Inorganica Chimica Acta 379 (2011) 81–89

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

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

^{1}D and ^{2}D Nuclear magnetic resonance of new silver(I) complexes with achiral and chiral bases as ligands: Crystal structure of $[Ag\{(S)\text{-}(6\text{-}CH_3)C_5H_3N\text{-}CHN\text{-}C{*}H(\alpha\text{-}CH_3)C_6H_5\}(PPh_3)_2](O_3SCF_3)$

Olga Cifuentes [a], Raúl Contreras [a,*], Antonio Laguna [b,*], Olga Crespo [b]

[a] Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago-6094411, Chile
[b] Departamento de Química Inorgánica, Universidad de Zaragoza-CSIC, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Pedro Cerbuna 12, 50009 Zaragoza, Spain

ARTICLE INFO

Article history:
Received 6 May 2011
Received in revised form 13 September 2011
Accepted 16 September 2011
Available online 24 September 2011

Keywords:
Silver
Schiff bases
Nuclear magnetic resonance

ABSTRACT

Treatment of equimolar amounts of substituted aniline or amine with substituted benzaldehyde leads to the corresponding achiral or chiral Schiff bases (L). The reaction of the bases with $[Ag(O_3SCF_3)(PPh_3)]$ leads to the preparation of three or four coordinated cationic complexes, $[Ag(k^1\text{-}L)(PPh_3)_n]^+$ ($n = 1$ or 2) which have been characterized by IR, ^{1}D and ^{2}D NMR spectroscopy. The crystal structure of $[Ag\{(S)\text{-}(6\text{-}CH_3)C_5H_3N\text{-}CHN\text{-}C{*}H(\alpha\text{-}CH_3)C_6H_5\}(PPh_3)_2](O_3SCF_3)$ is reported.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The chemistry of silver(I) complexes has attracted an increased interest during last years, due to both their structural features and their potential applications. Silver(I) complexes with nitrogen ligands have proved to be valuable candidates in medicine, catalysis or materials science. Polydentate ligands should offer different coordination sites, thus dictating different coordination geometries around the metal centre and the possibility to obtain monomeric or polymeric species [1–27]. The use of Schiff bases as ligands can increase the biological activity of many of their metallic coordination complexes, i.e. as anti-influenza, antibacterial or as antitumoral agents [28–36]. Nevertheless, not many complexes of this type have been described until now with silver(I) [37–46]. Among them, different types of Schiff bases, e.g. containing heteroaromatic benzimidazole and benzithiale rings [40], *N*,*N* chelating moieties [41], cryptands [38] or other substituents, have been used as ligands in the silver(I) chemistry.

Herein we describe the synthesis, characterization and reactivity of silver three or four coordinated complexes with the Schiff bases shown in Fig. 1 as ligands.

2. Experimental

2.1. General

The starting complex $[Ag(O_3SCF_3)(PPh_3)]$ [47] and the Schiff bases [48–52] were synthesized by similar procedures to those described in literature. FT-IR spectra (KBr pellet) were obtained on a model Vector-22 Bruker spectrophotometer. ^{1}H, ^{19}F, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AC-200P and Bruker-400 spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 in D_2O (^{31}P) (positive shifts downfield) as external standards, respectively. The values of the coupling constants ($^1J_{C-H}$) of the ligands and complexes synthesized were determined by means of the experiment of HMBC (^{2}D NMR).

2.2. Synthesis of the Schiff bases

The new Schiff bases used in this work (Fig. 1): $O_2NC_6H_4\text{-}CHN\text{-}CH_2C_6H_4(4\text{-}CH_3)$ (**L$_1$**), $(CH_3)_2NC_6H_4\text{-}CHN\text{-}CH_2C_6H_5$ (**L$_2$**), $(CH_3)_2NC_6H_4\text{-}CHN\text{-}CH_2C_6H_4(4\text{-}CH_3)$ (**L$_3$**), $C_6H_4N\text{-}CHN\text{-}CH_2C_6H_5$ (**L$_4$**), $C_6H_4N\text{-}CHN\text{-}CH_2C_6H_4(4\text{-}Cl)$ (**L$_5$**), $C_6H_4N\text{-}CHN\text{-}CH_2C_6H_4(4\text{-}CH_3)$ (**L$_6$**), (S)-(−)-$(6\text{-}CH_3)C_5H_3N\text{-}CHN\text{-}C{*}H(\alpha\text{-}CH_3)C_6H_5$ (**L$_7$-$*$C$_S$**) and (S)-(−)-$C_5H_4N\text{-}CHN\text{-}C{*}H(\alpha\text{-}CH_3)C_6H_5$ (**L$_8$-$*$C$_S$**) were synthesized by similar methods to those described in the bibliography [48–52], by condensing equimolar amounts of different amines and

---

* Corresponding authors.
E-mail address: alaguna@unizar.es (A. Laguna).

0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2011.09.033

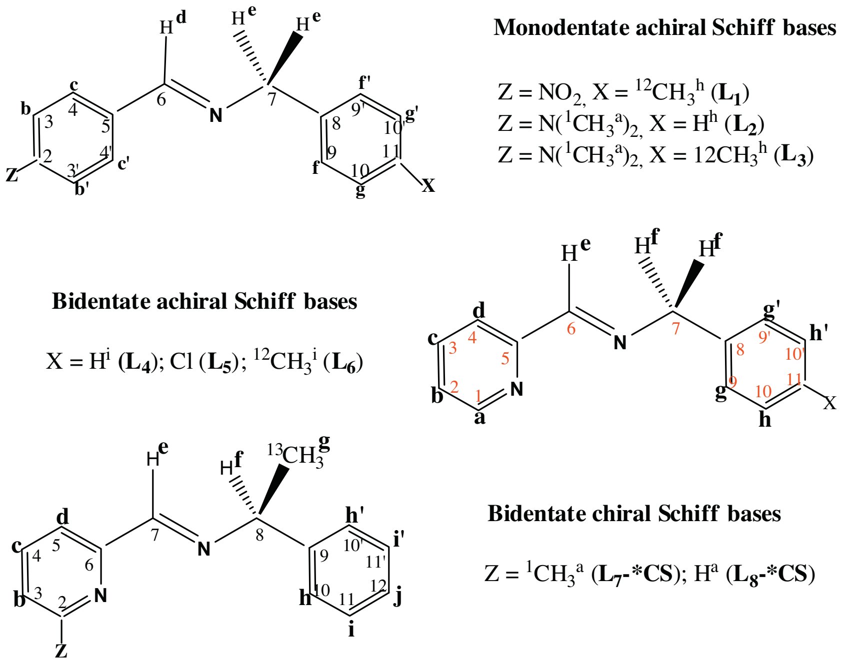

Fig. 1. Schiff bases $\mathbf{L}_1$–$\mathbf{L}_8$.

the respective substituted aldehydes, under continuous stirring. Reaction times and temperature (room or refluxing temperature) conditions are detailed below.

2.2.1. Monodentate achiral Schiff bases ($\mathbf{L}_1$–$\mathbf{L}_3$)

2.2.1.1. $O_2NC_6H_4$-CHN-$CH_2C_6H_4$(4-CH_3) ($\mathbf{L}_1$). A solution of 4-methylbenzylamine (1000 mg, 8.3 mmol), 4-nitrobenzaldehyde (1250 mg, 8.3 mmol) and glacial acetic acid (0.2 mL) in 3 mL of dichloromethane was stirred for 3 days at room temperature and protected from light. The solution was evaporated under vacuum and the beige residue washed with cold dichloromethane. Yield, 97%. FT-IR: $\nu_{(C=N)im} = 1638.2\ cm^{-1}$. *Anal.* Calc. for $C_{15}H_{14}N_2O_2$ ($M = 254.29$ g/mol): C, 70.85; H, 5.55; N, 11.0. Found: C, 71.2; H, 5.8; N, 11.9%. ^{1}H NMR (acetone-d_6): δ 8.60 (s, ^1H_d), 8.29 (d, $2H_{b,b'}$ $^3J = 8.8$ Hz,), 8.05 (d, $2H_{c,c}$, $^3J = 8.8$ Hz,), 7.25 (d, $2H_{f,f'}$, $^3J = 8.0$ Hz,), 7,16 (d, $2H_{g,g'}$, $^3J = 8.0$ Hz,), 4.82 (s, $2H_e$), 2.30 (d, ^1H_h). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 149.1 (C_2), 123.7 ($C_{3,3'}$, $^1J = 173.5$ Hz), 129.0 ($C_{4,4'}$, $^1J = 168.0$ Hz), 142.1 (C_5), 159.6 (C_6, $^1J = 162.8$ Hz), 64.5 (C_7, $^1J = 135.4$ Hz), 136.4 (C_8), 128.0 ($C_{9,9'}$, $^1J = 156.2$ Hz), 128.9 ($C_{10,10'}$, $^1J = 156.2$ Hz), 136.3 (C_{11}), 20.3 (C_{12}, $^1J = 125.0$ Hz).

2.2.1.2. $(CH_3)_2NC_6H_4$-CHN-$CH_2C_6H_5$ ($\mathbf{L}_2$). A solution of benzylamine (500 mg, 4.7 mmol) and 4-(dimethylamine)benzaldehyde (450 g, 3.0 mmol) in 3 mL of ethanol was stirred for 3 days at room temperature and protected from light. Upon cooling a beige solid precipitated, which was filtered, washed with cold ethanol and dried under vacuum. Yield, 41%. *Anal.* Calc. for $C_{16}H_{18}N_2$ ($M = 238.33$ g/mol): C, 80.63; H, 7.61; N, 11.75. Found: C, 79.64; H, 9.18; N, 11.64%. FT-IR: $\nu_{(C=N)im} = 1638.6\ cm^{-1}$. ^{1}H NMR (acetone-$d_6$): δ 8.31 (s, ^1H_d), 7.65 (d, $2H_{c,c'}$, $^3J = 9.0$ Hz), 7.34 (dd, $2H_{f,f'}$, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz), 7.32 (t, $2H_{g,g'}$, $^3J = 7.6$ Hz), 7.22 (dt, H_h, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz), 6.75 (d, $2H_{b,b'}$, $^3J = 9.0$ Hz), 4.71 (s, $2H_e$), 3.00 (s, $6H_a$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 40.3 (C_1, $^1J = 144.1$ Hz), 153.3 (C_2), 112.5 ($C_{3,3'}$, $^1J = 155.1$ Hz), 130.4 ($C_{4,4'}$, $^1J = 155.1$ Hz), 125.8 (C_5), 162.1 (C_6; ^1J = not resolved), 65.5 (C_7, $^1J = 137.7$ Hz), 141.8 (C_8), 128.8 ($C_{9,9'}$, $^1J = 158.8$ Hz), 129.1($C_{10,10'}$; $^1J = 158.8$ Hz), 127.4 (C_{11}, $^1J = 155.1$ Hz).

2.2.1.3. $(CH_3)_2NC_6H_4$-CHN-$CH_2C_6H_4$(4-CH_3) ($\mathbf{L}_3$). A solution of 4-methylbenzylamine (200 mg, 1.65 mmol) and 4-(dimethylamine)benzaldehyde (160 mg, 1.07 mmol) in 3 mL of ethanol was stirred for 3 days at room temperature and protected from light. Upon cooling a beige solid precipitated, which was filtered, washed with cold ethanol and dried under vacuum. Yield, 66%. *Anal.* Calc. for $C_{17}H_{20}N_2.0.75H_2O$ ($M = 264.87$ g/mol): C, 77.09; H, 8.18; N, 10.58. Found: C, 77.26; H, 9.75; N, 10.24%. FT-IR: $\nu_{(C=N)im} = 1634.7\ cm^{-1}$. ^{1}H NMR (acetone-$d_6$): δ 8.29 (s, ^1H_d), 7.64 (d, $2H_{c,c'}$, $^3J = 8.8$ Hz), 7.22 (d, $2H_{f,f}$, $^3J = 8.0$ Hz), 7.13 (d, $2H_{\acute{g},g'}$, $^3J = 8.0$ Hz,), 6.75 (d, $2H_{b,b'}$, $^3J = 8.8$ Hz), 4.67 (s, $2H_e$), 3.00 (s, $6H_a$), 2.30 (s, $3H_h$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 40.3 (C_1, $^1J = 140.3$ Hz), 153.3 (C_2), 112.5 ($C_{3,3'}$, $^1J = 155.8$ Hz), 130.3 ($C_{4,4'}$, $^1J = 155.8$ Hz); 125.9 (C_5), 161.8 (C_6, ^1J = not resolved), 65.4 (C_7, $^1J = 131.2$ Hz), 138.7 (C_8), 128.7 ($C_{9,9'}$, $^1J = 154.2$ Hz), 129,8 ($C_{10,10'}$, $^1J = 154.2$ Hz), 136.7 (C_{11}), 21.2 (C_{12}, $^1J = 124.4$ Hz).

2.2.2. Bidentate achiral Schiff bases ($\mathbf{L}_4$–$\mathbf{L}_6$)

2.2.2.1. C_5H_4N-CHN-$CH_2C_6H_5$ ($\mathbf{L}_4$). A solution of benzylamine (200 mg, 1.87 mmol) and 2-pyridinecarboxaldehyde (200 mg, 1.87 mmol in 3 mL of water was stirred for 3 days at refluxing temperature and protected from light. During this time it is observed the formation of a yellow oil, which was isolated. Yield, 65%. *Anal.* Calc. for $C_{13}H_{12}N_2.0.5H_2O$ ($M = 205.26$ g/mol): C, 76.07; H, 6.38; N, 13.65. Found: C, 76.92; H, 8.22; N, 13.50%. FT-IR: $\nu_{(C=N)im} = 1647.2$, $\nu_{(C=N)py} = 1586.7\ cm^{-1}$. ^{1}H NMR (acetone-$d_6$): δ 8.65 (d, H_d, $^3J = 4.8$ Hz), 8.51 (s, H_e), 8.08 (d, H_a, $^3J = 8.0$ Hz), 7.83 (t, H_b, $^3J = 8.0$ Hz), 7.41 (dd, $H_{g,g'}$, $^3J = 6.0$ Hz, $^4J = 1.2$ Hz, 2H), 7.39 (t, H_c, $^3J = 6.4$ Hz), 7.37 (t, $H_{h,h'}$, $^3J = 7.2$ Hz, 2H), 7.27 (dt, H_i, $^3J = 7.2$ Hz, $^4J = 1.2$ Hz), 4.87 (s, H_f, 2H). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 121.4 (C_1, $^1J = 144.1$ Hz), 137.3 (C_2, $^1J = 167.7$ Hz), 125.8 (C_3, $^1J = 167.7$ Hz), 150.3 (C_4, $^1J = 182.2$ Hz), 155.8 (C_5), 163.7 (C_6, $^1J = 165.3$ Hz); 65.3 (C_7, $^1J = 135.6$ Hz), 140.4 (C_8), 129.0 ($C_{9,9'}$, $^1J = 160.2$ Hz), 129.3 ($C_{10,10'}$, $^1J = 160.2$ Hz), 127.8 (C_{11}, $^1J = 156.5$ Hz).

2.2.2.2. C_5H_4N-CHN-$CH_2C_6H_4$(4-Cl) ($\mathbf{L}_5$). Following a procedure similar to the reported for $\mathbf{L}_4$, from a solution of 4-chlorobenzylamine (200 mg, 1.41 mmol) and 2-pyridinecarboxaldehyde (370 mg,

Download English Version:

https://daneshyari.com/en/article/1306158

Download Persian Version:

https://daneshyari.com/article/1306158

Daneshyari.com