Inorganica Chimica Acta xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Studies on the Ru(II) monocationic complexes $[RuCl_2(NO)(P–N)(PR_3)]PF_6$, where P–N = *o*-diphenylphosphino-*N*,*N*-dimethylaniline, and R = Ph and *p*-X-C_6H_4 (X = OMe, Me, F)

Juliana P. da Silva [a], Francisco D. Fagundes [a], Davi F. Back [b], Javier Ellena [c], Brian R. James [d], Márcio P. de Araujo [a,*]

[a] Departamento de Química, Universidade Federal do Paraná, Centro Politécnico, CP 19081, CEP 81531-980 Curitiba (PR), Brazil
[b] Departamento de Química, UFSM, CEP 97105-900 Santa Maria (RS), Brazil
[c] Instituto de Física de São Carlos, Universidade de São Paulo, CEP 13560-970 São Carlos (SP), Brazil
[d] Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada

ARTICLE INFO

Article history:
Received 27 September 2015
Received in revised form 23 November 2015
Accepted 29 November 2015
Available online xxxx

Keywords:
Ruthenium nitrosyl
Phosphorus–nitrogen ligand
Triarylphosphines
^{31}P NMR
Electrochemistry
ESI-MS

ABSTRACT

Reaction of *fac*-$[RuCl_3(NO)(P–N)]$ **(1)** with the triarylphosphines PR_3 in MeOH allows for isolation of the monocationic Ru(II) complexes $[RuCl_2(NO)(P–N)(PR_3)]PF_6$; P–N = *o*-diphenylphosphino-*N*,*N*-dimethylaniline, and R = *p*-MeO-C_6H_4 (complex **2**), *p*-Me-C_6H_4 (**3**), Ph (**4**), and *p*-F-C_6H_4 (**5**). The complexes were characterized by elemental analysis, $^{31}P\{^1H\}$, ^1H NMR and IR spectroscopies, ESI-MS, CV, and X-ray structural data for complexes **3**–**5**. The $^{31}P\{^1H\}$ spectra display two doublets with $^2J_{pp}$ values consistent with *cis* P-atoms. The ESI-MS spectra reveal the molecular ion $[RuCl_2(NO)(P–N)(PR_3)]^+$ and the fragmentation ions $[M–PR_3]^+$, $[M–PR_3–Cl]^+$, and $[M–PR_3–2Cl]^+$. CV data show a one-electron, quasi-reversible reduction process centred at the Ru–NO unit that depends on the pK_a of the PR_3. The IR spectra reveal ν_{NO} bands for coordinated NO^+. A known, empirical inverse correlation between the δ_P value and the Ru–P bond length of the P–N ligand that exists for a series of *cis*- and *trans*-$RuX_2(L)(P–N)(PR_3)$ complexes (X = Cl or Br), where L is a range of small molecules, is extended with L = NO^+ and now covers the respective ranges of about 30–80 ppm and 2.39–2.17 Å.

1. Introduction

The chemistry of transition metal nitrosyl complexes is extensive, resulting from the flexibility of NO to coordinate in forms ranging from NO^+ to NO^- [1]. Ruthenium nitrosyl complexes have raised special interest in the inorganic medicinal field because of photolytic release of the biologically important NO [2]; indeed the importance of this topic has led a journal entitled 'Nitric Oxide' that deals with research basic and clinical topics [3].

On more inorganic aspects, coordinated NO^+ provides one of the strongest *trans* structural effects [4]. The NO^+ affects not only the *trans* metal-L bond [4], but also all the coordinated ligands; coordinated NO^+ dramatically changes the electron density over the metal center, due to strong M → NO^+ π-back-bonding. These changes become evident through the M–$L_{(cis\ or\ trans)}$ bond strength, NMR chemical shifts and coupling constants, and metal-centered electron-transfer processes [5].

One of our groups has reported on *fac*-$[RuCl_3(NO)(P–N)]$ (complex **1**), the first Ru nitrosyl to contain a phosphorus–nitrogen ligand, specifically *o*-diphenylphosphino-*N*,*N*-dimethylaniline; exposure of this complex to white light generates the structurally characterized *mer*,*trans*-isomer, where NO is trans to the P-atom [6,7]. Both complexes are $Ru^{II}(NO^+)$ species, with the typical Ru–N–O bond angle of ~180° [1,6–8].

The current paper reports on an initial test reaction of **1** with PPh_3 in the presence of NH_4PF_6 that generates $[RuCl_2(NO)(P–N)(PPh_3)]PF_6$ (complex **4**), again a $Ru^{II}(NO^+)$ species, and we realized that this was an analogue of the known series of *cis*- and *trans*-$RuX_2(L)(P–N)(PR_3)$ complexes (X = Cl or Br), where L is a range of small molecules [9], L now being NO^+. In this series (some 10 species with R = Ph or *p*-tolyl), a noteworthy, empirical inverse correlation between the δ_P chemical shift and the Ru–P bond length (of the P–N ligand) exists over the respective ranges of ~40–80 ppm and 2.34–2.17 Å [9]. To our pleasant surprise, the ^{31}P and structural data for the cationic species **4** extend the correlation significantly (see Section 3.3), and a theoretical DFT study on the $RuX_2(L)(P–N)(PR_3)$ (R = Ph, *p*-tolyl) complexes to attempt to interpret the

* Corresponding author.
E-mail address: mparaujo@ufpr.br (M.P. de Araujo).

http://dx.doi.org/10.1016/j.ica.2015.11.030
0020-1693/

correlation is in progress [10]. As a further step in a theoretical understanding of the correlation, wider variation in the PR_3 ligand was considered a worthwhile study, and this paper reports on the isolation and extensive characterization of $[RuCl_2(NO)(P–N)(PR_3)]PF_6$ complexes (R = Ph, and *p*-X-C_6H_4 where X = OMe, Me, F) in order to later probe and interpret theoretically any observed trends.

2. Experimental

2.1. Materials and instrumentation

$RuCl_3{\cdot}3H_2O$ was generously donated by Johnson Matthey plc., and was used as received. The PR_3 phosphines were also used as received; the R = Ph, *p*-Me-C_6H_4, and *p*-F-C_6H_4 phosphines were Aldrich products, whereas the R = *p*-OMe compound was obtained from Acros. The P–N ligand [11] and *fac*-$[RuCl_3(NO)(P–N)]$ (**1**) [6,7] were made by the reported methods. Solvents were dried and degassed before use, and manipulations involving solutions of the complexes were performed under Ar using standard Schlenk techniques. The strong IR bands for the coordinated NO were recorded (in cm^{-1}, resolution of 2 cm^{-1}) as KBr pellets, and in CH_2Cl_2 solution, on a Bomem-Michelson 102 spectrophotometer. Cyclic voltammetry (CV) experiments were carried out at r.t. (room temperature, ~20 °C) on an Ivium Compacstat potentiostat/galvanostat with stationary, Pt foil working and auxiliary electrodes, and an Ag/AgCl reference electrode in a Luggin capillary probe. A 0.10 M MeCN solution of $Bu_4N^+ClO_4^-$ (Fluka Purum grade) was used as supporting electrolyte; in these conditions, the $E_{1/2}$ of the Fc^+/Fc couple was 516 mV with $E_{pa} - Epc$ = 79 mV. ESI-MS experiments were conducted on a Thermo Fisher Scientific Inc. LTQ XL Linear Ion Trap Mass Spectrometer with Software Xcalibur 2.1 processing, the sample concentrations in CH_2Cl_2 being ~10 μg/mL. Elemental analyses were performed in the Chemistry Department of the Universidade Federal de São Carlos, using a Fisons CHNS, mod. EA 1108 elemental analyzer. NMR data (81 MHz for $^{31}P\{^1H\}$, and 200 MHz for ^1H) were acquired at r.t. in CH_2Cl_2 for $^{31}P\{^1H\}$, and in $CDCl_3$ for ^1H (except for complex **2** when CD_2Cl_2 was used for solubility reasons), on a Bruker DRX-200 spectrometer. Chemical shifts are reported with respect to the phosphorus signal of 85% H_3PO_4 for ^{31}P and the residual solvent proton for ^1H. Multiplicities were abbreviated as follows: s, singlet; d, doublet; m, multiplet; bs, broad singlet; and bd, broad doublet. *J* values are given in Hz.

2.2. Syntheses of the $[RuCl_2(NO)(P–N)(PR_3)]PF_6$ complexes

PR_3 and NH_4PF_6 were added to a solution of *fac*-$[RuCl_3(NO)(P–N)]$ (**1**) in MeOH (5 mL) and the resulting orange suspension was refluxed for 3 h, except for the P(*p*-Me-C_6H_4)$_3$ system when reaction occurred at r.t. After being cooled to room temperature, the resulting yellow suspensions of complexes **3**–**5** were filtered to give a yellow solid that was washed with H_2O (2 × 5 mL), MeOH (2 × 5 mL) and Et_2O (2 × 5 mL), and then dried *in vacuo*. In the case of complex **2**, the reaction generated a clear yellow solution; the solvent was removed *in vacuo* to give a yellow residue that was then largely dissolved in CH_2Cl_2 (5 mL), and the mixture was filtered through Celite. Addition of *n*-hexane (15 mL) yielded a yellow solid that was then treated as described above. The *mer*, *trans*-isomer of **1** [6,7] could also be used as the precursor for syntheses using the same methodology, which gave similar product yields.

2.2.1. $[RuCl_2(NO)(P–N)\{P(p\text{-}MeO\text{-}C_6H_4)_3\}]PF_6$ (**2**)

Complex **1** (50 mg, 0.092 mmol), P(*p*-MeO-C_6H_4)$_3$ (36 mg, 0.102 mmol) and NH_4PF_6 (75 mg, 0.460 mmol) yielded 65 mg of **2** (70%). *Anal.* Calc. for $C_{41}H_{41}N_2O_4Cl_2F_6P_3Ru$: C, 49.0; H, 4.1; N, 2.8. Found: C, 49.2; H, 4.0; N, 2.8%. IR: ν_{NO} 1867 s (KBr) and 1872 s (CH_2Cl_2). $^{31}P\{^1H\}$ NMR: δ 30.4 (d, *P*–N), 24.6 (d, *P*R_3); $^2J_{PP}$ = 18.65. ^1H NMR: δ 8.00–6.78 (m, 26H, aromatic), 3.82 (s, 9H, *p*-OMe), 3.66 (bd, 3H, NMe), 3.18 (bd, 3H, NMe).

2.2.2. $[RuCl_2(NO)(P–N)\{P(p\text{-}Me\text{-}C_6H_4)_3\}]PF_6$ (**3**)

Complex **1** (50 mg, 0.092 mmol), P(*p*-Me-C_6H_4)$_3$ (33 mg, 0.110 mmol) and NH_4PF_6 (75 mg, 0.460 mmol) yielded 66 mg (75%) of **3**. *Anal.* Calc. for $C_{41}H_{41}N_2OCl_2F_6P_3Ru$: C, 51.5; H, 4.3; N, 2.9. Found: C, 51.9; H, 4.2; N, 2.8%. IR: ν_{NO} 1863 s (KBr) and 1874 s (CH_2Cl_2). $^{31}P\{^1H\}$ NMR: δ 30.5 (d, *P*–N), 25.8 (d, *P*R_3); $^2J_{PP}$ = 18.50. ^1H NMR: δ 8.06–6.74 (m, 26H, aromatic); 3.69 (bd, 3H, NCH_3); 3.20 (bs, 3H, NCH_3); 2.34 (s, 9H, P(*p*-CH_3-C_6H_4)$_3$).

2.2.3. $[RuCl_2(NO)(P–N)(PPh_3)]PF_6$ (**4**)

Complex **1** (50 mg, 0.092 mmol), PPh_3 (26 mg, 0.101 mmol) and NH_4PF_6 (75 mg, 0.460 mmol) yielded 80 mg of **4** (95%). *Anal.* Calc. for $C_{38}H_{35}N_2OCl_2F_6P_3Ru$: C, 49.9, H, 3.9, N, 3.1. Found: C, 49.5; H, 3.8; N, 3.0%. IR: ν_{NO} 1853 s (KBr) and 1875 s (CH_2Cl_2). $^{31}P\{^1H\}$ NMR: δ 30.9 (d, *P*–N), 26.3 (d, *P*R_3); $^2J_{PP}$ = 17.80. ^1H NMR: δ 8.05–6.78 (m, 29H, aromatic); 3.71 (bd, 3H, NCH_3); 3.25 (bd, 3H, NCH_3).

2.2.4. $[RuCl_2(NO)(P–N)\{P(p\text{-}F\text{-}C_6H_4)_3\}]PF_6$ (**5**)

Complex **1** (50 mg, 0.092 mmol), P(*p*-F-C_6H_4)$_3$ (32 mg, 0.101 mmol) and NH_4PF_6 (75 mg, 0.460 mmol) yielded 85 mg of **5** (95%). *Anal.* Calc. for $C_{38}H_{32}N_2OCl_2F_9P_3Ru$: C, 47.1; H, 3.3; N, 2.9. Found: C, 46.9; H, 3.2; N, 2.9%. IR: ν_{NO} 1870 s (KBr) and 1877 s (CH_2Cl_2). $^{31}P\{^1H\}$ NMR: δ 31.5 (d, *P*–N), 24.3 (d, *P*R_3); $^2J_{PP}$ = 18.72. ^1H NMR (CD_2Cl_2): δ 8.02–6.83 (m, 26H, aromatic); 3.72 (bd, 3H, NCH_3); 3.20 (bd, 3H, NCH_3).

2.3. X-ray crystallography

X-ray quality, single-crystals of **3**·CH_2Cl_2, **4** and **5** were grown by slow evaporation of CH_2Cl_2 solutions of the complexes, and the molecular structures were solved at 293 K using graphite-monochromatized Mo Kα radiation (0.71073 Å). Such a crystal for **2** could not be made. Data for **3** were acquired on a Bruker APEX II CCD diffractometer, and the structures were solved by direct method using SHELXS [12]. Subsequent Fourier-difference map analyses provided the positions of the non-H-atoms with refinements carried out with the SHELXL package using full-matrix least squares on F^2 with anisotropic displacement parameters [13]. H-atoms were included in the refinement at the calculated positions. Data for **4** and **5** were acquired using the COLLECT program [14] on an Enraf-Nonius Kappa-CCD diffractometer. The final unit cell parameters were based on all reflections that were integrated and scaled with the HKL Denzo-Scalepack programs system [15], a Gaussian absorption correction being applied [16]. The structures were solved by direct methods, with the aid of the SHELXS-97 program [12], with refining done by full-matrix least squares on F^2 using SHELXL-97 [13]. All H-atoms were stereochemically positioned and refined with the riding model [17]. Table S1 (Supplementary information) summarizes selected crystallography data.

3. Results and discussion

3.1. Synthesis and characterization of complexes **2**–**5**

The syntheses of complexes **2**–**5** are outlined in Chart 1; the solid state structures of **3**–**5** were established by X-ray crystallography, and NMR data in $CDCl_3/CD_2Cl_2$ solutions are consistent with the same structure.