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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