_2\{CNC_6H_3(2,6\text{-}Me_2)\}_2]$ and $Ph_2C{=}NH$ in 1:2 molar ratio

A solution of $Ph_2C{=}NH$ (0.036 g, 0.20 mmol) in $CHCl_3$ (5 mL) was added to a suspension of **II** (0.053 g, 0.10 mmol) in $CHCl_3$ (10 mL) and the reaction mixture was refluxed for *ca.* 2 h until homogenization forming a bright yellow solution. This solution was evaporated to dryness at 20–25 °C under a stream of dry N_2, and the yellow solid residue formed was washed with two 10-mL portions of diethyl ether and dried in air at room temperature. Slow evaporation of an acetone solution of the obtained solid in air at 20–25 °C for 1 d leads to crystals of **V** suitable for X-ray diffraction.

$[PtCl\{CNC_6H_3(2,6\text{-}Me_2)\}\{C(NH_2)N(H)C_6H_3(2,6\text{-}Me_2)\}(Ph_2C{=}NH)]Cl$ (**V**). *Anal.* Calc. for $C_{31}H_{32}N_4Cl_2Pt$: C, 51.24; H, 4.44; N, 7.71. Found: C, 51.34; H, 4.67; N, 7.53%. IR spectrum (selected bands), cm^{-1}: 3284 mw ν(N–H), 2196 s ν(C≡N), 1652 w ν(C=N), 1620 s ν(C=N), 1598 s ν(C=N), 1473 s ν(C=C), 775 s δ(C–H). ESI^+-MS, *m*/*z*: 691 $[M_{cation}-H]^+$. ^1H NMR spectrum in $(CD_3)_2CO$, δ: 2.32 (s, 6*H*, Me), 2.46 (s, 6*H*, Me), 7.10–7.78 (m, 16*H*, aryls). $^{13}C\{^1H\}$ NMR in $(CD_3)_2CO$, δ: 18.5 and 19.2 (Me), 119.2, 121.8, 128.9, 129.3, 130.2, 138.3, 140.2, 143.2 (aryls), 118.8 (C≡NR), 179.2 (N=*C*Ph_2), 194.6 (C=N). ^{195}Pt NMR in $(CD_3)_2CO$, δ: −2014 (120 Hz).

2.3. X-ray structure determinations

Intensity data for complexes **IV** and **V** were collected using a Bruker AXS-KAPPA APEX II diffractometer using graphite monochromated Mo Kα radiation. Data was collected at 150 K using omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all the observed reflections. Absorption corrections were applied using SADABS. Structure was solved by direct methods by using the SHELXS-97 package

[32] and refined with SHELXL-97 [33] with the WINGX graphical user interface [34]. All hydrogens were inserted in calculated positions. Least square refinement with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms gave $R_1 = 0.0299$ (**IV**) and 0.0390 (**V**). The maximum and minimum peaks in the final difference electron density maps are close to the platinum atoms.

3. Results and discussion

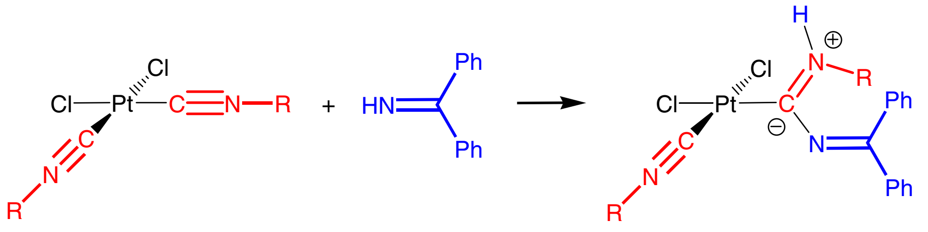
For this study we addressed, on one hand, the platinum(II) isonitrile complex *cis*-[PtCl$_2${*C*NC$_6$H$_3$(2,6-Me$_2$)}$_2$] and, on the other hand, benzophenone imine, Ph$_2$C=NH, which represents a stable imine useful as a model for reactivity studies [10–14].

A common method for preparation of isonitrile complexes of the type *cis*-[PtCl$_2$(CNR)$_2$] employs "the Magnus salts" [Pt(CNR)$_4$][PtCl$_4$], obtained from K$_2$[PtCl$_4$] and RNC in water, followed by thermolysis of [Pt(CNR)$_4$][PtCl$_4$] to furnish *cis*-[PtCl$_2$(CNR)$_2$] [35]. Other synthetic routes leading to *cis*-[PtX$_2$(CNR)$_2$] are also known and they include, e.g., substitution of two X$^-$ ligands in K$_2$[PtX$_4$] (X = Cl [36], SCN [37]) or replacement of 1,5-cyclooctadiene in *cis*-[PtCl$_2$(COD)] [38] with RNC. In our study, the complex *cis*-[PtCl$_2${*C*NC$_6$H$_3$(2,6-Me$_2$)}$_2$] (**II**) was prepared by substitution of the propiononitrile ligands from *cis*/*trans*-[PtCl$_2$(EtCN)$_2$] (**I**) (containing *ca.* 80% of the *cis* isomer; based on the data of ^{1}H NMR spectroscopy) with C≡NC$_6$H$_3$(2,6-Me$_2$). Thus, the reaction of **I** with C≡NC$_6$H$_3$(2,6-Me$_2$) in a molar ratio 1:2 in CHCl$_3$ upon reflux for *ca.* 2 h results in formation of **II**, which was isolated in *ca.* 90% yield; the mixture, based on ^{1}H NMR spectroscopy data, contains *ca.* 95% of the *cis*-isomer.

Complex **II** was characterized by elemental analyses, ESI mass-spectrometry, IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopies. In the IR spectrum, **II** shows no ν(N≡C) vibrations from the starting nitrile complex (2314 and 2342 cm^{-1}) [31], but the spectrum displays two very strong stretches at 2205 and 2230 cm^{-1}, corresponding to ν(C≡N) of the isonitrile ligands. The latter bands allow the assignment of the *cis*-configuration of **II** because usually in the corresponding symmetric *trans*-forms only one ν(C≡N) signal is observed [35]. In the ^{195}Pt NMR spectrum measured in CDCl$_3$, one resonance emerges at −2031 ppm and it corresponds to the sole isomer, while in the ^{13}C{^{1}H} spectrum, a weak and very broad (due to the unresolved ^{13}C–^{195}Pt coupling) signal at *ca.* 117 ppm, corresponding to the Pt-bound isonitrile moiety is observed.

The interaction between the isonitrile species in **II** and Ph$_2$C=NH has been studied in CDCl$_3$ by ^{1}H and ^{13}C{^{1}H} NMR and ESI-MS and it was found that this interplay results in *the previously unreported addition of an imine to one isonitrile* ligand leading to the aminoimino-carbene complex *cis*-[PtCl$_2${*C*NC$_6$H$_3$(2,6-Me$_2$)}-{*C*(N=CPh$_2$)N(H)C$_6$H$_3$(2,6-Me$_2$)}] (**III**) (Scheme 1). Thus, after mixing equimolar amounts of **II** and Ph$_2$C=NH, only one signal (*ca.* 178 ppm) corresponding to δ(C=N) from the free unreacted Ph$_2$C=NH was observed in the low-field region (150–200 ppm) of the ^{13}C{^{1}H} spectrum. After heating of the reaction mixture at 55 °C for 2 h, two new signals emerge (at *ca.* 196 and 172 ppm) and they belong to the *C*=N(H)R and N=*C*Ph$_2$ imine moieties from the newly formed *C*(N=CPh$_2$)N(H)C$_6$H$_3$(2,6-Me$_2$) ligand. The inspection of the low-field region of the ^{13}C{^{1}H} spectrum (Fig. 1S; see Supplementary material) of this reaction mixture allows the recognition not only of the resonances from those groups (including corresponding aryl/phenyl signals from carbene and imine species), but also of the aryl/phenyl resonances of the unreacted isonitrile ligand, and of the free Ph$_2$C=O originating from the hydrolysis of Ph$_2$C=NH (this was proved upon addition of commercially available Ph$_2$C=O to a sample of a reaction solution and repeated run of the spectrum). The ^{1}H and ^{13}C{^{1}H} peak assignment performed using the conventional 2D ^{1}H,^{1}H-COSY, ^{1}H, ^{13}C-HMQC/^{1}H,^{13}C-HSQC, and ^{1}H,^{13}C-HMBC correlation experiments supports the formulation of **III**. ESI$^+$ and ESI$^-$ mass-spectra of the reaction mixture measured after heating for 2 h shows the presence of the molecular ion and certain fragmentation peaks, whose isotopic patterns are in a good agreement with the calculated ones (ESI$^+$-MS, *m*/*z*: 748 [M+K]$^+$, 691 [M−Cl+OH]$^+$; ESI $^-$-MS, *m*/*z*: 748 [M+K]$^-$, 708 [M−H]$^-$, 364 [M+OH]$^{2-}$).

In the experiment, we also observed that **III** is not stable in solution, even at room temperature, and it is gradually converts to the diamino-carbene complex *cis*-[PtCl$_2$-{*C*NC$_6$H$_3$(2,6-Me$_2$)}{*C*(NH$_2$)N(H)C$_6$H$_3$(2,6-Me$_2$)}] (**IV**); all our attempts to isolate **III** as a solid failed. Complex **IV** (Fig. 1) is at least formally a known product of the addi-



II **III**

Scheme 1.

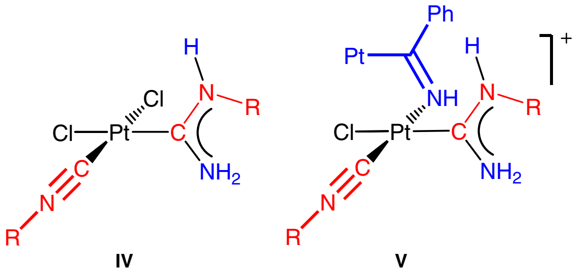


Fig. 1.

tion of ammonia to a Pt-bound isonitrile [8] and it could be formed by one of the following routes: (i) hydrolytic decomposition of **III** with formation of **IV** and liberating of the free $Ph_2C{=}O$, (ii) nucleophilic attack on platinum-bound RNC by ammonia, formed upon the hydrolysis of the free $Ph_2C{=}NH$. However, the current system does not allow the discrimination between these routes.

The influence of the molar ratio between the reactants (**II** and $Ph_2C{=}NH$) on the composition of products in the final reaction mixture and on the reaction rates in different solvents was additionally studied. Thus, when the molar ratio was 1:1, the reaction mixture after 2 h refluxing comprised **III** and **IV** in *ca.* equal proportions, while after 12 h under reflux it contained *ca.* 80% of **IV**. After one week at 20–25 °C, the reaction mixture contained *ca.* 50% of **IV**, along with some yet unidentified by-products. When the reaction was performed in a 1:2 molar ratio, $[PtCl\{\mathit{C}NC_6H_3(2,6\text{-}Me_2)\}\{\mathit{C}(NH_2)N(H)C_6H_3(2,6\text{-}Me_2)\}(Ph_2C{=}\mathit{N}H)]Cl$ (**V**), containing one coordinated benzophenone imine ligand was the isolated solid in *ca.* 80% yield.

The identification of **III**–**V** was performed using ESI-MS, 1D (^1H, $^{13}C\{^1H\}$) and 2D (^1H,^1H-COSY, ^1H,^{13}C-HMQC, ^1H,^{13}C-HSQC, and ^1H,^{13}C-HMBC) NMR experiments and X-ray diffraction (for **IV** and **V**). In addition, **V** was isolated in a pure form and characterized by elemental analyses (C, H, N).

The structures of **IV** and **V** have been determined by X-ray single-crystal diffraction (Figs. 2 and 3), and represent the first *crystallographic* evidence for the ammonia–isonitrile coupling products ligated to a Pt^{II} center. In the crystal unit of **IV**, two similar molecules are detected. In **IV**, the chlorides are in the *cis*-position [Pt(1)–Cl(11) 2.3228(16), Pt(1)–Cl(12) 2.366(2) Å] and one isonitrile $CNC_6H_3(2,6\text{-}Me_2)$ and one diamino-carbene $C(NH_2)N(H)C_6H_3(2,6\text{-}Me_2)$ complete the slightly distorted square planar environment [Cl(11)–Pt(1)–C(1) 177.38(18)°, Cl(12)–Pt(1)–C(11) 179.07(17)°]. The newly formed diamino-carbene ligand is in the *E*-configuration, and the $Pt–C_{carbene}$ [Pt(1)–C(11) 1.983(7) Å] bond distance is in a good agreement with that previously observed in the related complex $[Pt\{\eta^2\text{-}(S,S')\text{-}S_2C{=}C(C(O)Me)\}(CNBu^t)\{C(NEt_2)(NHBu^t)\}]$ [2.053(2) Å] [39], while the $C_{carbene}–N$ [C(11)–N(11) 1.295(8)] distance is slightly shorter than that in the former [1.334(3) Å] [39]. The C(1)–N(1) triple bond of the unreacted isonitrile moiety [1.152(9) Å] is of a typical value for platinum complexes containing the $CNC_6H_3(2,6\text{-}Me_2)$ ligand, e.g., as reported in $[Pt\{\eta^2\text{-}(S,S')\text{-}S_2C{=}C\{C(O)Me\}_2\}\{CNC_6H_3\text{-}(2,6\text{-}Me_2)\}_2]$ [1.152(3) Å] [39]. All other bond lengths are of normal values and agree with those observed in related platinum(II) aminocarbene and isonitrile complexes [8,9].

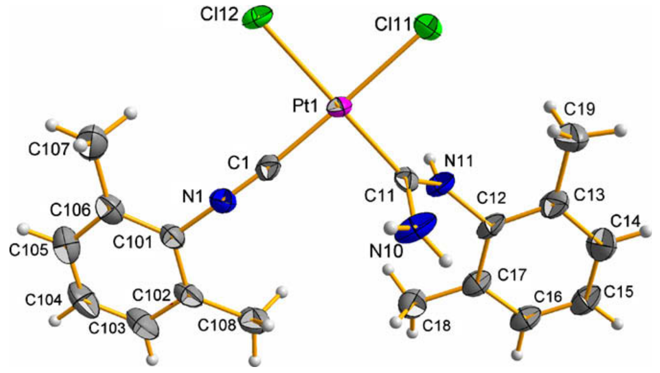


Fig. 2. Thermal ellipsoid view of complex **IV** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (°): Pt(1)–C(1) 1.884(6), Pt(1)–Cl(11) 2.3228(16), C(1)–N(1) 1.152(9), Pt(1)–C(11) 1.983(7), C(11)–N(10) 1.333(9), C(11)–N(11) 1.295(8), N(11)–C(12) 1.435(10), N(1)–C(101) 1.385(9), Pt(1)–C(1)–N(1) 175.8(7), Cl(11)–Pt(1)–C(1) 177.38(18), Cl(12)–Pt(1)–C(11) 179.07(17), C(1)–N(1)–C(101) 170.5(6), C(11)–N(11)–C(12) 128.0(6).

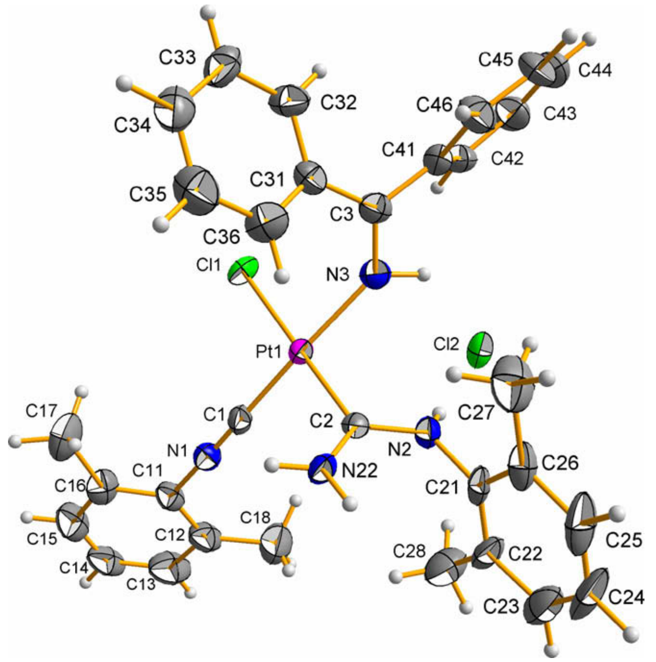


Fig. 3. Thermal ellipsoid view of complex **V** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (°): Pt(1)–C(1) 1.890(7), Pt(1)–C(2) 1.995(6), Pt(1)–Cl(1) 2.3613(15), Pt(1)–N(3) 2.038(6), C(1)–N(1) 1.151(9), C(2)–N(2) 1.330(8), N(3)–C(3) 1.279(9), C(2)–N(22) 1.310(8), N(1)–C(11) 1.415(9), N(2)–C(21) 1.441(8), Cl(1)–Pt(1)–(C2) 179.13(17), C(1)–Pt(1)–N(3) 171.6(3), Pt(1)–C(1)–N(1) 172.2(6), Pt(1)–C(2)–N(2) 119.8(4), Pt(1)–N(3)–C(3) 135.6(5), C(1)–N(1)–C(11) 175.2(7), C(2)–N(2)–C(21) 125.2(6).

The coordination polyhedron of **V** is a slightly distorted square plane [Cl(1)–Pt(1)–(C2) 179.13(17)°, C(1)–Pt(1)–N(3) 171.6(3)°]. In **V**, the chloride is in the *trans* position to the diamino-carbene ligand $C(NH_2)N(H)C_6H_3(2,6\text{-}Me_2)$, with the coordinated benzophenone imine $Ph_2C{=}NH$ and one isonitrile $CNC_6H_3(2,6\text{-}Me_2)$ completing the coordination environment. The carbene ligand is in the *E*-configuration and both $Pt{-}C_{carbene}$ [Pt(1)–C(2) 1.995(6) Å] and $C_{carbene}{-}N$ [C(2)–N(2) 1.330(8) Å] distances are in a good agreement with those previously observed in the related diamino-carbene complex $[Pt\{\eta^2\text{-}(S,S')\text{-}S_2C{=}C(C(O)Me)\}(CNBu^t)\{C(NEt_2)(NHBu^t)\}]$ [2.053(2) and 1.334(3) Å, correspondingly] [39]. The C(1)–N(1) triple bond of the isonitrile ligand [1.151(9) Å] is of a normal value for the triple CN bond and coherent with that observed in the related isocyanide platinum complex $[Pt\{\eta^2\text{-}(S,S')\text{-}S_2C{=}C\{C(O)Me\}_2\}\{CNC_6H_3(2,6\text{-}Me_2)\}_2]$ [1.152(3) Å] [39]. The Pt(1)–N(3) distance [2.038(6) Å] between the metal atom and the ligated $Ph_2C{=}NH$ agrees with that reported in the related (benzophenone imine)Pt^{II} complexes, e.g., $[PtCl_2(Ph_2C{=}NH)(R_2SO)]$ [2.017–2.024 Å] [40]. In the $Ph_2C{=}NH$ moiety, the distance C(3)–N(3) [1.279(9) Å] is of a typical C=N bond, and its value correlates with that in $[PtCl_2(Ph_2C{=}NH)(R_2SO)]$ [1.26–1.29 Å] [40]. All other bond lengths are of normal values and they agree with those reported for related platinum(II) aminocarbene and isonitrile complexes [8,9].

In both complexes **IV** and **V**, the $C{=}N(H)C_{aryl}$ moiety of the diamino-carbene ligands is roughly planar and the C=N bond has a double bond character, what is accounted for by the greater weight of the form $^{-}C({=}N^{+}HR)(NH_2)$ relatively to $^{-}C(NHR)({=}N^{+}H_2)$.

4. Conclusions

To summarize, we observed the first example of reaction between a Pt-bound isonitrile and an imine, i.e., $Ph_2C{=}NH$, which results in the addition of the latter to the former species to give the aminoimino-carbene complex *cis*-$[PtCl_2\{CNC_6H_3(2,6\text{-}Me_2)\}\{C(N{=}CPh_2)N(H)C_6H_3(2,6\text{-}Me_2)\}]$ (**III**). This addition product is not stable in solution, even at room temperature, and it converts to *cis*-$[PtCl_2\{CNC_6H_3(2,6\text{-}Me_2)\}\{C(NH_2)N(H)C_6H_3(2,6\text{-}Me_2)\}]$ (**IV**). Further works of our group in this direction will be focused on the extension of this type of reaction to other imines and isonitriles with the aim to discover more chemically stable systems and to investigate their properties.

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Appendix A. Supplementary material

CCDC 670267 and 670268 contain the supplementary crystallographic data for *cis*-$[PtCl_2\{CNC_6H_3(2,6\text{-}Me_2)\}\{C(NH_2)N(H)C_6H_3(2,6\text{-}Me_2)\}]$ and $[PtCl\{CNC_6H_3(2,6\text{-}Me_2)\}\{C(NH_2)N(H)C_6H_3(2,6\text{-}Me_2)\}(Ph_2C{=}NH)]Cl$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.02.026.

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