#### Polyhedron 50 (2013) 418-424

Contents lists available at SciVerse ScienceDirect

### Polyhedron



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

# Synthesis and characterization of tin complexes [Sn(L)Hal<sub>4</sub>] (L = *N*-alkyl-(pyridin-2-yl)aldimine; Hal = Cl, Br): A structural study

Edmundo Guzmán-Percástegui, Carlos A. Reyes-Mata, Diego Martínez-Otero, Noemí Andrade-López, José G. Alvarado-Rodríguez \*

Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Hidalgo, km. 4.5 Carretera Pachuca-Tulancingo, Col. Carboneras, C.P. 42184, Mineral de la Reforma, Hidalgo, Mexico

#### ARTICLE INFO

Article history: Received 14 August 2012 Accepted 19 November 2012 Available online 29 November 2012

Keywords: Tin compounds X-ray crystal structures Schiff base Intermolecular interactions

#### ABSTRACT

The reactions of the ligands *N*-methyl-(pyridin-2-yl)aldimine (**a**), *N*-ethyl-(pyridin-2-yl)aldimine (**b**), and *N*-benzyl-(pyridin-2-yl)aldimine (**c**) with SnCl<sub>4</sub> and SnBr<sub>4</sub> led to the formation of compounds [Sn{( $C_5H_4N$ ) HC=NMe}Cl<sub>4</sub>] (**1**), [Sn{( $C_5H_4N$ )HC=NMe}Br<sub>4</sub>] (**2**), [Sn{( $C_5H_4N$ )HC=NEt}Cl<sub>4</sub>] (**3**), [Sn{( $C_5H_4N$ )HC=NEt}Br<sub>4</sub>] (**4**), [Sn{( $C_5H_4N$ )HC=NBn}Cl<sub>4</sub>] (**5**), and [Sn{( $C_5H_4N$ )HC=NBn}Br<sub>4</sub>] (**6**) in good yields. All the compounds were characterized by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>119</sup>Sn{<sup>1</sup>H} NMR, vibrational IR-Raman spectroscopy, elemental analyses, and X-ray diffraction analysis. The structural studies confirmed the formation of the respective six-coordinate tin complexes as a result of the chelation of the iminic and pyridinic nitrogen atoms of the ligands towards the tin atom; the Sn–N distances were shortened as the Lewis acid character at the tin atom was increased. In all the molecular structures the tin atom displayed a distorted octahedral local geometry.

© 2012 Elsevier Ltd. All rights reserved.

#### 1. Introduction

Polydentate Schiff ligands play an important role in coordination chemistry owing to their ease of synthesis by means of condensation reactions under mild conditions and their outstanding ability to bind a vast variety of metallic atoms [1]. Within the wide diversity of organic compounds which can be prepared by this route, the coordination of N-substituted-aldimine-based ligands via the pyridinic and the iminic nitrogen atoms provides a valuable and versatile tool in organometallic [2] and supramolecular synthesis [3]. As a result, this has led to the formation of several metal complexes displaying remarkable applications; for example, some complexes containing transition metals such as Ni [4,5], Pd [6,7], Mo [8], and Cu [9] exhibit interesting catalytic activity in diverse polymerization reactions. In this sense, in the last decades new developments in the chemistry of these ligands have been extended to main group elements; what is more, an increasing attention has been devoted to the synthesis of organotin halide octahedral complexes derived from the coordination of polydentate N-donor Schiff bases and organotin(IV) moieties in view of their antibacterial [10,11], antifungal [12], and in vitro antitumor activity [13,14].

As the activity of many of these compounds has been associated to their structural features [15], attempts to correlate structural

Corresponding author.
 E-mail address: jgar@uaeh.edu.mx (J.G. Alvarado-Rodríguez).

data and antitumor activity have been carried out; consequently, it has been concluded that biologically active complexes have Sn–N bond lengths near 2.4 Å [16]. This fact suggests that dissociation of ligands is an important step in their mechanism of action. In this regard, it has been usually assumed that the organic fragment would facilitate the transport of the complex across cell membranes, while the antitumor activity would be accomplished via a dissociation mechanism of the organotin(IV) moieties [17]. These achievements have encouraged new research work in the design, synthesis and structural study of novel octahedral organotin and tin halide complexes systematically substituted. Since the biochemical activity of organotin(IV) Schiff-base complexes seems to be greatly influenced by structural features and because the mechanism of the activity requires gaining a greater insight in the understanding of structure, herein we describe the synthesis, characterization, structural study and coordination behavior of six tin(IV) halide complexes of Schiff bases derived from N-substituted-(pyridin-2-yl)aldimine ligands with SnCl<sub>4</sub> and SnBr<sub>4</sub>.

#### 2. Experimental

#### 2.1. Materials and physical methods

All the starting reagents were of analytical grade and used without further purification. Solvents were dried by standard methods and distilled prior to use. 2-Pyridinecarboxaldehyde, methylamine, ethylamine, benzylamine, SnCl<sub>4</sub> and SnBr<sub>4</sub> were purchased from



<sup>0277-5387/\$ -</sup> see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2012.11.022

Aldrich and used as supplied. Ligands *N*-methyl-(pyridin-2-yl)aldimine (**a**), *N*-ethyl-(pyridin-2-yl)aldimine (**b**) and *N*-benzyl-pyridin-2-yl)aldimine (**c**) ligands were prepared as reported [18]. Melting points of the compounds were determined on a Mel-Temp II instrument and are reported without correction. Elemental analyses were recorded on a Perkin Elmer Series II CHNS/O Analyzer 2400. The IR spectra (4000–400 cm<sup>-1</sup>) were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer as either KBr pellets or CsI films. The Raman spectra in solid state (4000–100 cm<sup>-1</sup>) were recorded on a Perkin-Elmer Spectrum GX NIR FT-RAMAN spectrometer with 10–280 mW laser power and 4 cm<sup>-1</sup> resolution. NMR studies were carried out on a Varian VNMRS 400 instrument. Standard references were used: TMS and SnMe<sub>4</sub>. All the spectra were acquired at room temperature (20 °C).

## 2.2. General synthesis of tetrahalogenate tin(IV) complexes [Sn(L)Hal<sub>4</sub>] (1–6)

A ligand L (L = a-c) was dissolved in dichloromethane and magnetically stirred for 10 min; then, the tin halide was added at once. The mixture was stirred overnight and the resulting precipitate was filtered, washed thoroughly with dichloromethane and recrystallized from a mixture 1:1 of either acetone–hexane or acetoni-trile–chloroform mixtures for compounds 1-4 and 5-6, respectively.

#### 2.2.1. $[Sn\{(C_5H_4N)HC=NCH_3\}Cl_4]$ (1)

a (100 mg, 0.83 mmol), dichloromethane (25 mL), SnCl<sub>4</sub> (0.097 mL, 0.83 mmol). Compound 1 was obtained as a very pale yellow solid. Yield: 77% (243 mg). M.p.: 196 °C (dec.). Anal. Calc. for C<sub>7</sub>H<sub>8</sub>Cl<sub>4</sub>N<sub>2</sub>Sn: C, 22.09; H, 2.12; N, 7.36. Found: C, 23.25; H, 2.28; N, 6.35%. IR: 1658 v(C=N<sub>(imine)</sub>), 334 v(Sn-Cl). <sup>1</sup>H NMR  $(CD_3)_2CO, 20 \circ C]: \delta = 9.44$ = 28.40,  ${}^{3}J_{H5-H4} = 5.60, {}^{4}J_{H5}$ (ddd, [400 MHz, 1H. H5.  ${}^{4}J_{\rm H5-H3}$  = 1.52, <sup>5</sup>Јн5- ${}^{3}J_{\rm H5-119/117\,Sn}$  = 28.40, <sub>H2</sub> = 0.80 Hz), 9.32 (dq, 1H, H6,  ${}^{3}J_{H6-119/117}Sn = 108.04$ ,  ${}^{4}J_{H6-119/117}Sn = 108.04$ ,  ${}^{4}J_{H6-11$  $_{\rm H7}$  = 1.70 Hz), 8.70 (ddd, 1H, H3,  $^{3}J_{\rm H3-H4}$  = 8.00,  $^{3}J_{\rm H3-H2}$  = 7.60,  $^{4}J_{\rm H3-H2}$ <sub>H5</sub> = 1.54,  ${}^{5}J_{\text{H3}-119/117}\text{Sn}$  = 7.69 Hz), 8.54 (ddd, 1H, H2,  ${}^{3}J_{\text{H2}-\text{H3}}$  = 7.51,  ${}^{4}J_{H2-H4} = 1.11, \, {}^{5}J_{H2-H5} = 0.82, \, {}^{4}J_{H2-119/117}s_{n} = 7.74 \, Hz), \, 8.34 \, (ddd, \, 1H, \, 10.11)$  ${}^{3}J_{\rm H4-H3} = 7.80,$  ${}^{3}J_{\rm H4-H5} = 5.34,$  ${}^{4}J_{\rm H4-H2}$  = 1.33, H4,  ${}^{4}J_{H4-119/117}{}_{Sn}$  = 7.97 Hz), 3.93 (d, 3H, H7,  ${}^{3}J_{H7-119/117}{}_{Sn}$  = 32.10,  ${}^{4}J_{H7-119/117}{}_{Sn}$  $_{H6} = 1.72 \text{ Hz}$ ).  $^{13}C{^{1}H}$  [100 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta = 159.4$  (C6,  ${}^{2}J_{C6-119Sn}$  = 23.8 Hz), 146.5 (C5,  ${}^{2}J_{C5-119Sn}$  = 20.3 Hz), 145.3 (C3,  ${}^{4}J_{C3-119}{}_{Sn} = 5.3 \text{ Hz}$ , 140.1 (C1), 132.3 (C2,  ${}^{3}J_{C2-119}{}_{Sn} = 14.1 \text{ Hz}$ ), 131.7 (C4,  ${}^{3}J_{C4-119}{}_{Sn} = 12.2 \text{ Hz}$ ), 43.3 (C7,  ${}^{2}J_{C7-119}{}_{Sn} = 19.0 \text{ Hz}$ ). <sup>119</sup>Sn{<sup>1</sup>H} [149 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta$  = -555.9.

#### 2.2.2. $[Sn\{(C_5H_4N)HC=NCH_3\}Br_4]$ (2)

**a** (100 mg, 0.83 mmol), dichloromethane (25 mL), SnBr<sub>4</sub> (365 mg, 0.83 mmol). Pale yellow solid. Yield: 59% (275 mg). M.p.: 198 °C (dec.). *Anal.* Calc. for C<sub>7</sub>H<sub>8</sub>Br<sub>4</sub>N<sub>2</sub>Sn: C, 15.05; H, 1.44; N, 5.02. Found: C, 17.01; H, 1.71; N, 4.59%. IR: 1655  $\nu$ (C=N<sub>(imine)</sub>), 201  $\nu$ (Sn–Br). <sup>1</sup>H NMR [400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta$  = 9.57 (dd, 1H, H5, <sup>3</sup>J<sub>H5-119/117Sn</sub> = 93.52 Hz), 8.69 (td, 1H, H3, <sup>3</sup>J<sub>H3-H4</sub> = 7.77, <sup>4</sup>J<sub>H3-H5</sub> = 1.54, <sup>5</sup>J<sub>H3-119/117Sn</sub> = 7.72 Hz), 8.54 (d, 1H, H2, <sup>3</sup>J<sub>H2-H3</sub> = 7.71 Hz), 8.36 (ddd, 1H, H4, <sup>3</sup>J<sub>H4-H3</sub> = 7.81, <sup>3</sup>J<sub>H4-H5</sub> = 5.42, <sup>4</sup>J<sub>H4-H2</sub> = 1.21 Hz), 3.92 (d, 3H, H7, <sup>3</sup>J<sub>H7-119/117Sn</sub> = 32.60, <sup>4</sup>J<sub>H7-H6</sub> = 1.72 Hz). <sup>13</sup>C{<sup>1</sup>H} (100 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C):  $\delta$  = 158.1 (C6, <sup>2</sup>J<sub>C6-119Sn</sub> = 17.2 Hz), 131.9 (C4, <sup>3</sup>J<sub>C4-119Sn</sub> = 7.8 Hz), 42.6 (C7). <sup>119</sup>Sn{<sup>1</sup>H} NMR [149 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta$  = -1206.1.

#### 2.2.3. $[Sn{(C_5H_4N)HC=NCH_2CH_3}Cl_4]$ (3)

**b** (100 mg, 0.75 mmol), dichloromethane (25 mL), SnCl<sub>4</sub> (0.087 mL, 0.75 mmol). Yellow solid. Yield: 74% (219 mg). M.p.: 170 °C (dec.). *Anal.* Calc. for  $C_8H_{10}Cl_4N_2Sn$ : C, 24.34; H, 2.55; N,

7.10. Found: C, 24.28; H, 2.38; N, 6.74%. IR: 1653 v(C==N<sub>(imine)</sub>), 336 v(Sn–Cl). <sup>1</sup>H NMR [400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta$  = 9.45 (ddd, 1H, H5, <sup>3</sup>J<sub>H5-119/117Sn</sub> = 26.89, <sup>3</sup>J<sub>H5-H4</sub> = 5.42, <sup>4</sup>J<sub>H5-H3</sub> = 1.82, <sup>5</sup>J<sub>H5-H2</sub> = 1.00 Hz), 9.33 (td, 1H, H6, <sup>3</sup>J<sub>H6-119/117Sn</sub> = 111.61, <sup>4</sup>J<sub>H6-H7</sub> = 1.42, <sup>4</sup>J<sub>H6-H2</sub> = 0.91 Hz), 8.69 (td, 1H, H3, <sup>3</sup>J<sub>H3-H4H2</sub> = 7.70, <sup>4</sup>J<sub>H3-H5</sub> = 1.60, <sup>5</sup>J<sub>H3-119/117Sn</sub> = 7.70 Hz), 8.53 (ddd, 1H, H2, <sup>3</sup>J<sub>H2-H3</sub> = 7.70, <sup>4</sup>J<sub>H2-H4</sub> = 1.31, <sup>5</sup>J<sub>H2-H5</sub> = 0.91, <sup>4</sup>J<sub>H2-119/117Sn</sub> = 7.43 Hz), 8.33 (ddd, 1H, H4, <sup>3</sup>J<sub>H4-H3</sub> = 7.82, <sup>3</sup>J<sub>H4-H5</sub> = 5.40, <sup>4</sup>J<sub>H4-H2</sub> = 1.31, <sup>4</sup>J<sub>H4-119/117Sn</sub> = 8.12 Hz),

 ${}^{3}_{H4-H3} = 7.82, {}^{3}_{H4-H5} = 5.40, {}^{4}_{JH4-H2} = 1.31, {}^{4}_{H4-119/117_{Sn}} = 8.12 \text{ Hz}),$ 4.30 (qd, 2H, H7,  ${}^{3}_{JH7-119/117_{Sn}} = 32.62, {}^{3}_{JH7-H8} = 7.20, {}^{4}_{JH7-146} = 1.42 \text{ Hz}),$  1.59 (t, 3H, H8,  ${}^{3}_{JH8-H7} = 7.20 \text{ Hz}). {}^{13}C{}^{1}H{}$ [100 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta = 158.4$  (C6), 146.3 (C5), 145.3 (C3), 140.2 (C1), 132.3 (C2), 131.8 (C4), 51.2 (C7), 15.5 (C8). {}^{119}Sn{}^{1}H{} NMR [149 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta = -559.0.$ 

#### 2.2.4. $[Sn\{(C_5H_4N)HC=NCH_2CH_3\}Br_4]$ (4)

**b** (300 mg, 2.24 mmol), dichloromethane (25 mL), SnBr<sub>4</sub> (980 mg, 2.24 mmol). Yellow solid. Yield: 77% (992 mg). M.p.: 172 °C (dec.). *Anal.* Calc. for C<sub>8</sub>H<sub>10</sub>Br<sub>4</sub>N<sub>2</sub>Sn: C, 16.78; H, 1.76; N, 4.89. Found: C, 16.95; H, 1.64; N, 4.65%. IR: 1649  $\nu$ (C=N<sub>(imine)</sub>), 209  $\nu$ (Sn-Br). <sup>1</sup>H NMR [400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta$  = 9.63 (ddd, 1H, H5, <sup>3</sup>J<sub>H5-119/117Sn</sub> = 29.08, <sup>3</sup>J<sub>H5-144</sub> = 5.40, <sup>4</sup>J<sub>H5-H3</sub> = 1.42, <sup>5</sup>J<sub>H5-142</sub> = 0.70 Hz), 9.29 (td, 1H, H6, <sup>3</sup>J<sub>H6-119/117Sn</sub> = 98.95, <sup>4</sup>J<sub>H6-H7</sub> = 1.40, <sup>4</sup>J<sub>H6-H2</sub> = 0.91 Hz), 8.74 (td, 1H, H3, <sup>3</sup>J<sub>H3-H4,H2</sub> = 7.70, <sup>4</sup>J<sub>H3-H5</sub> = 1.52, <sup>5</sup>J<sub>H3-119/117Sn</sub> = 7.62 Hz), 8.58 (ddd, 1H, H2, <sup>3</sup>J<sub>H2-H3</sub> = 7.68, <sup>4</sup>J<sub>H2-H4</sub> = 1.38, <sup>5</sup>J<sub>H2-H5</sub> = 0.77 Hz), 8.40 (ddd, 1H, H4, <sup>3</sup>J<sub>H4-H3</sub> = 7.77, <sup>3</sup>J<sub>H4-155</sub> = 5.40, <sup>4</sup>J<sub>H4-H2</sub> = 1.42, <sup>4</sup>J<sub>H4-119/117Sn</sub> = 6.70 Hz), 4.39 (qd, 2H, H7, <sup>3</sup>J<sub>H7-119/117Sn</sub> = 31.82, <sup>3</sup>J<sub>H7-H8</sub> = 7.20, <sup>4</sup>J<sub>H7-H6</sub> = 1.42 Hz), 1.71 (t, 3H, H8, <sup>3</sup>J<sub>H8-H7</sub> = 7.20 Hz). <sup>13</sup>C{<sup>1</sup>H} [100 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta$  = 157.0 (C6, <sup>2</sup>J<sub>C6-119Sn</sub> = 16.8 Hz), 145.3 (C3, <sup>4</sup>J<sub>C3-119Sn</sub> = 4.6 Hz), 145.2 (C5, <sup>2</sup>J<sub>C5-119Sn</sub> = 7.7 Hz), 139.0 (C1), 132.1 (C2, <sup>3</sup>J<sub>C2-119Sn</sub> = 7.8 Hz), 132.0 (C4, <sup>3</sup>J<sub>C4-119Sn</sub> = 12.2 Hz), 50.3 (C7, <sup>2</sup>J<sub>C7-119Sn</sub> = 18.0 Hz), 15.6 (C8). <sup>119</sup>Sn{<sup>1</sup>H} NMR [149 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta$  = -1209.7.

#### 2.2.5. $[Sn\{(C_5H_4N)HC=NCH_2(C_6H_5)\}Cl_4]$ (5)

**c** (300 mg, 1.53 mmol), dichloromethane (25 mL),  $SnCl_{4}$ (0.178 mL, 1.53 mmol). Compound 5 was obtained as beige solid. Yield: 89% (621 mg). M.p.: 243 °C. Anal. Calc. for C13H12Cl4N2Sn: C, 34.18; H, 2.65; N, 6.13. Found: C, 34.10; H, 2.52; N, 5.91%. IR: 1650 v(C=N<sub>(imine)</sub>), 329 v(Sn-Cl). <sup>1</sup>H NMR [400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta$  = 9.52 (ddd, 1H, H5,  ${}^{3}J_{\text{H5}-119/117}\text{Sn}$  = 28.15,  ${}^{3}J_{\text{H5}-\text{H4}}$  = 5.40,  ${}^{4}J_{\rm H5-H3}$  = 1.42,  ${}^{5}J_{\rm H5-H2} = 0.71 \text{ Hz}$ , 9.03 (td, 1H, H6.  ${}^{3}J_{\text{H6}-119/117}\text{Sn}$  = 107.67,  ${}^{4}J_{\text{H6}-\text{H7}}$  = 1.80,  ${}^{4}J_{\text{H6}-\text{H2}}$  = 0.80 Hz), 8.70 (td, 1H, H3,  ${}^{3}J_{H3-H4,H2} = 7.70$ ,  ${}^{4}J_{H3-H5} = 1.40$ ,  ${}^{5}J_{H3-^{119/117}Sn} = 7.72$  Hz), 8.55 (ddd, 1H, H2,  ${}^{3}J_{H2-H3} = 7.60$ ,  ${}^{4}J_{H2-H4} = 1.30$ ,  ${}^{5}J_{H2-H5} = 0.81$  Hz), 8.37 (ddd, 1H, H4,  ${}^{3}J_{H4-H3} = 7.70$ ,  ${}^{3}J_{H4-H5} = 5.38$ ,  ${}^{4}J_{H4-H2} = 1.39$ ,  ${}^{4}J_{\text{H4}-{}^{119/117}\text{Sn}} = 6.81 \text{ Hz}$ , 7.59 (dd, 2H, H9,  ${}^{3}J_{\text{H9}-\text{H10}} = 7.70$ ,  ${}^{4}J_{\text{H9}-\text{H10}}$ H11 = 1.60 Hz), 7.54-7.42 (m, 3H, H10-H11), 5.46 (d, 2H, H7,  ${}^{3}J_{\text{H7}-119/117}\text{Sn} = 21.09, {}^{4}J_{\text{H7}-\text{H6}} = 1.80 \text{ Hz}$ ).  ${}^{13}\text{C}{}^{1}\text{H}$  [100 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta = 159.0$  (C6,  ${}^{2}J_{C6-119Sn} = 24.4$  Hz), 146.4 (C5.  ${}^{2}J_{C5-119Sn}$  = 20.6 Hz), 145.2 (C3,  ${}^{4}J_{C3-119Sn}$  = 5.5 Hz), 140.2 (C1), 134.2 (C8), 132.4 (C2,  ${}^{3}J_{C2-119}Sn} = 14.4 Hz$ ), 132.2 (C4,  ${}^{3}J_{C4-119}$  = 12.5 Hz), 131.2 (C9), 130.0 (C10), 129.8 (C11), 57.9 (C7). <sup>119</sup>Sn{<sup>1</sup>H} NMR [149 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta = -560.4$ .

#### 2.2.6. $[Sn\{(C_5H_4N)HC=NCH_2(C_6H_5)\}Br_4]$ (6)

**c** (300 mg, 1.53 mmol), dichloromethane (25 mL), SnBr<sub>4</sub> (670 mg, 1.53 mmol). Beige solid. Yield: 70% (680 mg). M.p.: 239 °C. *Anal.* Calc. for C<sub>13</sub>H<sub>12</sub>Br<sub>4</sub>N<sub>2</sub>Sn: C, 24.61; H, 1.91; N, 4.41. Found: C, 25.16; H, 1.90; N, 4.07%. IR: 1649  $\nu$ (C=N<sub>(imine)</sub>), 206  $\nu$ (Sn–Br). <sup>1</sup>H NMR [400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta$  = 9.65 (ddd, 1H, H5, <sup>3</sup>J<sub>H5-119/117Sn</sub> = 29.62, <sup>3</sup>J<sub>H5-H4</sub> = 5.40, <sup>4</sup>J<sub>H5-H3</sub> = 1.42, <sup>5</sup>J<sub>H5-H2</sub> = 0.71 Hz), 8.85 (td, 1H, H6, <sup>3</sup>J<sub>H3-H4,H2</sub> = 7.70, <sup>4</sup>J<sub>H3-H5</sub> = 1.40, <sup>5</sup>J<sub>H3-119/117Sn</sub> = 7.80 Hz), 8.54 (ddd, 1H, H2, <sup>3</sup>J<sub>H2-H3</sub> = 7.60, <sup>4</sup>J<sub>H2-H4</sub> = 1.40, <sup>5</sup>J<sub>H2-H5</sub> = 0.70 Hz), 8.39 (ddd, 1H, H4, <sup>3</sup>J<sub>H4-H3</sub> = 7.70, <sup>3</sup>J<sub>H4-H5</sub> = 5.41,

Table 1	
Collection data and refinement parameters	s for compounds 1-6.

	1	2	3	4	5	6
Empirical formula	C7H8Cl4N2Sn	C7H8Br4N2Sn	C <sub>8</sub> H <sub>10</sub> Cl <sub>4</sub> N <sub>2</sub> Sn	C <sub>8</sub> H <sub>10</sub> Br <sub>4</sub> N <sub>2</sub> Sn	C13H12Cl4N2Sn	C <sub>13</sub> H <sub>12</sub> Br <sub>4</sub> N <sub>2</sub> Sn
Formula weight	380.64	558.48	394.67	572.51	456.74	634.58
Temperature (K)	293(2)	295(2)	295(2)	295(2)	293(2)	293(2)
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
Space group	Pna21	Pna2 <sub>1</sub>	$P2_1/n$	$P2_1/n$	ΡĪ	$P2_1/n$
a (Å)	14.3901(3)	14.7587(6)	8.6653(3)	8.8202(2)	7.1091(2)	9.3178(6)
b (Å)	9.17622(18)	9.3690(4)	15.9215(5)	16.4530(3)	9.1933(3)	17.9554(11)
c (Å)	9.34778(18)	9.7874(4)	9.7194(3)	10.0408(2)	13.1180(4)	10.7817(8)
β (°)	90	90	90.330(3)	90.7023(9)	87.881(2)	91.976(6)
$V(Å^3)$	1234.34(4)	1353.35(10)	1340.91(8)	1457.00(5)	837.02(4)	1802.8(2)
Z	4	4	4	4	2	4
Absorption coefficient (mm <sup>-1</sup> )	2.899	13.665	2.673	12.697	2.155	10.275
F(000)	728	1016	760	1048	444	1176
$\theta$ range (°)	3.11-26.50	3.01-26.48	3.14-26.05	3.06-26.05	2.93-26.36	2.95-26.37
Reflections collected	16350	10755	21285	20968	17265	19270
Unique reflections	2570	2764	2645	2871	3411	3689
Completeness to $\theta$	99.9	99.9	99.9	99.9	99.9	99.9
Data/restraints/parameters	2570/1/134	2764/1/133	2645/0/141	2871/0/141	3411/0/181	3689/0/182
GOF on F <sup>2</sup>	1.054	1.020	1.080	1.053	1.069	1.024
Final indices $[I > 2\sigma(I)]$	0.0183, 0.0456	0.0289, 0.0621	0.0192, 0.0395	0.0244, 0.0505	0.0295, 0.0683	0.0381, 0.0713
$R_1$ and $wR_2$ indices all data	0.0194, 0.0465	0.0365, 0.0654	0.0257, 0.0424	0.0337, 0.0537	0.0392, 0.0740	0.0650, 0.0807
Largest residuals (e Å $^{-3}$ )	0.238 and -0.224	0.377 and -0.595	0.269 and -0.444	0.374 and -0.654	0.744 and -0.378	1.503 and -1.003

<sup>4</sup>*J*<sub>H4-H2</sub> = 1.39, <sup>4</sup>*J*<sub>H4-119/117Sn</sub> = 6.82 Hz), 7.61 (dd, 2H, H9, <sup>3</sup>*J*<sub>H9-H10</sub> = 7.70, <sup>4</sup>*J*<sub>H9-H11</sub> = 1.50 Hz), 7.54–7.45 (m, 3H, H10–H11), 5.51 (d, 2H, H7, <sup>3</sup>*J*<sub>H7-119/117Sn</sub> = 19.72, <sup>4</sup>*J*<sub>H7-H6</sub> = 1.80 Hz). <sup>13</sup>C{<sup>1</sup>H} [100 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta$  = 156.5 (C6, <sup>2</sup>*J*<sub>C6-119Sn</sub> = 16.9 Hz), 144.4 (C5), 144.3 (C3), 138.1 (C1), 133.0 (C8), 131.7 (C2, <sup>3</sup>*J*<sub>C2-119Sn</sub> = 7.7 Hz), 131.3 (C4, <sup>3</sup>*J*<sub>C4-119Sn</sub> = 12.7 Hz), 130.4 (C9), 129.2 (C10), 129.1 (C11), 56.1 (C7). <sup>119</sup>Sn{<sup>1</sup>H} NMR [149 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 20 °C]:  $\delta$  = -1201.3.

#### 2.3. X-ray crystallography and structure solution

Compounds 1-4 were successfully recrystallized from a 1:1 acetone-hexane mixture whereas 5 and 6 were crystallized from a 1:1 acetonitrile-chloroform solution. Single crystals of suitable quality were glued on a glass fiber. X-ray diffraction data of 1-6 compounds were collected at room temperature on an Oxford Diffraction Gemini CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data were integrated, scaled, sorted, and averaged using the CrysAlis software package [19]. An analytical numeric absorption correction using a multifaceted crystal model was applied by using the CrysAlis software. The structures were solved by direct methods, using SHELXTL NT Version 5.10 and refined by full-matrix least squares against  $F^2$  [20]. The displacement parameters of non-hydrogen atoms were anisotropically refined. The positions of the hydrogen atoms were kept fixed with a common isotropic displacement parameter. The collection data details are collected in Table 1.

#### 3. Results and discussion

#### 3.1. Synthesis

The reaction of the aldiminic ligands  $\mathbf{a-c}$  dissolved in dichloromethane with the corresponding tin tetrahalide compound at room temperature gave the corresponding coordination compounds  $\mathbf{1-6}$  with yields ranging from 59% to 89%, Scheme 1; the numbering scheme for the NMR assignment is also showed. All compounds are soluble in acetone, insoluble in low-polar solvents as chloroform and dichloromethane; they experience dissociation in solvents with high dielectric constant as dimethylsulfoxide and methanol.



Scheme 1. Synthesis of compounds 1-6.

Selected vibration frequencies (cm<sup>-1</sup>) for ligands **a**-**c** and compounds **1**-**6**.

	a	b	с	1	2	3	4	5	6
R	Me	Et	Bn	Me	Me	Et	Et	Bn	Bn
Hal	-	-	-	Cl	Br	Cl	Br	Cl	Br
C=N <sub>(iminic)</sub>	1634	1650	1647	1658	1655	1653	1649	1650	1649
Sn-Hal	-	-	-	334	201	336	209	329	206

#### 3.2. Vibrational spectroscopy

The analyses of the FT-IR spectra revealed the formation of the complexes owing to the shift of the  $C=N_{(iminic)}$  stretching band of free ligands upon reaction with tin(IV) halides, indicating the participation of the aldiminic nitrogen atoms in the coordination to tin (Table 2). These shifts are toward higher

frequencies; this is similar to that observed for other tin-complexes containing the imino functional group [21]. In addition, this band is shifted to higher frequencies, seemingly due to an electron density transfer from the SnHal<sub>4</sub> moiety to the ligand, strengthening the C=N bond; this effect may occur for these ligands when they coordinate to main-group elements [22,23].

Additionally, the analysis of the Raman spectra in the  $350-200 \text{ cm}^{-1}$  region revealed the presence of a very strong band aris-

ing from the vibration Sn–Hal (see, for example, the Supplementary Material, Figure 1S). These values are similar to those found for analogous tin halide complexes [11].

#### 3.3. NMR spectra

NMR spectra of all the compounds were recorded in  $(CD_3)_2CO$  solutions at 20 °C. The assignment of the signals was carried out



by homonuclear and heteronuclear correlation of two dimensional experiments (COSY, HSQC and HMBC). The general numbering for compounds **1–6** is showed in Scheme 1.

All the proton signals were found shifted to higher frequencies when compared to the signals in the corresponding free ligands (see, for example, the Supplementary Material, Figure 2S). In solution the pyridinic rings display an ABCD pattern for all six complexes (see the Supplementary Material, Figure 3S). The chemical shifts of the 2, 3, and 4 protons do not present considerable differences among the six complexes. The H5 signal was observed as the most shifted one around 9.65-9.44 ppm. The aldiminic proton H6 displays a signal in the 9.34–8.85 ppm range and was observed that this proton in compounds 1, 3, and 5 is found at higher frequencies compared to those protons in compounds **2**. **4**. and **6**: this could be attributed to the enhancement of Lewis acidity on the tin atom when more electron withdrawing ligands such as chloro compared to bromo, are attached to it. In addition, due to the nature of the phenyl group and its diamagnetic ring-current, the H6 proton experiences an even more noticeable upfield shifting in the **5** and **6** compounds. H6 protons also exhibit  ${}^{3}J({}^{119/117}Sn-{}^{1}H)$ satellite couplings with the tin nucleus, evidencing that the ligand L is bonded to the tin atom in acetone solution. Values for the <sup>3</sup>*I*(<sup>119/117</sup>Sn-<sup>1</sup>H) range from 91 to 111 Hz; similar values have been also observed for other (pyridin-2-yl)aldimine tin complexes [24]. The magnitude of  ${}^{3}J({}^{(119)117}Sn{}^{-1}H)$  might be used to estimate the strength of N-Sn coordination since the larger constants are found in the chloro compounds 1, 3, and 5. Finally, the H7 protons also display signals accompanied by satellite couplings with tin nucleus (see the Supplementary Material, Figure 4S).

Discrete <sup>13</sup>C signals for all the individual carbons are identified in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra. The signals for the aldiminic carbon C6 appeared in the 159.5–156.5 ppm range, the signals for C5 range from 146.5 to 144.4 ppm and signals for C1 are near 139 ppm. The signals for C1, C6, and C5 showed a significant shift to low frequencies in all the complexes compared to the resonances in the free ligands owing to the electron density transfer effect since these carbons are directly bound to the nitrogen atoms; C1 undergoes the larger shift ( $\Delta \approx 16$  ppm) indeed. In contrast, signals for the remaining carbons are shifted to higher frequencies.

The <sup>119</sup>Sn{<sup>1</sup>H} NMR spectra of compounds **1–6** show only one sharp resonance confirming the existence of one tin species. The <sup>119</sup>Sn chemical shifts for the chloro compounds **1**, **3**, and **5** span from -555 to -561 ppm (Scheme 1); these chemical shifts are in the range of hexacoordinate tin species [25]. Nevertheless, even though the <sup>119</sup>Sn chemical shifts are depending on the coordination number [26] and, in turn, the coordination number must be

Table 3

Selected bond lengths (Å), angles (°), and geometrical parameters of compounds 1-6.

the same along the series of the **1–6** compounds, when the chloro ligands were replaced by the bromo ligands, the <sup>119</sup>Sn nuclei were considerably shifted to lower frequencies resulting in chemical shifts around -1205 ppm. This trend of chemical shift can be related to the effect of the heavy atom induced on the tin nucleus by the bromo ligands [27]. In addition, this shift to lower frequencies may be due to the less electron-withdrawing inductive effect of the bromo compared to chloro as well as to the possibility of additional  $\pi$  back-bonding contribution to the Sn–Br bonds which would shield the nucleus in a greater extent [28].

#### 3.4. X-ray diffraction

The crystal structures of the compounds were determined by single crystal X-ray diffraction analyses. The molecular drawings of **1–6** are depicted in Fig. 1 and selected bond lengths, angles and some relevant structural features are given in Table 3. The methyl derivatives **1** and **2** crystallized in the orthorhombic system and same space group,  $Pna2_1$ ; the ethyl derivatives **3** and **4** crystallized in the monoclinic system with the same space group  $P2_1/n$ . In these pairs of compounds the enlargement of cell parameters in **2** and **4** is due to the presence of four larger bromo ligands in comparison to the tetrachloro compounds **1** and **3**. Benzyl compounds **5** and **6** crystallized in the triclinic and monoclinic systems, respectively; the difference in crystal systems can be attributed to the conformational freedom of the benzyl groups where the C6–N2–C7–C8 torsion angles are 75.1(4)° and 11.9(8)° for **5** and **6**, respectively.

All the tin complexes are isostructural and some common aspects are observed from the analysis of the crystallographic data. In all cases an hexacoordination based upon a [SnN<sub>2</sub>Hal<sub>4</sub>] core is observed (Hal = Cl, Br), with similar N–Sn–N bite angles regardless of the different R groups and halogen ligands. The Sn-N<sub>(iminic)</sub> and Sn-N<sub>(pyridinic)</sub> distances are in the range of 2.220–2.257 and 2.236– 2.274 Å respectively, and they are in general shorter when the exocyclic pendant groups are chloro ligands, suggesting that the coordination of the bidentate Schiff ligand is stronger in 1, 3, and 5. These averaged distances are also shorter than those reported for similar compounds derived from the coordination of equivalent N-substituted-(pyridin-2-yl)aldimine ligands towards "BuSnCl<sub>3</sub> and Me<sub>2</sub>SnCl<sub>2</sub> [16,21,24]. From the above, it is observed that the Sn-N distances are shortened as the Lewis acid character at the tin atom increases. In addition, it can be noted that the Sn-N distances are significantly the same in the *N*-methyl compounds **1** and **2**, despite the nature of the halogen atom: a different situation is observed in the N-ethyl and N-benzyl compounds, where the

	1	2	3	4	5	6
Sn-N(1)	2.236(2)	2.253(5)	2.2548(19)	2.274(3)	2.236(3)	2.261(4)
Sn-N(2)	2.230(2)	2.244(5)	2.220(2)	2.241(3)	2.226(2)	2.257(4)
Sn-Hal(1)	2.3665(9)	2.5283(8)	2.3765(6)	2.5382(4)	2.3663(9)	2.5406(7)
Sn-Hal(2)	2.3954(7)	2.5571(6)	2.3899(6)	2.5777(5)	2.3872(9)	2.5508(8)
Sn-Hal(3)	2.3625(7)	2.5154(7)	2.3691(6)	2.5247(5)	2.3626(10)	2.5208(7)
Sn-Hal(4)	2.4122(7)	2.5679(7)	2.4171(6)	2.5490(5)	2.4336(8)	2.5650(7)
N(2)-C(6)	1.266(4)	1.264(8)	1.276(3)	1.265(5)	1.268(4)	1.258(6)
N(1)-Sn-N(2)	73.92(10)	73.0(2)	74.05(8)	73.49(13)	74.47(9)	73.53(16)
Hal(1)-Sn-Hal(2)	94.14(4)	91.10(3)	93.03(2)	91.227(15)	92.42(3)	93.55(3)
Hal(1)-Sn-Hal(4)	91.04(3)	91.10(3)	90.90(2)	93.585(16)	91.42(3)	93.96(2)
Hal(3)-Sn-Hal(1)	99.00(3)	98.87(3)	99.74(2)	99.466(10)	97.63(4)	99.52(3)
Hal(3)-Sn-Hal(2)	92.55(3)	92.66(3)	92.33(2)	92.551(17)	95.77(4)	94.93(3)
Hal(2)-Sn-Hal(4)	171.88(3)	170.89(3)	173.47(2)	172.499(17)	170.72(3)	168.12(3)
Hal(3)-Sn-Hal(4)	92.81(3)	93.49(3)	92.14(2)	92.329(17)	92.09(4)	92.89(3)
C6-N2-C7-C8	-	-	100.3(3)	97.9(5)	75.1(4)	11.9(8)
Sum of internal angles around Sn <sup>a</sup>	1583.99	1581.82	1585.70	1584.13	1584.40	1578.15

<sup>a</sup> The sum of the internal angles for a central atom in an ideal octahedral arrangement equals to 1620°, see text.



Fig. 2. Hal---H hydrogen bonding in 1 and 2 along the twofold screw axis (Hal = Cl, Br).

Sn-N distances are longer in the bromo compounds, reflecting the steric effects of the larger N-substituents as well as the bromo ligands. On the other hand, it is interesting to note that the Sn-Hal distances can be sorted in two sets. The first set contains the shortest distances formed by the linking of the tin atom with the halogen ligands located in the plane of the chelate ring; in the chloro compounds 1, 3, and 5 the distances range from 2.3625(7) to 2.3765(6)Å and for the bromo compounds 2, 4 and 6 from 2.5154(7) to 2.5406(7) Å. The second set is formed by the larger Sn-Hal bond distances perpendicular to that plane ranging from 2.3872(9) to 2.4336(8) and 2.5490(5) to 2.5777(5) Å for the chloro and bromo compounds, respectively. This effect is also observed within the series of a small number of examples of tin(IV) tetrachloro and tetrabromo compounds derived from the coordination of N,N' bidentate ligands where the Hal–Sn distances perpendicular to the ligand plane are larger than the co-planar ones [29–31]. In this respect, the coordination geometry at tin atom is described as distorted octahedral. The greatest deviations from the ideal angles in an octahedral geometry are those for the N(2)-Sn-N(1), N(1)-Sn-Hal(3) and N(2)-Sn-Hal(1) which range between 73-75°, 165–169°, and 165–168° respectively; these data reflect the restricted bite angle of the ligand. Moreover, by means of the analysis of the sum of internal angles around tin, the distortion from the ideal octahedral geometry can be estimated, where a value of 1620° is calculated for an ideal octahedral arrangement [32]. The data are listed in Table 3. Thus, in 6 the tin atom displays the most distorted geometry from the ideal octahedral arrangement, where the sum of the angles around Sn is 1578.15° and can be attributed to the larger steric effect of the bromo ligands and the phenyl group attached to the iminic nitrogen atom; the other compounds exhibit similar sum of internal angles data.

The hexacoordinate [SnN<sub>2</sub>Hal<sub>4</sub>] core in all compounds hinders any possible intermolecular interaction where the large tin atom might be involved; a different situation has been observed in the analogous compounds with smaller coordination numbers like [Zn{**a**}Cl<sub>2</sub>]<sub>2</sub> [33], [Cu{**c**}Cl<sub>2</sub>]<sub>2</sub> [34], and [Hg{**c**}Cl<sub>2</sub>]<sub>2</sub>·HgCl<sub>2</sub> [35], where the coordination of the **a** and **c** ligands to Zn(II), Cu(II), and Hg(II) leads to  $\mu$ -dichloro dimeric structures. Nevertheless, it is worth noting that some interesting features remain in structures 1-6 since they display a series of non-covalent interactions Hal---H as well as H---aromatic interactions offset-stacked parallel-displaced and face-tilted T-shaped [36], exhibiting a variety of motifs and chains in the crystalline structure. For example, the molecules in the isostructural compounds 1 and 2 generate a chain motif through Hal---H non-covalent intermolecular interactions ranging from 2.797 to 2.917 Å with the iminic H6 and one of the pyridinic protons; the motifs are related by a twofold screw axis along the chain in the c direction (Fig. 2). Besides the interactions above mentioned, the structures also showed relevant Cl3---H7 intermolecular contacts related by a glide plane, generating a different chain linked via the methyl groups.



Fig. 3. Dimeric intermolecular associations via  $\pi$ ---H interactions in 5.

Likewise, the molecules in the structure of **5**, besides of the Cl4---H non-covalent interactions with the iminic H6 proton [Cl4---H6 (2.796 Å)] displayed, form a centrosymmetric dimeric association via H---aromatic rings interactions (Fig. 3).

#### 4. Conclusions

Six new tetrahalide tin(IV) complexes have been synthesized from the reaction of the Schiff bases *N*-R-(pyridin-2-yl)aldimine (R = Me, Et, Bn) and SnHal<sub>4</sub> (Hal = Cl, Br). On the basis of the spectral and structural evidence the ligands are coordinated to the tin tetrahalides in a bidentate mode via the pyridinic and the iminic nitrogen atoms. As a result, the tin atom displays a distorted octahedral geometry in all the complexes which are isomorphic indeed. The different organic groups attached to the aldiminic nitrogen do not seem to impact the coordination behavior as the different halogen substituents around the tin atom do. This is reflected in how the structural parameters, such as the bond lengths, are affected in a different way in chloro and bromo derivatives suggesting that the binding effect is stronger when chloro substituents are present given that the Lewis acid character on tin is enhanced.

#### Acknowledgments

E.G.P. fully acknowledges CONACYT for his fellowship. This research was supported by CONACyT (Project 83157).

#### Appendix A. Supplementary data

CCDC 893891, 893892, 893893, 893894, 893895, and 893896 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, **5**, and **6**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2012.11.022.

#### References

- [1] R.W. Layer, Chem. Rev. 63 (1962) 489.
- [2] N.E. Borisova, M.D. Reshetova, Y.A. Ustynyuk, Chem. Rev. 107 (2007) 46.
- [3] L. Fabbrizzi, A. Poggi, Transition Metals in Supramolecular Chemistry, Kluwer Academic Publishers, The Netherlands, 1994.
- [4] B.K. Bahuleyan, J.H. Kim, H.S. Seo, J.M. Oh, I.Y. Ahn, C.S. Ha, D.W. Park, I. Kim, Catal. Lett. 126 (2008) 371.
- [5] S. Song, T. Xiao, L. Wang, C. Redshawb, F. Wang, W.H. Sun, J. Organomet. Chem. 699 (2012) 18.
- [6] R. Chen, J. Bacsa, S.F. Mapolie, Inorg. Chem. Commun. (2002) 724.
  [7] H. Zhang, J.E. Enman, M.L. Conrad, M.J. Manning, C.S. Turner, S.L. Wheaton, C.M.
- Vogels, S.A. Westcott, Transition Met. Chem. 31 (2006) 13. [8] A.C. Gomes, S.M. Bruno, S. Gago, R.P. Lopes, D.A. Machado, A.P. Carminatti, A.A.
- Valente, M. Pillinger, I.S. Gonçalves, J. Organomet. Chem. 696 (2011) 3543.
  [9] G.A. Ardizzoia, S. Brenna, F. Castelli, S. Galli, Inorg. Chim. Acta 362 (2009) 3507.
- [10] L.S. Zamudio-Rivera, R. George-Tellez, G. López-Mendoza, A. Morales-Pacheco, E. Flores, H. Höpfl, V. Barba, F.J. Fernández, N. Cabirol, H.I. Beltrán, Inorg. Chem. 44 (2005) 5370.
- [11] T. Sedaghat, M. Naseh, H.R. Khavasi, H. Motamedi, Polyhedron 33 (2012) 435.
- [12] W. Rehman, A. Badshah, S. Khan, L.T. Anh Tuyet, Eur. J. Med. Chem. 44 (2009) 3981.
- [13] T.S. Basu Baul, S. Basu, D. de Vos, A. Linden, Invest. New Drugs 27 (2009) 419.
- [14] T.A. Kabanos, P. Anastasios, D. Keramidas, D. Mentzafos, U. Russo, A. Terzisb, J.M. Tsangaris, J. Chem. Soc., Dalton Trans. (1992) 2729.

- [15] Z. Rappoport, The Chemistry of Organic Germanium, Tin and Lead Compounds, vol. 2, John Wiley & Sons, Ltd., England, 2002.
- [16] S.G. Teoh, S.B. Teo, L.K. Lee, H.K. Fun, J. Coord. Chem. 33 (1994) 69.
- [17] R.P. Irwin, Organometallic Chemistry Research Perspectives, Nova Science Publishers, New York, 2007.
- [18] P. Bamfield, R. Price, R.G.J. Miller, J. Chem. Soc., A (1969) 1447.
- [19] Oxford Diffraction, CrysAlis Software System, Version 1.171.33.31, Oxford Diffraction Ltd., Abingdon, UK, 2009.
- [20] SHELXTL, Version 5.10, Bruker AXS, Inc., Madison, WI, USA, 1998.
- [21] S.G. Teoh, S.B. Teo, L.K. Lee, Y.L. Chong, E.R.T. Tiekink, Polyhedron 14 (1995) 2275.
- [22] P.H.M. Budzelaar, Eur. J. Inorg. Chem. (2012) 530.
- [23] J. Scott, S. Gambarotta, I. Korobkov, Q. Knijnenburg, B. de Bruin, P.H.M. Budzelaar, J. Am. Chem. Soc. 127 (2005) 17204.
- [24] G. Matsubayashi, T. Tanaka, S. Nishigaki, K. Nakatsu, J. Chem. Soc., Dalton Trans. (1979) 501.
- [25] J. Holecek, M. Nadvornik, K. Handlir, J. Organomet. Chem. 241 (1983) 177.
- [26] J.B. Lamber, The Multinuclear Approach to NMR Spectroscopy, Kluwer Academic Publishers, Scotland, 1982.
- [27] J. Mason, Multinuclear NMR, Plenum, New York, 1987.
- [28] C. Pettinari, F. Marchetti, R. Pettinari, D. Martini, A. Drozdov, S. Troyanov, Inorg. Chim. Acta 325 (2001) 103.
- [29] N.J. Hill, G. Reeske, J.A. Moore, A.H. Cowley, Dalton Trans. (2006) 4838.
- [30] V.N. Zakharov, A.V. Yatsenko, A.L. Kamyshnyi, L.A. Aslanov, Koord. Khim. (Russ.) (Coord. Chem.) 17 (1991) 789.
- [31] B.Z. Momeni, F. Rominger, S.S. Hosseini, Acta Crystallogr., Sect. E 65 (2009) 690.
- [32] D.G. Vargas-Pineda, T. Guardado, F. Cervantes-Lee, A.J. Metta-Magana, K.H. Pannell, Inorg. Chem. 49 (2010) 960.
- [33] M. Schulz, M. Klopfleisch, H. Görls, M. Kahnes, M. Westerhausen, Inorg. Chim. Acta 362 (2009) 4706.
- [34] H.W. Lee, N. Sengottuvelan, H.J. Seo, J.S. Choi, S.K. Kang, Y.I. Kim, Bull. Korean Chem. Soc. 29 (2008) 1711.
- [35] Y.I. Kim, Y.K. Song, S.J. Yun, I.C. Kim, S.K. Kang, Acta Crystallogr., Sect. E 67 (2011) 52.
- [36] W.B. Jennings, B.M. Farell, J.F. Malone, Acc. Chem. Res. 34 (2001) 885.